

QUANTUM CHEMICAL INVESTIGATIONS ON MIXED-VALENCE SYSTEMS

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*No science has ever made more rapid
progress in a shorter time than chemistry.*

*-- Martin Heinrich Klaproth, 1791
(first professor of chemistry at the
University of Berlin)*

ABSTRACT

Organic mixed-valence (MV) compounds are the focus of recent research because they represent simple and suitable model systems for the investigation of electron-transfer (ET) processes. Usually, these MV systems consist of at least two redox centers in different redox states, linked by a saturated or unsaturated bridge unit. Quantum chemical studies on the localization/delocalization of the electron hole or of the odd electron in such radicals have been scarce, due to severe limitations of the available methods. In a nutshell, using Hartree-Fock (HF) theory, the hole is always too localized, whereas with density functional theory (DFT) and common functionals it is too delocalized. Furthermore, accurate post-HF *ab initio* methods currently tend to be too demanding for organic MV systems of realistic size. In addition, since solvents have a large impact on the charge localization/delocalization in such radicals, solvent effects have to be modeled in quantum chemical calculations.

Consequently, the main part of this work is the development of a reliable and quantitative quantum chemical protocol for the treatment of organic MV systems based on non-standard hybrid functionals. This protocol is originally validated on four bis-triarylamine radical cations containing bridge units of different length. A hybrid functional with 35% of exact-exchange (HF-) admixture (BLYP₃₅) is combined with a conductor-like screening model (COSMO) to simulate the dielectric solvent effects. Extensions to further bis-triarylamine radical cations as well as neutral perchlorotriphenylmethyl-triarylamine radicals confirm the scope of this protocol. Improvement of this protocol is achieved by the direct COMSO-RS *ansatz*, an extension for real solvents (RS) to the COSMO approach. This facilitates a realistic description of dinitroaromatic or diquinone radical anions even in protic solvents. The calculated quantities (e.g. ET barriers, dipole moments, hyperfine coupling constants (HFCs), inter-valence charge transfer (IV-CT) energies, transition dipole moments, etc.) are compared with experimental reference values, where possible. In cases, where such values are (partly) missing, the protocol provides good predictions for experimental measurements, e.g. for the diquinone radical anions or paracyclophane-bridged bis-triarylaminines. Furthermore, electron coupling in squaraine dyes is investigated by a slightly modified protocol.

ZUSAMMENFASSUNG

Organische, gemischtvalente Systeme (MV) stehen im Fokus aktueller Forschung, da sie einfache und geeignete Modellsysteme für die Untersuchung von Elektronentransferprozessen (ET) darstellen. Üblicherweise bestehen derartige gemischtvalente Systeme aus mindestens zwei Redoxzentren in unterschiedlichen Oxidationsstufen, welche über eine gesättigte oder ungesättigte Brücke miteinander verbunden sind. Quantenchemische Untersuchungen zur Lokalisierung/Delokalisierung des Elektronenlochs bzw. des ungepaarten Elektrons in derartigen Radikalen sind aufgrund schwerwiegender Limitierungen der vorhandenen Methoden rar. Kurz zusammengefasst ist das Elektronenloch immer zu lokalisieren wenn es über die Hartree-Fock (HF) Theorie beschrieben wird, wohingegen es mittels Dichtefunktionaltheorie (DFT) und üblichen Funktionalen immer als zu delokalisiert dargestellt wird. Genaue post-HF *ab initio* Methoden sind jedoch zu zeitaufwändig für organische, gemischtvalente Systeme mit realistischer Größe. Zuletzt müssen aufgrund des Einflusses von Lösemittelmolekülen auf die (De-)Lokalisierung der Ladung ebenfalls Lösemittelleffekte in quantenchemischen Berechnungen berücksichtigt werden.

Folglich besteht das Hauptaugenmerk dieser Arbeit darin, ein verlässliches, quantenchemisches Protokoll für die Beschreibung organischer, gemischtvalenter Systeme zu entwickeln. Dieses Protokoll ist ursprünglich auf der Basis von vier Bistriarylamin-Radikalkationen abgeleitet worden, welche Brücken unterschiedlichster Länge besitzen, wobei ein Hybridfunktional mit 35% exaktem (HF-) Austausch mit einem Kontinuumsolvensmodell (COSMO) zur Simulation der Lösungsmittelleffekte kombiniert wurde. Berechnungen für weitere Bistriarylamin-Radikalkationen sowie neutrale Perchlortriphenylmethyl-Triarylamin-Radikale bestätigen die Bandbreite des Protokolls. Weitere Verbesserungen werden durch den direkten COSMO-RS Ansatz erzielt, einer Erweiterung des COSMO Modells für realistische Lösungsmittel (RS), wodurch sogar eine realistische Beschreibung von Dinitroaromatischen- oder Dichinon-Radikalanionen in protischen Lösungsmitteln ermöglicht wird. Die berechneten Eigenschaften (z.B. ET Barrieren, Dipolmomente, etc.) werden jeweils mit experimentellen Referenzwerten verglichen. Sofern derartige Werte nicht zur Verfügung stehen, dienen die berechneten Werte des Protokolls als gute Vorhersagen für experimentelle Messungen. Des Weiteren werden die elektronischen Kopplungen in Squarain-Farbstoffen durch ein gering modifiziertes Protokoll untersucht.

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- [9] Manuel Renz and Martin Kaupp, “Predicting the Localized/Delocalized Character of Mixed-Valence Diquinone Radical Anions: Towards the Right Answer for the Right Reason.” *J. Phys. Chem. A* **2012**, 116, 10629-10637.
- [8] Manuel Renz, Martin Kess, Michael Diedenhofen, Andreas Klamt and Martin Kaupp, “Reliable Quantum Chemical Prediction of the Localized/Delocalized Character of Organic Mixed-Valence Radical Anions. From Continuum Solvent Models to Direct-COSMO-RS.” *J. Chem. Theory Comput.* **2012**, 8, 4189-4203.
- [7] Sebastian F. Völker, Manuel Renz, Martin Kaupp and Christoph Lambert, “Squaraine Dyes as Efficient Coupling Bridges between Triarylamine Redox Centres.” *Chem. Eur. J.* **2011**, 17, 14147-14163.
- [6] Marina M. Safont-Sempere, Peter Osswald, Matthias Stolte, Matthias Grüne, Manuel Renz, Martin Kaupp, Krzysztof Radacki, Holger Braunschweig and Frank Würthner, “Impact of Molecular Flexibility on Binding Strength and Self-Sorting of Chiral π -Surfaces.” *J. Am. Chem. Soc.* **2011**, 133, 9580-9591.
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- [9] *Internationale Konferenz des GRK1221*, Würzburg, September **2011**.
- [8] *JCF-Frühjahrssymposium*, Göttingen, March **2010**.
- [7] *Workshop on Modern Methods in Quantum Chemistry*, Mariapfarr (A), March **2010**.
- [6] *Berichtskolloquium zur Verlängerung des GRK1221*, Würzburg, December **2009**.
- [5] *2. Fränkisches Theoretikertreffen*, Würzburg, November **2009**.
- [4] *Workshop des GRK 1221*, Niederstetten, Oktober **2009**.
- [3] *Workshop on Modern Methods in Quantum Chemistry*, Mariapfarr (A), March **2009**.
- [2] *Seminar zu neuen Methoden in der Quantenchemie*, Würzburg, January **2008**.
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Posters

- [13] *GDCh-Wissenschaftsforum*, Bremen, September **2011**.
- [12] *Workshop on Modern Methods in Quantum Chemistry*, Mariapfarr (A), March **2011**.
- [11] *Chem-SyStM*, Würzburg, December **2010**.
- [10] *46th Symposium on Theoretical Chemistry (STC)*, Münster, September **2010**.
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- [2] *GDCh-Wissenschaftsforum*, Ulm, September **2007**.
- [1] *JCF-Frühjahrssymposium*, Chemnitz, March **2007**.

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LIST OF ABBREVIATIONS

CI	Configuration Interaction
COSMO	C Onductor-like Screening M odel
CPCM	Conductor-like P olarizable C ontinuum M odel
CT	Charge Transfer
DCM	D i C hloro M ethane
D-COSMO-RS	D irect C Onductor-like Screening M odel for R eal Solvents
DFT	D ensity F unctional T heory
DMF	D i M ethyl F ormamide
DMSO	D i M ethyl S ulf O xide
DN	D i N itro(-aromatic)
DQ	D i Q uinone
EOA	E lectro- O ptical Absorption
ESR	E lectron S pin R esonance
ET	E lectron T ransfer
EtOAc	E thylacetate
E_{xx}	E xact- e xchange admixture
Go3	G aussian o 3
Go9	G aussian o 9
GGA	G eneralized G radient A pproximation
GMH	G eneralized- M ulliken- H ush
HF	H artee- F ock
HFC	H yper F ine C oupling constant
HMPA	H exa M ethyl P hosphor A mid
IR	I nfra R ed
IV-CT	I nter V alence- C harge T ransfer
L(S)DA	L ocal (S pin) D ensity A pproximation
MD	M olecular D ynamics
MeCN	Acetonitrile/ M ethyl c yanide
MeOH	M ethanol
MV	M ixed- V alence
NIR	N ear- I nfra R ed

PC	ParaCyclophane
PCTM	PerChloroTriphenylMethyl
PES	Potential Energy Surface
SCF	Self-Consistent Field
SCRf	Self-Consistent Reaction Field
SIE	Self-Interaction Error
SVP	Split Valence Polarization (basis set)
TAA	TriArylAmine
TBM _{5.10}	TurBoMole 5.10
TBM _{6.3}	TurBoMole 6.3
TD	Time-Dependent
TDDFT	Time-Dependent Density Functional Theory
THF	TetraHydroFuran
TTF	TetraThiaFulvalene
TZVP	Triple Zeta Valence Polarization (basis set)
UHF	Unrestricted Hartree-Fock
UV	UltraViolett
vdW	van-der-Waals
vis	visible
XC	EXchange-Correlation

Chapter 1

Erwin (Schrödinger) with his Psi can do calculations quite a few. But one thing has not been seen just what does Psi really mean.

-- Walter Hückel

1 Introduction

Mixed valency is a 50 year old definition in chemistry which was for the first time termed by Klotz in 1958 in conjunction with a $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ complex.^[1] However, mixed-valence (MV) compounds have been established far earlier in many applications. Plenty of pigments discovered in the early days of chemistry belong to this class, e.g. the Prussian Blue ($\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]_3$) scientifically investigated for the first time at the beginning of the 18th century^[2, 3] – a MV compound all chemistry students are exposed to in one of their first lab courses. Today, the term mixed-valence is typically associated with binuclear transition-metal complexes, with the Creutz-Taube ion being the most prominent example reported for the first time in 1969.^[4] Nevertheless, since the 1960's, there are an increasing number of purely organic systems that may also be regarded as mixed-valence systems.^[5, 6] These organic MV compounds are widely used as simple model systems in order to investigate basic aspects of electron transfer (ET).^[7-10] Such ET processes in organic and inorganic MV systems are of fundamental importance in many technological fields, from molecular, heterogeneous or bio-catalysis to molecular electronics, quantum computing, conductivity, energy transduction, and so on.^[5, 8, 11-14]

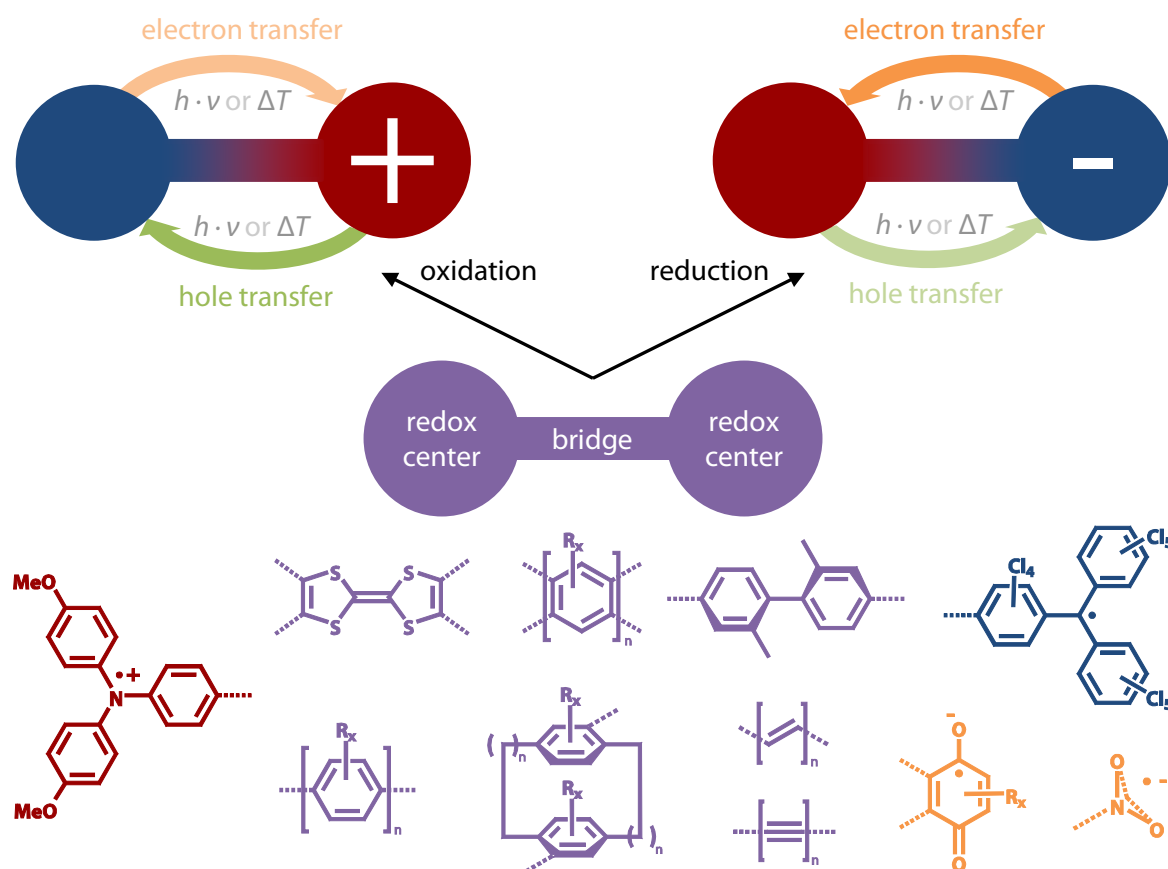


Figure 1.1. Typical arrangement of MV systems containing two (equivalent) redox centers connected via a bridge (center). Upon oxidation/reduction, radicals are obtained and a charge transfer, which can be described as hole transfer (for cations, *left*) or electron transfer (for anions, *right*), is induced either by a photon or by heating (top). Typical organic redox centers are given in their radical state (bottom): **radical cations** like triarylamines, **radical anions** like quinones or nitro groups as well as methyl radicals, which are already radicals in their **neutral** form. At least two (degenerate) redox centers are connected by typical **bridge units**.

In general, MV systems usually consist of two (or more) degenerate redox centers in different oxidation states that are connected by conjugated or non-conjugated bridges (see Figure 1.1). Typical organic redox centers are for example triarylamines (TAA),^[15-20] perchlorotriphenylmethyl radicals (PCTM),^[21-23] dimethoxybenzenes,^[24, 25] hydrazines,^[26, 27] or quinones,^[28, 29] which are connected by conjugated bridge units (Figure 1.1) like ethylene, acetylene, arylene,^[15, 17] and tetrathiafulvalene,^[30] or by non-conjugated ones such as paracyclophanes.^[20, 31, 32] Oxidation or reduction of such a redox center forms a radical cation or radical anion, respectively. In radical cations, the oxidized redox center acts as an electron acceptor (Figure 1.1, left), whereas the reduced redox center in radical anions is an electron donor (Figure 1.1, right). The charge transfer (CT) between the redox centers is usually

described as hole transfer in the former case and as electron transfer (ET) in the latter one. The two possible CT pathways, either optically ($h\nu$) or thermally (ΔT) induced (Figure 1.2), are both anyhow denoted as electron transfer (ET) in general. The optical ET is associated with the so-called inter-valence charge transfer (IV-CT) band λ , which usually appears in the near-infrared (NIR) region and which is also called the Marcus reorganization energy. The thermal ET is described by the free energy barrier $\Delta G^\ddagger$. Various subjects have been investigated so far, for instance the dependence of the electron transfer on the distance of the redox centers,^[15, 33] the influence of local bridge states (electron-rich vs. electron-deficient),^[17, 18] as well as temperature,^[34, 35] solvent^[36, 37] and counter-ion effects.^[38]

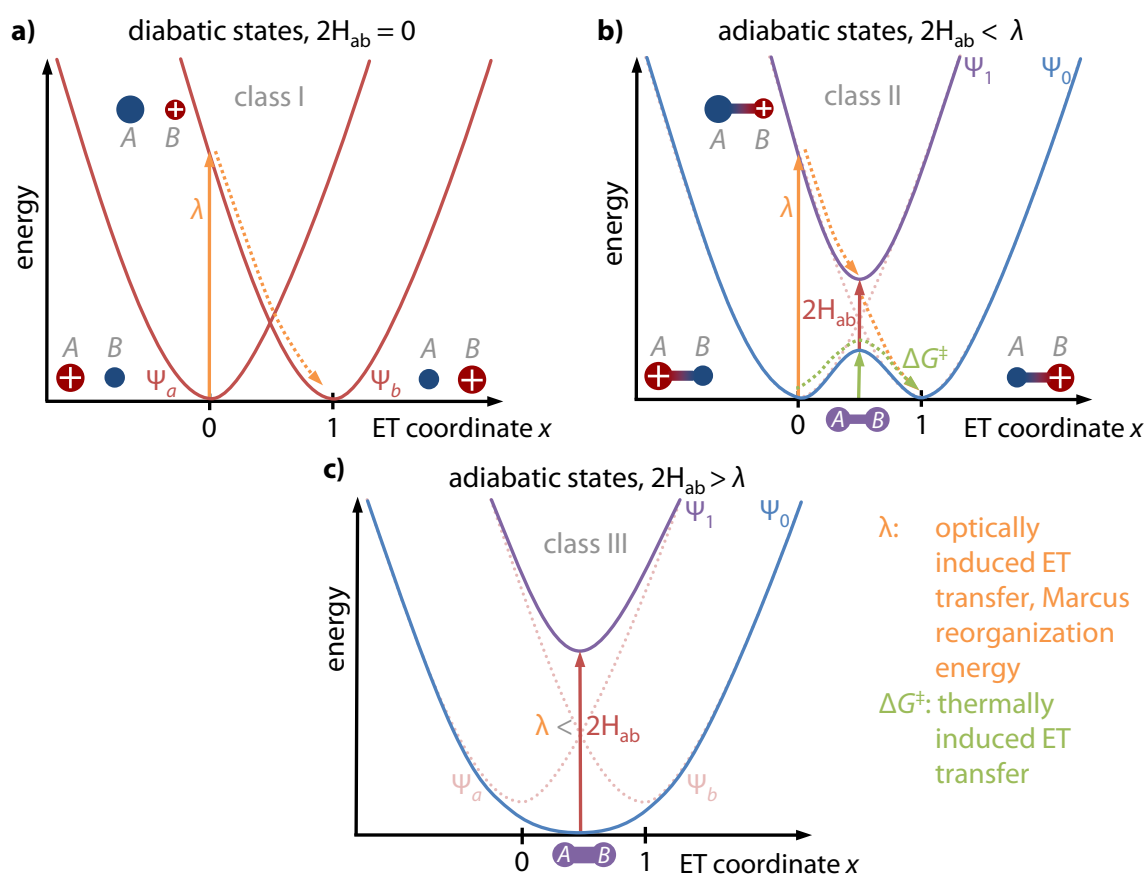


Figure 1.2. Robin-Day classification of MV systems: a) class I – diabatic states, no coupling, fully localized. b) class II – adiabatic states, weak coupling, partly localized. c) class III – adiabatic states, strong coupling, fully delocalized.

The major aspect in mixed-valence (MV) systems is the question of charge localization or delocalization. The latter is often found in organic MV compounds because these are mostly connected by π -conjugated bridges forcing the delocalization of the charge.^[33] Charge

localization is obtained e.g. by large bridge units and thus a large distance between the redox centers, by bridges with a biphenyl-axis causing bad overlap of the π -orbitals due to rotation or by saturated bridges. This situation can be described by two diabatic states Ψ_a and Ψ_b representing the charge localized on redox center A or B , respectively. In an adiabatic model these two states are coupled. In 1967, Robin and Day introduced a general scheme to classify MV systems according the shape of their ground (Ψ_0) and excited state (Ψ_1) potential energy surfaces (Figure 1.2).^[39] They distinguish between three different classes depending on the electronic coupling $2H_{ab}$ of the two states Ψ_a and Ψ_b that describes the localization of the electron on either one of the redox centers A or B :

- class I:* diabatic states, no coupling between the two states ($2H_{ab} = 0$), the charge is fully localized at one of the redox centers (Figure 1.2a)
- class II:* adiabatic states, weak coupling between the two states ($2H_{ab} < \lambda$), the charge is partly localized at one of the redox centers, thermal ET barrier $\Delta G^\ddagger$ from A to B or vice versa (Figure 1.2b)
- class III:* adiabatic states, strong coupling between the two states ($2H_{ab} > \lambda$), the charge is fully delocalized (Figure 1.2c)

MV systems belonging to the latter class are not really mixed-valent by definition because the redox centers are indistinguishable due to the delocalized charge. However, they are often termed mixed-valent, and the optical transition is also called IV-CT. In contrast, MV compounds belonging to class I are truly mixed-valent but unfavorable for studying electron transfer. Accordingly, research focuses on class-II systems or systems at the borderline of class II/III as these MV systems exhibit tunable ET barriers, electronic couplings and IV-CT bands. Classification of MV systems is hence the major issue in this field. Unfortunately, experimental classification of MV compounds is often challenging (see section 2.4.1) just as substantial computational obstacles have prohibited a quantitative theoretical description until recently.

As the more sophisticated post-Hartree-Fock *ab initio* methods (see section 2.4.2.1) are computationally too demanding at present to be applied routinely to the study of realistic

organic MV systems,^[40, 41] the attention so far has been concentrated on both semi-empirical MO methods with some type of configuration interaction on top (see section 2.4.2.1), and on density functional theory (DFT). For reasons explained in more detail below (see section 2.4.2.2), neither DFT with standard functionals nor the semi-empirical methods were able to reliably and quantitatively describe the molecular and electronic structures of MV species in cases when they are close to the class II/III borderline. In addition, as most experiments are done in solution, inclusion of environmental effects especially during structure optimization is essential (see section 2.4.2.3), but has been applied only in rare cases so far.^[42, 43] This work thus deals with both the derivation and application of a reliable quantum chemical protocol for the characterization of organic mixed-valence compounds.

In chapter 3, a set of four bis-triarylamine (TAA) radical cations (**TAA1-4**) close to the class II/III borderline is evaluated by hybrid density functionals with a non-standard HF-exchange admixture (see section 2.2.1) and polarizable continuum solvent models (see section 2.3). The question of localization/delocalization is answered by comparing ground state properties after full structure optimizations (besides optimizations without symmetry constraints calculations in C_i -symmetry are performed). Symmetry breaking is indicated by significant dipole moments, ET barriers and structural distortions in equivalent bonds of both redox centers which are all missing in C_i -symmetrical structures. Supported by excited state properties a proper classification of MV compounds is feasible. This quantum chemical protocol has already been published in the *Journal of the American Chemical Society*.^{[44][A]} In chapter 4 the same computational protocol is applied to further bis-triarylamine radical cations (**TAA5-10**) and to MV triarylamine-perchlorotriphenylmethyl (PCTM) radical systems with non-degenerate redox centers (**TAA11-17**). Since these compounds are uncharged, comparison of computed and experimental dipole moments (see section 2.4.2.2) also assists illustrating the reliability of the computational protocol. In addition, the question of localization or delocalization is supported by ^{14}N -hyperfine coupling constants (HFCs) showing one HFC in the localized and two HFCs for the delocalized case. This part of this thesis has been published recently in *Physical Chemistry Chemical Physics*.^{[45][B]} Chapter 5 expands the protocol to bis-triarylamine radical cations

with non-conjugated bridge units ([n.n]paracyclophanes) **PC1-6**. Here, two kinds of ET mechanism are possible: ET via the σ -bonds or ET through space (π - π). The main question in this context is which one is favored. In order to deal with the π - π -interactions, dispersion energy corrections to DFT are applied.

Chapter 6 deals with a set of six small dinitroaromatic radical anions (**DN1-6**). Their system size allows an in-depth survey of different density functionals and of the size of basis sets. The exposed negative charge at the nitro group displays the limitations of the present solvent model in protic solvents, especially due to the lack of hydrogen bonding. Hence, a more realistic solvent model (D-COSMO-RS, see section 2.3) is employed to these MV compounds allowing a proper classification even in protic solvents. This part of the work has already been published in the *Journal of Chemical Theory and Computation* as one of the first investigations dealing with D-COSMO-RS.^{[46][C]} The enhanced protocol is furthermore applied to a set of diquinone radical anions (**DQ1-4**) in chapter 7, which has been recently accepted for publication in the *Journal of Physical Chemistry A*.^{[47][D]} In contrast to previous studies, it enables accurate descriptions of the class II systems without using constraints, and has thus a much higher predictive power since only few experimental data are available.

Finally, the electron coupling in various squaraine-based systems (**SQ1**, **CN1**, **TA1-3**, **TACN1**) is investigated in chapter 8, which has already been published in *Chemistry – A European Journal*.^{[48][E]} Although the distance between the redox centers is quite large in some of these compounds, they exhibit strong electronic coupling and are categorized consequently as class III systems. Since these compounds are thus rather single chromophores than MV systems, a density functional with lower exact-exchange admixture (B3LYP) has been found necessary, in contrast to the computational protocol described in the previous chapters. Furthermore, the di- and trications in different electronic configurations (singlet vs. open-shell singlet vs. triplet) are compared with respect to experimental spectra.

Chapter 2

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

-- Paul A. M. Dirac

2 Theoretical and Experimental Background

2.1 Elementary Quantum Chemistry

2.1.1 Schrödinger Equation

The basic equation of quantum chemistry is the time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad (2.1)$$

which represents the ground state of many-particle systems such as atoms, molecules or solids. The Hamilton operator $\hat{H}$ includes quantum-mechanical operators for all interactions that occur in the system and the wave function Ψ provides all information about the system. Within the Born-Oppenheimer approximation, where nuclei are fixed, the electronic Hamiltonian for a system with N electrons and M nuclei is given as (in a.u.)

$$\hat{H}_{el} = \hat{T} + \hat{V}_{ne} + \hat{V}_{ee} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 \right) - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}. \quad (2.2)$$

The individual contributions are the kinetic energy of the electrons $\hat{T}$, the Coulomb attraction between electrons and nuclei $\hat{V}_{ne}$ and the electron-electron repulsion $\hat{V}_{ee}$.

2.1.2 Hartree-Fock Theory

One of the main tasks in quantum chemistry is finding a solution for the Schrödinger equation (2.1). Unfortunately, an exact solution can be obtained only for one electron systems like the hydrogen atom or the helium cation. Systems with more than one electron can be treated by Hartree-Fock (HF) theory.^[49] The wave function in the ground state Ψ_0 is approximated by a so-called Slater determinant, corresponding to an antisymmetrized product of N one-electron wave functions $\chi_i(x_i)$:

$$\Psi_0 \approx \Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \cdots & \chi_N(x_1) \\ \vdots & \ddots & \vdots \\ \chi_1(x_N) & \cdots & \chi_N(x_N) \end{vmatrix}. \quad (2.3)$$

The one-electron functions $\chi_i(x_i)$ are called spin orbitals, and are composed of a spatial orbital $\varphi_i(r)$ and one of the two spin functions, $\alpha(s)$ or $\beta(s)$

$$\chi(x) = \varphi(r)\sigma(s), \quad \sigma = \alpha, \beta. \quad (2.4)$$

The total electronic energy given as the expectation value of the Hamiltonian can be separated into one- and two electron parts

$$E = \langle \Phi_{SD} | \hat{H} | \Phi_{SD} \rangle = \sum_i^N (i | \hat{h} | i) + \frac{1}{2} \sum_i^N \sum_j^N (ii | jj) - (ij | ji). \quad (2.5)$$

The first term is the contribution to the kinetic energy and the second term is further divided into the so-called Coulomb- and exchange integrals. Constrained minimization of the Hartree-Fock energy E^{HF} with respect to the orbitals (under the constraint of orthonormalized orbitals) leads to the HF equations

$$\hat{f}_i \chi_i = \varepsilon_i \chi_i, i = 1, 2, 3, \dots, N, \quad (2.6)$$

with the one-electron Fock-operator

$$\hat{f}_i = -\frac{1}{2} \nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}} + V_{HF}(i). \quad (2.7)$$

The Lagrangian multipliers ε_i are the eigenvalues of the Fock-operator and represent the orbital energies. The HF potential

$$V_{HF}(x_1) = \sum_j^N \left(\hat{J}_j(x_1) - \hat{K}_j(x_1) \right) \quad (2.8)$$

is now a one-electron operator where the electron-electron repulsion is taken into account only on average and has two components: the Coulomb-operator

$$\hat{J}_j(x_1) = \int |\chi_j(x_2)|^2 \frac{1}{r_{12}} dx_2 \quad (2.9)$$

and the exchange-operator

$$\hat{K}_j(x_1) \chi_j(x_1) = \int \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_2) dx_2 \chi_j(x_1). \quad (2.10)$$

In eq. (2.5), the term $i = j$ arises and describes the Coulomb interaction of one electron with itself. This self-interaction is physical nonsense (e.g. if one considers the hydrogen atom, where no electron-electron interaction can take place), but is cancelled exactly in the exchange term of the HF potential (see eq. (2.10)). Unfortunately, this is not the case for density functional theory since the exact functional is unknown (see below in section 2.2).

Since the HF potential and thus the Fock-operator depends on the spin orbitals, the HF equations have to be solved iteratively leading to a self-consistent field (SCF) where a set of orbitals is used as initial guess to solve the HF equations. The resulting new set of orbitals is then used in the next iteration until the difference in energy falls below a given threshold.

For a closed-shell system, the HF solution is usually characterized by having doubly occupied spatial orbitals, i.e., two spin orbitals χ_α and χ_β share the same spatial orbital φ_i connected with an α - or a β -spin function, and exhibit the same orbital energy. This is then called restricted Hartree-Fock (RHF). For open-shell systems, two possible descriptions are available: the restricted open-shell HF (ROHF) and the more popular unrestricted Hartree-Fock variant (UHF) which allows each spin orbital to have its own spatial part (this leads to different orbital energies for α - and β -orbitals). The UHF Slater determinant is thus no longer an eigenfunction of the total spin operator $\hat{S}^2$. The deviation of the expectation value $\langle S^2 \rangle$ from the correct value (with S as total spin of the system), given through $S(S+1)$, is a reference for the physical quality of the calculation. This so-called spin contamination is due to mixing with states of higher spin multiplicity.

According to Löwdin,^[50] the electron correlation energy is defined as

$$E_C^{HF} = E_0 - E_{HF} . \quad (2.11)$$

This quantity describes the correlation of electrons due to instantaneous repulsion not covered by the HF potential and is often divided into two terms: the dynamical and the non-dynamical or static correlation. The former one is a short range effect which originates from the actual motions of the individual electrons. The latter one is especially important in open-shell systems where several ground state Slater determinants with comparable energies are required to describe the true ground state. The absence of electron correlation in RHF leads to a too ionic picture, even in UHF (where electron correlation is somewhat covered). A byproduct in the latter case is, however, spin-contamination and wave functions, which do not resemble the singlet ground state at the dissociation of H_2 . Several post-HF methods like “Configuration Interaction” (CI), “Møller-Plesset perturbation theory” (e.g. second order – MP2) or “Coupled-Cluster” theory (CC) are dealing with dynamical correlation. CC theory also includes some part (left-right correlation) of non-dynamical correlation. Strong non-dynamical correlation effects can be introduced by multi-configuration SCF (MCSCF) techniques like, for instance, a complete-active-space SCF

(CASSCF).^[49, 51] However, all these methods are computationally demanding for systems of chemical interest.

2.2 Density Functional Theory

Density Functional Theory (DFT)^[52] can also handle electron correlation and is widely used even for larger molecules in chemistry. This method is based on the so-called Hohenberg-Kohn theorem, which was introduced in 1964 stating that the total energy of a system is a functional of the electron density $\rho(r)$.^[53] For this case, the energy of the electronic ground state and hence further properties can be determined. The total electron energy is the sum of the kinetic energy of the electrons $T[\rho]$, the electron-electron interaction $V_{ee}[\rho]$ and the nuclei-electron interaction $V_{ne}[\rho]$

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{ne}[\rho]. \quad (2.12)$$

Some terms in this equation are system dependent ($V_{ne}[\rho]$) and some are system-independent ($T[\rho]$ and $V_{ee}[\rho]$). The latter are therefore universally valid and merged to the Hohenberg-Kohn functional $F_{HK}[\rho]$. Consequently, the total electron energy is:

$$E[\rho] = F_{HK}[\rho] + V_{ne}[\rho] \quad (2.13)$$

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho] \quad (2.14)$$

Following from this second Hohenberg-Kohn theorem the smallest energy value is obtained from the ground state density. In other words the variational principle holds in DFT. This implies that each energy value, which is calculated by a different electron density but the exact electron density, is higher than the exact ground state energy. Nevertheless, the main challenge is the unknown Hohenberg-Kohn functional $F_{HK}[\rho]$, especially the unknown kinetic energy of the electrons $T[\rho]$. One year after Hohenberg and Kohns first theorem in 1965, Kohn and Sham identified a way to approximate the kinetic energy of the electrons $T[\rho]$. In this case, $T[\rho]$ is defined as the sum of the kinetic energy of a non-interacting reference system $T_s[\rho]$ and a correlation term $T_c[\rho]$ for the interacting system.^[54] The electron-electron interaction $V_{ee}[\rho]$ is split up into a classical Coulomb-like

term $J[\rho]$ and an unknown part which is merged with $T_c[\rho]$ into the exchange-correlation (XC) functional $E_{xc}[\rho]$

$$E_{HK}[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]. \quad (2.15)$$

The total energy of the system is then defined as

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + V_{ne}[\rho]. \quad (2.16)$$

The kinetic energy of the electrons $T_s[\rho]$ in a non-interacting reference system (i.e. Slater determinant) can be described in a following way:

$$T_s[\rho] = -\frac{1}{2} \sum_{i=1}^N \langle \varphi_i | \nabla_i^2 | \varphi_i \rangle. \quad (2.17)$$

The XC functional contains the non-classical electron-correlation energy $E_{nc}[\rho]$ and a contribution to the kinetic energy $T_c[\rho]$

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] = T_c[\rho] + E_{nc}[\rho]. \quad (2.18)$$

This means, that the exchange-correlation energy is a functional which contains everything that cannot be handled exactly. These are not only the non-classical effects of self-interaction correction, correlation and exchange, but also a part belonging to the kinetic energy. The main challenge of DFT is the proper approximation of $E_{xc}[\rho]$. Similarly to the Hartree-Fock approximation the wave function of the non-interacting reference system is represented by a Slater determinant Θ_s with Kohn-Sham orbitals φ_i . Minimizing the energy under the constraint of orthonormal orbitals thus leads to the Kohn-Sham equations

$$\left[-\frac{1}{2} \nabla^2 + V_s(r) \right] \varphi_i = \varepsilon_i \varphi_i \quad (2.19)$$

with the Kohn-Sham operator

$$\hat{f}_{KS} = \left[-\frac{1}{2} \nabla^2 + V_s(r) \right] \quad (2.20)$$

$$V_s(r) \equiv V_{eff}(r) = \int \frac{\rho(r_2)}{r_{12}} dr_2 + V_{xc}(r) - \sum_A^M \frac{Z_A}{r_{1A}}. \quad (2.21)$$

The exchange-correlation potential $V_{xc}(r)$ is defined as the functional derivative of E_{xc} with respect to ρ

$$V_{xc} \equiv \frac{\delta E_{xc}}{\delta \rho}. \quad (2.22)$$

This equation would give, in principle, the exact solution of the Schrödinger equation, if the exact forms of V_{xc} and E_{xc} were known. As described above for HF theory, open-shell systems can be calculated similarly by unrestricted Kohn-Sham DFT allowing the orbitals to differ in their spatial parts. As a consequence, symmetry breaking of the electronic wave function is enabled.

Several ways have been developed to approximate the exchange-correlation energy. The first of such approximations was the “local spin-density approximation” (LSDA) which describes the electron density $\rho(r)$ at each point in space as electron density of a uniform electron gas. In the unrestricted case the XC energy is a functional of the α - and β -electron densities

$$E_{xc} \approx E_{xc}^{LSDA} = \int e_{xc}[\rho_\alpha, \rho_\beta] d^3r. \quad (2.23)$$

In case of equal numbers of α - and β -electrons the system is called closed-shell and LSDA becomes the “local density approximation” (LDA).

Usually the XC functional is divided into an exchange- and correlation part

$$E_{xc}^{LSDA} = E_x^{LSDA} + E_c^{LSDA}. \quad (2.24)$$

An example for such XC functionals is the combination of Slater-Dirac exchange (S),^[55, 56] which is exact for the uniform electron gas, and the correlation functional by Vosko, Wilk

and Nusair (VWN) which is based on analytical fits to data from Monte-Carlo simulations.^[57] Functionals based on the LSDA for the exchange-correlation energy are denoted as “local” functionals.

This approximation works quite well for metals or solids, where the electrons could be described more or less as an electron gas. In contrast, the electron density in molecules is strongly position dependent making its characterization by a uniform electron gas inadequate. As a logical first step, not only the information about the density $\rho(r)$ at a particular point r was used, but also the gradient of the charge density $\nabla\rho_\alpha$ and $\nabla\rho_\beta$ leading to the “generalized gradient approximation” (GGA)

$$E_{XC} \approx E_{XC}^{GGA} = \int e_{XC}[\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta] d^3r. \quad (2.25)$$

As for LSDA, the exchange-correlation energy can be split up into an exchange- (E_x) and correlation-term (E_c) for GGA functionals (see eq. (2.24)). One popular example for this class of functionals is the Becke-exchange functional (B88),^[58] in combination with a correlation functional by Perdew (P86)^[59] or one by Lee, Yang and Parr (LYP).^[60] This class of functionals is often called “semi-local”.

GGA functionals can be further improved if higher derivatives of the density and/or the kinetic energy density are taken into account. These functionals are then called meta-GGA functionals.

2.2.1 Hybrid functionals

In general, the exchange contributions are significantly larger than the corresponding correlation effects. As the exchange energy of a Slater determinant can be computed exactly, a combination of exact-exchange energy with electron correlation by approximate functionals seems to be straightforward

$$E_{XC} = E_x^{exact} + E_c^{KS}. \quad (2.26)$$

Unfortunately, this gives reasonable results only for atoms but not for molecules. The first and simplest so-called hybrid functional (functionals without exact exchange are therefore often called “pure” functionals, see above) was introduced by Becke using a half-and-half combination of equal weights of exact exchange and the LSDA XC functional^[61]

$$E_{XC}^{HandH} = \frac{1}{2}E_X^{HF} + \frac{1}{2}(E_X^{LSDA} + E_C^{LSDA}). \quad (2.27)$$

Further improvement of hybrid functionals was obtained by the introduction of three semi-empirical coefficients into the exchange-correlation functional^[62]

$$E_{XC}^{B3} = (1-a)E_X^{LSDA} + a \cdot E_X^{HF} + b \cdot \Delta E_X^{B88} + c \cdot \Delta E_C^{PW91} + E_C^{LSDA}. \quad (2.28)$$

The parameters determine the amount of exact exchange and the weight of non-local correction to B88-exchange and PW91-correlation respectively. The probably most popular functional B3LYP is based on equation (2.28) with the parameters set to $a = 0.20$, $b = 0.72$, $c = 0.81$ (as compared to the originally proposed exchange-correlation functional by Becke, the correlation part is replaced by the LYP correlation functional).^[63] The number of parameters can be further reduced to one, if only the amount of exact-exchange a will be varied (this type of functional will be used mostly in this work)

$$E_{XC} = (1-a)(E_X^{LSDA} + \Delta E_X^{B88}) + a \cdot E_X^{HF} + E_C^{LYP}. \quad (2.29)$$

Functionals based on equation (2.28) and (2.29) are so-called global hybrid functionals, since the exact-exchange admixture a is constant in space. Further developments are obtained by applying variable exact-exchange admixtures. One *ansatz* are the so-called range-separated functionals (where short- and long-range interactions are split, the former mostly described by pure DFT exchange, the latter usually by exact exchange) like CAM-B3LYP^[64] or LC- ω PBE,^[65-68] or a general long-range correction (LC) to exchange-correlation functionals.^[69] Another approach are local hybrid functionals where a is replaced by a suitable position-dependent local mixing function (LMF) $g(r)$.^[70-80] These types of functionals could solve some of the problems of DFT methods (see section 2.2.2) in the future as they are still undergoing an intense development.

2.2.2 Delocalization and Correlation Errors in Density Functional Calculations

One of the major problems in DFT is the so-called self-interaction error (SIE).^[81] In a one-electron system, there is no electron-electron interaction and the sum of $J[\rho]$ and $E_{xc}[\rho]$ (see eq. (2.16)) must be equal to zero. Unfortunately, this is not the case for most approximated density functionals since the exact form of $E_{xc}[\rho]$ is unknown. The SIE is then defined as

$$SIE = J[\rho_q] + E_{xc}[\rho_q] \quad (2.30)$$

for a q -electron system ($0 < q \leq 1$).^[82] For many-electron systems, where this effect is often called delocalization error,^[83] Perdew and Zunger^[84] defined the SIE for the entire system as sum over all SIE of the orbital density in analogy to eq. (2.30).^[85, 86] However, this method is working well for atoms but merely limited for molecules.^[87] The basis of the SIE can be easily described considering the H_2^+ -molecule: DFT stabilizes states with fractional charge (half of the charge at each hydrogen atom) at the dissociation limit compared to the exact case where a hydrogen atom and a proton at infinite distance is obtained (which is reproduced exactly by HF).^[82] These fractional charges for DFT have been introduced by Perdew in 1982.^[88] In this case, DFT (LDA and GGA) achieves lower energies leading to unphysical delocalization of the electron/spin density.^[89] In contrast, HF theory suffers from a localization error, obtaining too high energies for fractional charges (but note, for one-electron systems, HF would give the exact solution).^[85, 90] Consequently, hybrid functionals contain the energy errors from LDA or GGA functionals (convex behavior with respect to exact energies considering fractional charges) and HF energies (concave behavior). As the errors have opposite signs, hybrid functionals benefit in some cases from this error cancellation. Larger a values (see eq. (2.29)) will diminish SIE but enhance spin polarization. However, too large exact-exchange admixtures in hybrid functionals are expected to lead to artifacts arising from spin contamination, and from missing simulation of left-right correlation. Efforts to directly reduce the SIE in exchange-correlation functionals include so-called range-separated hybrid functionals,^[91] local hybrid functionals with position-dependent exact-exchange admixture,^[70, 71, 92] and other approaches classified generally as hyper-GGA

functionals.^[77, 93-98] In fact, Yang *et al.* have recently introduced and defined a specific “delocalization error” in DFT.^[83, 99]

These delocalization errors in DFT are well known in many areas, from solid-state physics^[100, 101] via transition-metal ligand bonding^[102, 103] to organic π -systems.^[104-109] The latter are most closely related to the organic MV systems studied in this work, but extended studies are lacking so far. The aim of this work is to provide a basis for such investigations by examining the decisive aspects that control the outcome of DFT calculations. In this context, the ability of global hybrid functionals, based on eq. (2.29), to reduce the delocalization errors will be evaluated to get a proper description of organic MV systems.

2.2.3 Time-dependent Density Functional Theory

Excited states of molecules can be described quite well by wave-function-based methods like CI or CASSCF.^[110, 111] One of the cheapest excited state *ansatz* is the CI with singlet excitations (CIS).^[112] Further improvements, which also include correlation effects, are for example CIS(D) where effects of doublet excitations are introduced as a perturbation in a scheme similar to MP2.^[113, 114] In a time-dependent (TD) extension to Kohn-Sham DFT, it is also possible to calculate excited states by the linear response of the ground state electron density to a time-dependent perturbation.^[115] This is thus called time-dependent DFT (TDDFT). Starting from the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(r,t) = \hat{H}(r,t)\Psi(r,t) \quad (2.31)$$

the Runge-Gross theorem^[116] is the analogue of the Hohenberg-Kohn-theorem in the time-dependent case. The Hamiltonian additionally depends on an external potential, which is composed of one-particle potentials. The time-dependent Kohn-Sham equations are then defined as

$$i\frac{\partial}{\partial t}\varphi_i(r,t) = \left(-\frac{1}{2}\nabla_i^2 + V(r,t) + \int \frac{\rho(r^t,t)}{|r-r^t|} d^3r^t + \frac{\delta A_{xc}[\rho]}{\delta \rho(r,t)} \right) \varphi_i(r,t). \quad (2.32)$$

All exchange- and correlation effects are put together into $\delta A_{xc}[\rho]/\delta\rho(r,t)$ (except the classical Coulomb interaction). Up to this point, no approximations have been applied and the time-dependent Kohn-Sham theory is formally exact. However, in analogy to the Hohenberg-Kohn functional for the time-independent case the exact time-dependent exchange-correlation action functional (also called XC-kernel f_{xc} , which is the second functional derivative of the exchange-correlation energy) is unfortunately unknown and has to be approximated.^[115] One example is the so called “adiabatic local density approximation” (ALDA), where the non-local, time-dependent XC-kernel is substituted by a local and time-independent XC-kernel for a particular point of time while it is assumed that the density is changing only slowly with time.

In practice, excitation energies or oscillator strengths are mostly calculated by the linear response TDDFT which describes the response of the system to an external, time-dependent perturbation. Considering that excitations take place for infinitesimal perturbations, the following TDDFT equations are obtained (analogous to the TDHF equation)

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}, \quad (2.33)$$

with the matrix elements $\mathbf{A}$ and $\mathbf{B}$ defined as (two-electron integrals in Mulliken notation)

$$\begin{aligned} A_{ia,jb} &= \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia | jb) + (1 - c_{HF})(ia | f_{xc} | jb) - c_{HF}(ij | ab) \\ B_{ia,jb} &= (ia | bj) + (1 - c_{HF})(ia | f_{xc} | bj) - c_{HF}(ib | aj). \end{aligned} \quad (2.34)$$

Here, it is seen that the orbital eigenvalue difference of the ground state orbitals ($\epsilon_a - \epsilon_i$) is a first approximation of the excitation energy (for pure DFT functionals, $c_{HF} = 0$). A further simplification, called Tamm-Dancoff-approximation (TDA), is made by neglecting the matrix $\mathbf{B}$ yielding the simplified eigenvalue equation:^[117]

$$\mathbf{A}\mathbf{X} = \omega\mathbf{X}. \quad (2.35)$$

In this case, the excitation energy ω is much easier to derive if only pure DFT exchange-correlation functionals are used. For hybrid functionals ($c_{\text{HF}} \neq 0$) an additional term arises in the unperturbed Kohn-Sham-Hamiltonian. Hence, TDDFT is a suitable method for the description of excited states. It is also applicable to larger molecules due to its computational efficiency since calculations are only slightly more expensive than CIS (depending on the functional used).

However, TDDFT functionals fail in describing long-range charge transfer (CT) excitations sufficiently, especially if the overlap between ground and excited state is zero.^[115] This is mainly a result of the wrong asymptotic behavior ($\neq 1/R$) of the potential of most XC functionals. It is assumed that this error arises from the electron transfer self-interaction error which means that the transferred electron in the final state still experiences its own electrostatic field from the initial state. This error can be reduced if hybrid functionals are used in TDDFT (as in this work) – analogously to DFT functionals. In addition, since the overlap of ground and excited state is non-zero for most of the mixed-valence systems studied in this work, TDDFT calculations on these systems will be essentially protected against this CT problem.

2.3 Solvation models

All methods described so far are based on calculations in the gas phase. Experimental data for the MV systems studied here are, however, usually obtained in solution because most of them are charged and exhibit a significant dipole moment. Especially polar solvents have a strong impact on these molecules by stabilizing the charge and solubilizing them at all. The underlying solvent interactions can be divided into two groups:^[51] non-specific, long-range solvation (polarization and dipole orientation) and specific, short-range solvation (e.g. hydrogen bonds, van-der-Waals (vdW) interactions or charge-transfer effects). Calculations on specific solvent effects are really expensive, because at least the first solvation shell has to be modeled explicitly (Figure 2.1a) requiring several hundreds of solvent molecules. In this case, there are plenty of minima and one snapshot of a given point in time is not enough to describe this situation. This dynamic can be modeled by molecular dynamics (MD) or

Monte-Carlo (MC) simulations. For large molecules, this is more or less unfeasible for quantum mechanical (QM) methods. Hybrid methods (QM/MM) are using molecular mechanics (MM) for the solvent molecules and QM for the solute to reduce the computational effort. However, these methods are still expensive and cannot be used routinely for a huge number of calculations. Therefore, the most widely used methods describe the solvent effects implicitly considering basically long-range solvation interactions which cause a screening of charge interactions.^[118]

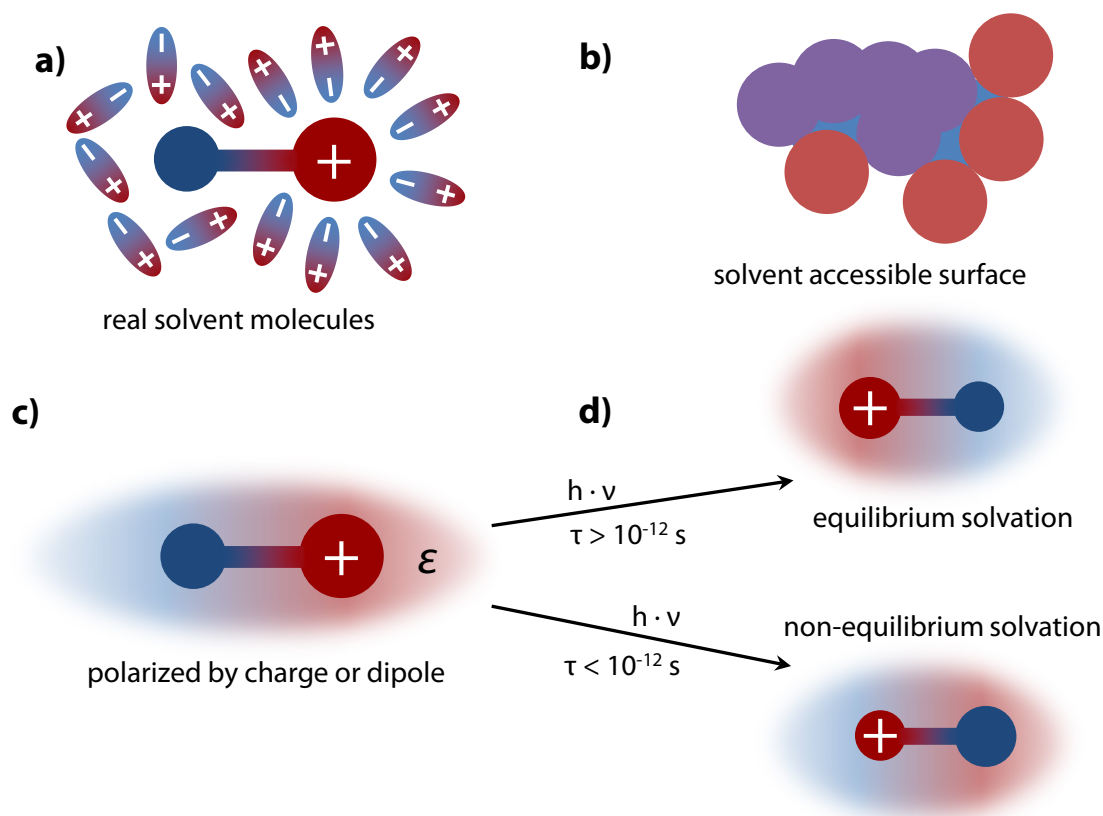


Figure 2.1. a) Realistic description of solute surrounded by a first shell of explicit solvent molecules (denoted as dipoles). b) Cavity construction, solute surface is composed of spheres (purple) and surrounded by solvent molecules (red). Solvent accessible surface (SAS) is the sum of purple and blue (which is the solvent excluded surface, SES). c) Solvent represented as continuum solvent model (CSM) with the solute placed in a (polarizable) dielectric continuum with a dielectric constant ϵ . d) Alternatives for an optical transition. *Top*: equilibrium solvation, excitation and electron/charge transfer including relaxation of solute nuclei and solvent, slow. *Bottom*: non-equilibrium solvation, Franck-Condon-type vertical excitation, no relaxation of solute nuclei and solvent, just electron/charge transfer, fast, closer to reality (time scales according to ref. [119])

One of these methods is the continuum solvation model (CSM).^[119] In this case, the solvent is described as a uniform polarizable medium with a dielectric constant ϵ , and with a hole – the so-called cavity where the solute is placed (Figure 2.1c). It is important to mention, that ϵ is the only parameter, which is solvent characteristic, and thus solvents with equal dielectric constants are indistinguishable (e.g. MeCN and DMF, $\epsilon \approx 37$, see Table 2.1). If the cavity in the continuum is constructed as sphere or ellipsoid, the interaction between the solute and the solvent can be calculated analytically. More realistically, the cavity is created according to the molecular shape, so each atom has its own sphere, which is based on the vdW radius – so-called van-der-Waals surfaces. Due to the overlap of the vdW spheres, small pockets in this cavity arise. Taking a solvent with a given radius, a so-called solvent accessible surface (SAS) is obtained (Figure 2.1b). In addition, one has to keep in mind that, unfortunately, various solvent and vdW radii (default radii are available in Table S6.1), which are e.g. based on universal force-field (UFF), united atom topological models (UAo) or crystal structures (Bondi) are applied in miscellaneous quantum chemical programs leading to unequal cavity constructions.^[119] In general, the solvent effects are implemented in a self-consistent reaction field (SCRF), where the calculated electric moments induce charges in the dielectric continuum. The back-polarization of the continuum again induces changes in the solute (this is done by adding a further potential to the Hamiltonian of the solute) so that this procedure is continued until the convergence is reached. In other words: the solute polarizes the dielectric medium and the response of the medium is the generation of screening charges on the cavity surface (which is built up from a number of surface segments), according to the following boundary condition for dielectric media:

$$4\pi\epsilon\sigma(r) = (\epsilon - 1) n(r) E(r) \quad (2.36)$$

where $\sigma(r)$ is the screening charge density at the position r of the surface, $E(r)$ the electric field arising from the solute as well as the screening charges on cavity surface, and $n(r)$ is the surface normal vector. However, this is a rather complicated boundary condition to obtain the screening charges. The boundary condition is much simpler in a conductor-like screening model (COSMO, CPCM)^[120, 121] where the total electrostatic potential on the surface vanishes

$$\Phi_{tot} = 0. \quad (2.37)$$

The dielectric constant is that of a conductor in this case ($\epsilon = \infty$). However, this vector is determined by the solute potential Φ_{sol} which arises from source charges $\mathbf{Q}$ on the segments, and a potential $\mathbf{A}\mathbf{q}$, originating in the surface charges $\mathbf{q}$:

$$\Phi_{tot} = \Phi_{sol} + \mathbf{A}\mathbf{q} = 0. \quad (2.38)$$

In this case, $\mathbf{A}$ is the Coulomb-matrix of the screening charge interactions. The screening charges $\mathbf{q}$ for a conductor are then defined as

$$\mathbf{q} = -\mathbf{A}^{-1}\Phi_{sol}. \quad (2.39)$$

To account for the finite dielectric constants in real solvents, the actual screening charges $\mathbf{q}^*$ are scaled by an ϵ -dependent correction factor^[120, 121]

$$f(\epsilon) = \frac{\epsilon - 1}{\epsilon + \frac{1}{2}} \text{ (COSMO)} \quad \text{or} \quad f(\epsilon) = \frac{\epsilon - 1}{\epsilon} \text{ (CPCM)} \quad (2.40)$$

and

$$\mathbf{q}^* = f(\epsilon) \mathbf{q}. \quad (2.41)$$

The relative error, which is included by this extension to finite dielectric constants is less than $\frac{1}{2}\epsilon^{-1}$. It follows that it is almost negligible for polar solvents, but significant for non-polar solvents (e.g. for hexane, $\epsilon = 1.89$, the error would be about 25%).^[120] The dielectric energy (this is the energy gained by the solvation process) is half of the solute-solvent interaction energy, and the total free energy of the system is then the sum of the isolated system, calculated with the solvated wave function and this dielectric energy

$$E = E(\Psi_{solv}) + \frac{1}{2}f(\epsilon)\mathbf{q}\Phi_{sol}. \quad (2.42)$$

This energy might be adjusted by the outlying charge correction,^[122] since there is an inconsistency caused by electron density outside the cavity.^[119] It has to be mentioned at this

point that there is a large number of further solvent models or refinements, within or beyond the polarizable continuum model (PCM).^[118, 119] However, this work focusses on COSMO and the comparable CPCM since these models are implemented in the programs used (i.e. TURBOMOLE only provides COSMO and thus CPCM is used in Gaussian for comparison).

However, one further improvement of COSMO will be described here. While the above-mentioned COSMO/CPCM are simple continuum solvation models, which take the polarization effects of the solvents only into account on a plain, electrostatic level, the COSMO model for real solvents (COSMO-RS)^[123-125] is a statistical thermodynamics treatment of the solute-solvent interactions. It is based on the COSMO polarization charge densities calculated on solute and solvent molecules in a conductor ($\epsilon = \infty$). The major advantage of COSMO-RS over COSMO and other dielectric CSMs is its ability to treat solute and solvent on the same quantum chemical basis as well as its possibility of considering hydrogen bonding, solvent mixtures and temperature effects. While the latter are always only performed at $\epsilon = \infty$ in COSMO-RS, the solvation thermodynamics are handled in a separate step after the quantum chemical calculations. This is a great advantage with respect to computational efficiency, especially in the treatment of solvent mixtures. However, calculations of geometrical or electronic response properties of the solute in a specific solvent are unsupported. The direct COSMO-RS (D-COSMO-RS)^[126] approach makes use of the specific solvent response function calculated in COSMO-RS, the so-called σ -potential, turns it into a response operator, which is only slightly more complicated than the COSMO operator itself, and uses this in the quantum chemical calculation of solute properties in the specific solvent. This σ -potential for an ensemble S (solvent or solvent mixture) originates from the chemical potential of an effective surface segment of area a_{eff} , the polarization charge densities σ and σ' and the σ -profile p_s

$$\mu_s(\sigma) = -\frac{kT}{a_{eff}} \ln \left[\int p_s(\sigma') \cdot \exp \left(\frac{-a_{eff} (e_{int}(\sigma, \sigma') + \mu_s(\sigma'))}{kT} \right) d\sigma' \right]. \quad (2.43)$$

The term $e_{int}(\sigma, \sigma')$ represents the energetic costs of making contact between the polarities σ and σ' . The energy term can be written as

$$E_{add,RS} = f(\epsilon)E_{diel}(\epsilon = \infty) + \sum_t a_t \hat{\mu}_s(\sigma_t'). \quad (2.44)$$

The correction factor $f(\epsilon)$ is defined according to eq. (2.40), a_t is the area of segment t , while the σ -potential operator $\hat{\mu}_s(\sigma_t')$ is itself again depending on the screening charge σ_t' . The σ -potential of the solvent combines a back-polarization factor f_p and a volume element α (depending on the effective radius)

$$\hat{\mu}_s(\sigma_t') = f_p \mu_s(\sigma_t') - \frac{\alpha}{2}(1 - f(\epsilon))(\sigma_t')^2. \quad (2.45)$$

Since the σ -potential can be calculated for almost any solvent and solvent mixture, even at variable temperature, and since it includes some hydrogen bonding contributions and many other effects beyond the dielectric continuum approximation, D-COSMO-RS has the potential to calculate solute geometries and spectra even in protic solvents (which will be shown in section 6.4.6).

As described in section 2.2.3, excited states can be calculated by TDDFT. In this case, solvent effects can be included with equilibrium solvation or via non-equilibrium solvation (Figure 2.1d).^[127-129] The latter only accounts for fast responses of the solvent (e.g. polarization, electronic effects) whereas the former also includes slow motions of the solvent (e.g. reorientation of the solvent molecules) and of solute nuclei. In a vertical excitation, only the fast terms should be included – according to the Franck-Condon principle, while equilibrium solvation is necessary in excited state geometry optimizations. In both cases, the electronic polarizability, which is part of the effective Hamiltonian, corresponds to an optical dielectric constant, which is the square of the refractive index η of the solvent. However, for comparison with experimental UV/vis transition energies in solution, calculated excitation energies using non-equilibrium solvation should give reliable results.

Specific dielectric constants which have been used in this work are summarized in Table 2.1. It has to be noted that the programs sometimes use different values for the same solvent, yet the differences are rather small. In addition, temperature dependence of ϵ is not taken into account.

Table 2.1. Dielectric constants ϵ and refractive indices η of several solvents used or for comparison

solvent	ϵ^a	η^b
<i>n</i> -hexane	1.89	1.385
ethyl acetate (EtOAc)	5.99	1.372
tetrahydrofuran (THF)	7.43	1.405
dichloromethane (DCM)	8.93	1.424
<i>n</i> -octanol	9.86	1.429
methanol (MeOH)	32.61	1.329
hexamethylphosphoramide (HMPA)	32.70 ^c	1.458
acetonitrile (MeCN)	35.69 (36.64) ^d	1.344
dimethylformamide (DMF)	37.22	1.430
dimethylsulfoxide (DMSO)	46.83	1.417

^a Default values in Gaussian 09 (also used in the D-COSMO-RS calculations). See, e.g., Helambe *et al.* or Kinart *et al.* for temperature dependence.^[130, 131] ^b Default values in Gaussian 09. If not stated otherwise, $\eta = 1.300$ was used in TURBOMOLE 6.3. Compared to realistic values deviations are $< 30 \text{ cm}^{-1}$.

^c Ref. [132]. ^d Gaussian 03 and TURBOMOLE default value in parenthesis.

2.4 Mixed-Valence Systems

One of the basic approaches when dealing with mixed-valence (MV) systems is Marcus theory.^[133] As already mentioned in the introduction, a typical MV system consists of at least two redox centers, connected via a bridge (see Figure 1.1). As the term “mixed-valence” only holds for symmetric systems, the electron transfer (ET) for systems with two redox centers can be described by two states: the initial state, where the electron is localized at redox center *A*, and the final state, where the electron is localized at redox center *B*. It has to be noted that this process can also be depicted as hole transfer^[5] – nevertheless, in this work, this process will always be called electron transfer. In the framework of Marcus theory, these two states can be described by two diabatic potentials Ψ_a and Ψ_b along a reaction coordinate x (Figure 2.2a and b). There are two pathways for the electron transfer: (a) the optically induced ET by vertical excitation of a photon with the energy λ (also called Marcus reorganization energy) and (b) the thermally induced ET with the free activation energy $\Delta G^\ddagger$. The energy λ in the former case can be described by the sum of the outer reorganization energy λ_o (e.g. from solvent reorganization, often also denoted as λ_s) and the inner reorganization energy λ_v , considering all structural changes (bond lengths and angles) within the molecule due to the change in the oxidation states of the redox centers. In non-

degenerate compounds like **TAA11-17** (see section 4.4.3), the free energy difference $\Delta G^{\circ 0}$ between the two degenerate states Ψ_a and Ψ_b is an additional term to the Marcus reorganization energy (otherwise, $\Delta G^{\circ 0}$ is zero in the following equations).^[5, 45]

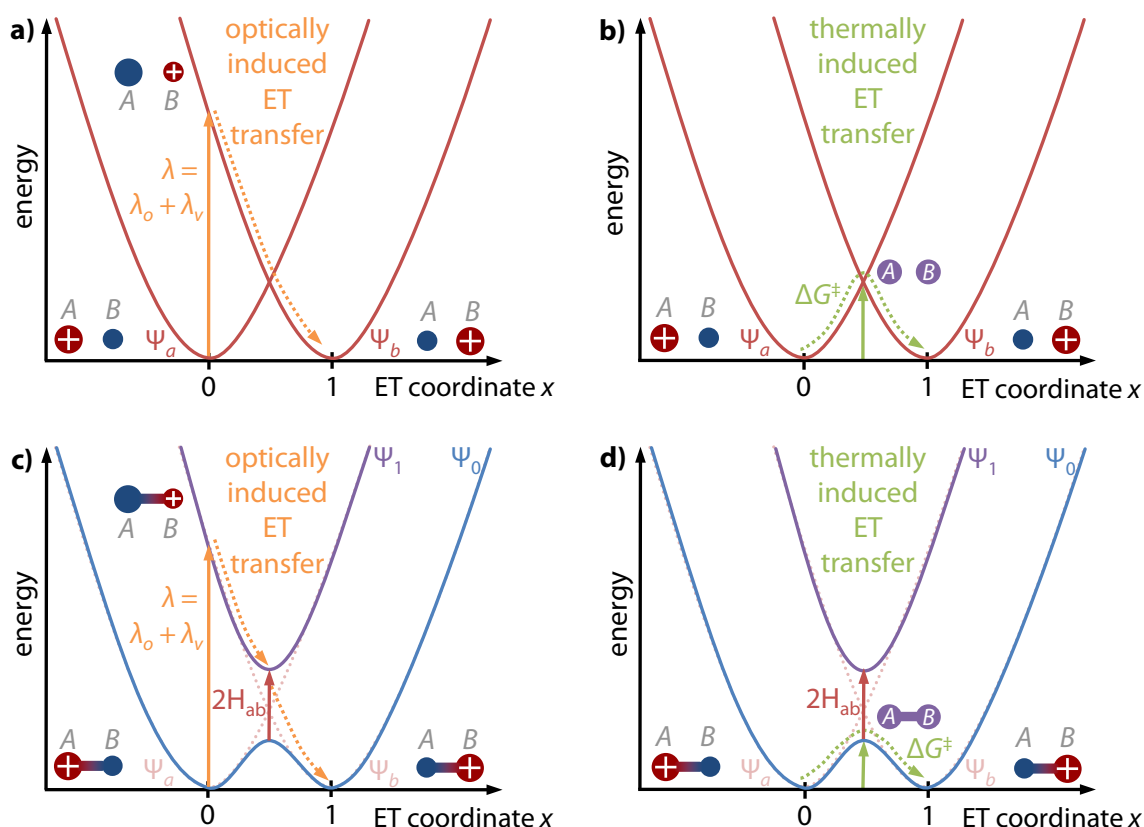


Figure 2.2. Top: Description of two diabatic states, represented by two non-interacting wave functions Ψ_a and Ψ_b – according to Marcus theory. a) Optically induced ET transfer from Ψ_a to Ψ_b requiring the energy λ . b) Thermally induced ET transfer from redox center A to redox center B requiring the energy $\Delta G^\ddagger$. Bottom: Adiabatic description according to Marcus-Hush/Mulliken-Hush theory: Mixing/coupling of the two wave functions Ψ_a and Ψ_b results into a ground state wave function Ψ_0 and an excited state wave function Ψ_1 with an electronic coupling $2H_{ab}$ between the two states Ψ_a and Ψ_b . Optically (c) and thermally (d) induced ET transfer is shown. Scaling of the redox centers corresponds to their geometrical arrangement. Additional vibrational modes in the potentials are omitted in all cases.

For a better understanding of ET processes, the behavior of the solvent molecules, which are directly linked to the ET transfer, as well as the solute itself, has to be looked into detail for both cases. In case (a), reorganization of the solvent molecules as well the inner reorganization is impossible within the time-scale of this Franck-Condon-type excitation of Ψ_a with a photon of the energy $h \cdot \nu$. Indeed, the charge is transferred to the other redox center (as vice versa for state Ψ_b), but there is no structural change (indicated by the size of

the redox centers in Figure 2.2a). In a CSM description (by extending classical Marcus theory to adiabatic states, see below), this corresponds to the non-equilibrium solvation (see Figure 2.1c). The solvent molecules and the molecule itself rearrange in the relaxation time τ , resulting in the final state Ψ_b , with relaxed solvent molecules and molecular structures of the solute. In the case of a thermally induced ET transfer (b), there is a continuous rearrangement of the solute and the solvent to the current charge distribution. Here charge transfer proceeds via a symmetrical transition state, where the charge is fully delocalized (Figure 2.2b). The rate constant k can then be calculated by an Arrhenius-type equation, using the free energy $\Delta G^\ddagger$.

However, the diabatic treatment of the two states in classical Marcus theory does not contain electronic coupling and is thus only valid for Robin-Day class I systems (see Figure 1.2a). An adiabatic treatment allowing the electronic communication between the two diabatic states Ψ_a and Ψ_b was introduced in Marcus-Hush theory.^[134] The electronic coupling is then defined as $2H_{ab}$ (Figure 2.2c and d), and the wave functions Ψ_0 (ground state) and Ψ_1 (first excited state) are linear combinations (with normalized coefficients) of Ψ_a and Ψ_b :

$$\Psi_0 = c_a \Psi_a + c_b \Psi_b \quad (2.46)$$

$$\Psi_1 = c_a \Psi_a - c_b \Psi_b. \quad (2.47)$$

The energies of the ground (E_0) and excited state (E_1) are then determined by solving the following secular determinant

$$\begin{vmatrix} H_{aa} - E & H_{ab} \\ H_{ab} & H_{bb} - E \end{vmatrix} = 0 \quad (2.48)$$

where the diabatic energies are defined as a function of the ET coordinate x

$$H_{aa} = \lambda x^2 \quad (2.49)$$

$$H_{bb} = \lambda(1-x)^2 + \Delta G^{00}. \quad (2.50)$$

If eqs. (2.49) and (2.50) are now inserted into the solution of eq. (2.48), the difference between E_1 and E_0 at the transition state structure is the electronic coupling $2H_{ab}$. As shown in Figure 2.2d, the barrier for thermal ET is lowered by H_{ab} compared to classical Marcus theory and can be calculated by

$$\Delta G^\ddagger = \frac{(\lambda - 2H_{ab})^2}{4\lambda}. \quad (2.51)$$

If harmonic potentials are used for the description of the diabatic states along the ET coordinate x , with the reorganization energy λ describing the curvature of the potential, an adiabatic double minimum potential is obtained if $2H_{ab}$ is smaller than λ (see Figure 1.2a and Figure 2.2c and d). This is the situation for typical class II systems. Increasing $2H_{ab}$ to λ leads to a class III system where the ET barrier separating the two minima vanishes and a single minimum (see Figure 1.2c) is achieved. In this strong coupling regime, where $2H_{ab}$ is at least as large as λ , the maximum of the IV-CT band corresponds exactly to the sum of the Marcus reorganization energy λ and ΔG^{00} (if present) (Figure 1.2c). The same applies for non-degenerate MV systems (**TAA11-15**) in which the redox centers are inequivalent, for example if different types of redox centers are employed.^[45] A special case arises for non-degenerate systems, if ΔG^{00} is as large as λ . In this case the barrier may vanish although the electronic coupling H_{ab} is still much smaller than λ .

One of the most important issues of the Mulliken-Hush theory (which is a generalization to the Marcus-Hush theory)^[134-136] is the extraction of the electronic coupling from the IV-CT band

$$H_{ab} = \frac{\mu_{t,1}(\lambda + \Delta G^{00})}{\Delta\mu_{ab}}. \quad (2.52)$$

To calculate the electronic coupling according to eq. (2.52), the transition dipole moment between the adiabatic states $\mu_{t,1}$ (ground and excited state) can be extracted from the IV-CT band by

$$\mu_{t,1}^2 = \frac{3hc\varepsilon_0 \ln 10}{2000\pi^2 N^2} \frac{9\eta}{(\eta^2 + 2)^2} \int \frac{E}{\nu} d\nu \quad (2.53)$$

and the diabatic dipole moment difference $\Delta\mu_{ab}$ according to

$$\Delta\mu_{ab} = \sqrt{\Delta\mu_{0,1}^2 + 4\mu_{t,1}^2}. \quad (2.54)$$

In these equations h is the Planck's constant, c the speed of light, ε_0 the permittivity of the vacuum, N is Avogadro's number, η the refractive index of the solvent, E the extinction coefficient and $\Delta\mu_{0,1}$ the difference between the dipole moments in the ground and first excited state.

As described above, classical Mulliken-Hush theory only takes two states into account. Since there are often additional absorption bands associated with charge transfer the so-called generalized Mulliken-Hush theory (GMH) was introduced.^[137-140] This approach includes a third state related to the localization of the charge at the bridge. Further aspects of this model are nicely reviewed by Heckmann and Lambert.^[5] It has to be noted that $2H_{ab}$ is also often labeled as $2V_{12}$ in literature. However, the electronic coupling will be denoted by $2H_{ab}$ in this work.

2.4.1 Experimental Classification

Experimental investigations on organic mixed-valence systems (especially on dinitroaromatic anions, see chapter 6) started in the 1960's by using electron spin resonance (ESR) to determine the electron transfer. At that time, the question of localization/delocalization was answered by analysis of hyperfine coupling constants (HFCs).^[141-152] Temperature-dependent ESR measurements in the early 1990's provide temperature-dependent rate constants k leading also to $\Delta H^\ddagger$ and $\Delta G^\ddagger$ extractable from Arrhenius plots.^[153-156] At the same time, analysis of the IV-CT band in UV/vis/NIR spectra according to Mulliken-Hush theory (see above) affords a classification of MV systems. While band shape analysis (the theoretical predictions are e.g. nicely reported by Brunschwig, Creutz and Sutin)^[7] of class II compounds lead to almost symmetric IV-CT bands, which can be fitted by Gaussian functions (to determine the maximum λ of the transition), compounds with a strong

electron coupling possess asymmetric IV-CT bands due to the cutoff of the (Boltzmann-weighted) transitions at the energy $2H_{ab}$.^[10, 15] The electronic coupling $2H_{ab}$ can then be obtained by eq. (2.52). However, the main challenge is the determination of the dipole moment difference between the diabatic states $\Delta\mu_{ab}$. As described above, it can be calculated by eq. (2.54) from the transition dipole moment $\mu_{t,1}$ between the adiabatic states and the dipole moment difference between the ground and the first excited state $\Delta\mu_{0,1}$. Hence, evaluation of the latter is crucial and can in principle be done by electro-optical absorption (EOA) spectroscopy.^[157-162] But such measurements require high electric fields which cannot be applied to liquid solutions of radical ions as these migrate in the electric field. For this reason only neutral systems like TAA11-17 can be investigated using this method. In rare cases, this value can be determined by Stark spectroscopy.^[157, 159, 160, 163] Nevertheless, this is the weak point of the Mulliken-Hush analysis. Furthermore, only limited direct experimental data is available on ground-state structures: just a handful of symmetrical structures have been characterized in the solid state, and the effect of crystal environment on symmetry breaking is being debated.^[164] Finally, experiments using photoelectron spectroscopy^[19, 165] and IR/Raman vibrational spectroscopy^[166] have been performed to classify MV compounds.

2.4.2 Theoretical Classification

2.4.2.1 Non-DFT methods

As experimental classification of MV compounds is challenging (e.g. the dipole moment difference between the adiabatic states $\Delta\mu_{0,1}$ is poorly determinable by experiments) it is thus often supported by quantum chemical methods. However, a full classification by such methods is lacking so far – for several reasons (see below).

Unrestricted Hartree-Fock (UHF) calculations, either *ab initio* or semi-empirical, tend to give structural symmetry breaking and thus localized charge and spin even in cases that are clearly on the delocalized side.^[15, 42, 167] This is accompanied by substantial spin contamination, and the predicted dipole moments are too large due to the overlocalization. This well-known observation reflects the lack of Coulomb correlation, which tends to delocalize charge to a certain extent. Keeping in mind the lack of a clear-cut separation, the correla-

tion can be distinguished loosely between non-dynamical correlation, with some near-degeneracy character (but also including the important left-right correlation in chemical bonds), and dynamical correlation that reflects the correlation cusp at small inter-electronic distances (see also section 2.1.2). The computational data available so far suggest that both types of correlation need to be taken into account simultaneously for a reliable picture of organic MV systems.

It is known that single-reference perturbation theory, e.g. MP2 theory, has difficulties with non-dynamical correlation. Indeed, there have apparently been no serious attempts so far to apply the MP2 method to such organic MV systems. Multi-configuration SCF calculations like, e.g., a complete-active-space SCF (CASSCF) account on the other hand for the non-dynamical correlation if a sufficiently extended active space is employed. Yet the dynamical correlation is missing in this case. Results of the few CASSCF calculations available so far on (relatively small) organic MV systems suggest that these do not sufficiently compensate for the tendency of UHF calculations to over-localize.^[41, 168-171]

A large configuration-interaction (CI) or coupled-cluster (CC) calculation that takes into account higher-order excitations, or a suitable multi-reference-CI or -perturbation calculation, account for both dynamical and non-dynamical correlation effects. As a consequence such methods should be adequate. However, when carried out within an *ab initio* framework, their computational cost and unfavorable scaling with system size makes such high-level post-HF calculations computationally too expensive to be currently applied to structural optimizations for the size of MV compounds of chemical or technological interest. With very few exceptions for small models, multi-reference techniques^[41, 171, 172] or, for example, CCSD(T) calculations^[173, 174] have so far not been applied to the question of symmetry breaking of organic MV systems. Note that a reasonably accurate treatment of the dynamical correlation part (of the correlation cusp) requires the use of rather large one-particle basis sets. This accounts in part for the very large computational effort involved, in addition to huge amount of states/determinants needed for multi-reference calculations.

Clark and coworkers^[42] and others^[16, 18, 33, 163, 167, 175-177] have applied semi-empirical CI calculations (AM1-CI) to a number of organic MV systems and obtained substantial insights. When used within a semi-empirical framework, the CI covers mainly the non-dynamical correlation part, whereas it is assumed that the semi-empirical parameterization of the method accounts for the dynamical correlation part (note that semi-empirical MO methods are mainly using minimal basis sets and thus could not provide the dynamical correlation explicitly with sufficient accuracy). Obviously, this limits somewhat the scope and quantitative predictive power of this method. The advantage is of course the low computational effort. So far there has been no systematic evaluation of semi-empirical CI methodology for organic MV systems near the class II/III borderline.

2.4.2.2 DFT methods

Today, the most widely used methodology to incorporate electron correlation for larger systems (within a formally single-determinant approach) is Kohn-Sham density functional theory (DFT, see section 2.2). Thus, DFT methods are currently the workhorse of applied quantum chemistry taking electron correlation implicitly into account. It is usually assumed that the exchange part of local or semi-local exchange-correlation functionals mimics to a certain extent non-dynamical correlation (see section 2.2). Obviously, the accuracy of Kohn-Sham DFT depends crucially on the quality of the (approximate) functional. In contrast to the post-HF methods, a systematic improvement of the functional towards an exact theory is usually not achieved (unless one applies the same kind of Hilbert-space expansions of electron correlation as for the former, with a correspondingly unfavorable computational scaling).^[178-181]

However, DFT with “pure” (i.e. local or gradient corrected) or standard hybrid exchange-correlation functionals has been found to give an overly delocalized description.^[34, 182] That is, even localized class II systems are typically computed to be delocalized. This has to do with the self-interaction error (SIE) in the standard functionals, which favors too pronounced delocalization (see section 2.2.2). In contrast to HF theory, most approximate exchange functionals do not correctly cancel the interaction of an electron with its own charge cloud that arises as part of the classical Coulomb term of Kohn-Sham theory. The

remaining SIE is a serious problem of most contemporary functionals and leads towards too delocalized density or spin-density distributions (see section 2.2.2). These problems extend way beyond organic MV systems but are particularly manifest for the latter. As a result, standard functionals with local or semi-local (GGA or related) character will artificially delocalize systems of distinctly localized character since they are not too far from the class II/III borderline. The latter condition seems to be met for most organic MV systems except for those where the two redox centers are largely de-coupled, e.g. by extended saturated spacers. Matters are different for mixed-valence multinuclear transition-metal complexes. In many cases, these seem to be sufficiently localized, in particular for 3d transition-metal systems, so that even standard GGA functionals provide a well-defined localization of spin on the different metal centers. This is important, in particular in the context of a computational treatment of molecular magnetism or of certain multinuclear metalloenzymes (e.g. for iron-sulfur clusters or the multinuclear manganese cluster in photosystem II). However, there is evidence that, e.g., the famous Creutz-Taube ion is insufficiently described by standard GGA functionals.

A way to reduce SIE is the inclusion of some amount of exact Hartree-Fock exchange into the exchange functional, replacing some of the (semi-)local exchange. This is done in the abovementioned hybrid functionals (see section 2.2.1). The most popular hybrid functional is the B3LYP functional.^[62] As remarked above, HF exchange cancels the Coulomb SIE exactly. However, an introduction of 100% exact exchange removes all of the local or semi-local exchange, which before mimicked some of the non-dynamical correlation. The latter would thus have to be reintroduced explicitly, a task that so far has not been solved completely with computationally efficient functionals (see below). Therefore one has to find some compromise between a reduction of SIE and a partial conservation of non-dynamical correlation contributions. In the case of B3LYP this leads to 20% HF exchange and 80% semi-local exchange (with some semi-empirical scaling of the gradient corrections to exchange and correlation). While this seems to provide reasonable thermo-chemical accuracy for many “normal” systems, the relatively low amount of exact exchange appears to be too low to fully correct the over-delocalization produced by (semi-)local functionals.

The suggested protocol which was derived during this work is thus based on hybrid functionals with higher exact-exchange admixture (see chapter 3). Due to low computational cost, this allows ground state structure optimizations with and without symmetry constraints (leading to ET barriers $\Delta H^\ddagger$, dipole moments μ_o , spin-density distributions, bond lengths, HFCs), and excited state calculations using TDDFT (leading to excitation energies $E_{i,\dots,n}$, transition dipole moments $\mu_{i,1\dots n}$, excited states dipole moments $\mu_{1\dots n}$ and electronic couplings $2H_{ab}$).

If calculated values are compared with experimental values, one has to keep in mind the following points: first of all, neither zero-point vibrational corrections nor thermal corrections have been applied to the internal energies of the asymmetrical minima ($E(C_1)$) and the symmetrical transition-state structures ($E(C_{i,2,s})$) to obtain the reported computational thermal ET barriers $\Delta H^\ddagger$ (this is the difference of computed absolute energies after full geometry optimization with- and without symmetry constraints, $E(C_{i,2,s}) - E(C_1)$). Note, however, that the various solvent models do include solvent thermal effects (and even some entropic contributions), but these approximations cause uncertainties in the computed activation enthalpies which are estimated to at least 5 kJ mol^{-1} . Furthermore, reported dipole moments are always given with respect to the center of charge because dipole moments of charged systems are not well defined. Anyhow, the dipole moments provide a very useful indicator for localization/delocalization, in particular when the delocalized structure features no dipole moment. Since mostly no experimental dipole moments are available this does not cause any problems. In addition, the maxima of experimental IV-CT bands λ are fitted by Gaussian functions leading to some uncertainty of these values which is especially challenging if neighboring bands exist.

2.4.2.3 Environmental Effects

Apart from the difficulties of including exchange as well as non-dynamical and dynamical correlation in a balanced way and avoiding SIE, other obstacles that may prevent the accurate computational description of organic MV systems in realistic experimental situations have to be taken into account as well: clearly, environmental effects have to be considered, as most experimental and spectroscopic studies are performed in a condensed-

phase environment. It is clear that the symmetry breaking or charge localization in, for example, solution or in crystals will differ from the gas-phase situation. In particular, electrostatic effects will tend to stabilize a charge-localized situation, and in this context a more polar environment will be more effective than a less polar one. Of course, matters are more complex, and solvent polarity (indicated by the dielectric constant ϵ) is not the only parameter that affects the symmetry breaking. Within a Mulliken-Hush picture (see Figure 2.1a and c), it is the solvent reorganization energy, λ_o , that is a main parameter governing the electron transfer.^[37, 42, 176, 183-186] A low λ_o will favor a delocalized situation, whereas a larger λ_o will enhance symmetry breaking and move the system towards a class II situation.^[5] Notably, a co-existence of localized and delocalized MV systems in the same (intermediate λ_o) solvent has very recently been reported for a dinitro-tolane MV radical anion (**DN5**).^[183]

A full description of microscopic solvation would require dynamical simulations that include both short-range specific solvation as well as long-range dielectric effects. Such simulations are computationally demanding and will currently not be possible for all MV systems of interest. Therefore, the protocol described below (see chapter 3 and ref. [44]) is so far based on a polarizable continuum solvent model (see section 2.3). Two types of limitations thus have to be kept in mind: On the one hand, even for the ground state, specific solvent effects may be important. For example, it has been argued that dinitroaromatic anions may act as donors towards acceptor solvent molecules like DMSO or DMF.^[176] Such specific solute-solvent interactions will be somewhat less important for the bulky cationic triarylamine systems, discussed in chapter 3-5, yet they will be important for the dinitroaromatic and diquinone systems in chapter 6 and 7. Thus, improvements of solvation models are necessary. On the other hand, the description of electron transfer, e.g. by TDDFT calculations of charge transfer excitation energies, require consideration of non-equilibrium solvation. The implications will be discussed further below in section 6.4.1.

It is to be expected that environmental effects will be most pronounced when dealing with overall charged MV systems, especially for ground state optimizations. This holds for the bis-triarylamine radical cations (**TAA1-10**) studied in the first validation study of the

computational protocol (chapter 3 and 4),^[44, 45] and it should hold even more for another well-known class of organic MV systems, the abovementioned dinitroaromatic radical anions (**DN1-6**),^[42, 156, 171, 176, 183, 185-190] for which the computational protocol was extended (see chapter 6 and ref. [46]). However, there are only few investigations using such solvent effects for ground state optimizations.^[42, 43]

Chapter 3

It is also a good rule not to put too much confidence in experimental results until they have been confirmed by theory.

-- Sir Arthur Eddington

3 Derivation of the Quantum Chemical Protocol

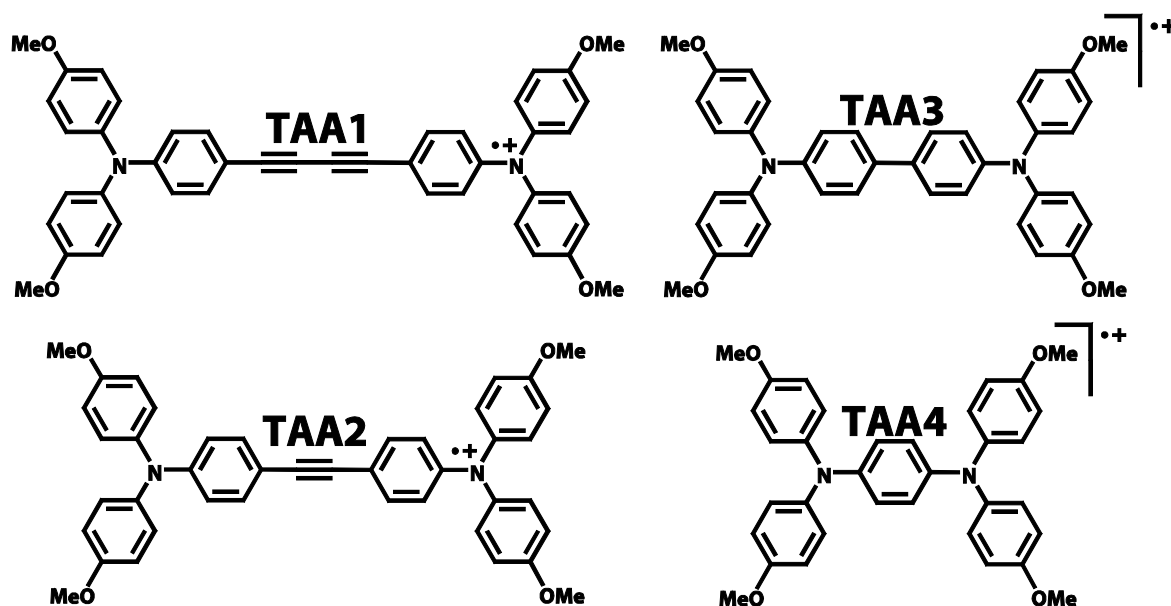
3.1 Introduction

The experimental and theoretical classification of (organic) mixed-valence (MV) systems is often difficult, especially for systems at the class II/III borderline, as described in section 2.4. The quantum chemical description of MV systems has been restricted so far to non-systematic studies mostly using that quantum chemical method which was able to describe the experimental observation closest (see section 2.4.2). So the predictive power of these methods is limited. A systematic quantum chemical study is thus highly desirable to enable a computational Robin-Day classification as well as the quantitative prediction of various properties of the ground and excited states of MV compounds.^[44] However, it has turned out that this is a challenge for the existing computational methodology which has already been described in section 2.4.2. Just in short, the combination of HF-theory and DFT in hybrid functionals (2.2.1) seems to be a reasonable and inexpensive approach to cope with the issue of describing the charge localization or delocalization in MV systems. In addition, solvent effects are expected to have a decisive influence on the point of symmetry breaking (especially on class II MV systems, see sections 2.3 and 2.4.2.3) so that these should be included in the computations to obtain a reliable description.

For this systematic validation study, a molecular test set is mandatory, fulfilling at least the following requirements:

- a.* The test set must contain class II as well as class III systems, and systems at the borderline of class II/III.
- b.* The molecules should exhibit systematic behavior, i.e. they should belong to the same class of molecules, to reduce the amount of parameters, which might have an influence on the results.
- c.* Experimental information is essential to calibrate the method, so only systems with enough experimental data (e.g. IV-CT bands, ET barriers) can be taken into account.
- d.* Specific, short-range solvent effects (e.g. hydrogen bonding) should not play a decisive role to avoid expensive molecular dynamics simulations, and since only long-range solvent effects are covered by common solvation models implemented in typical quantum chemical programs (see section 2.3).
- e.* Moderate-sized molecules are necessary due to computational efficiency.

These conditions are fulfilled for example by a series of four mixed-valence bis-triarylamine (TAA) radical cations (Scheme 3.1) that are all close to the class II/III borderline (condition *a*), but all to a different extent. They have been studied experimentally in detail as well as by standard DFT and TDDFT calculations, albeit only symmetrical ground-state structures are considered and solvent effects are neglected (condition *c*).^[182] Furthermore, these cations differ exclusively in the bridge unit between the two triarylamine centers (condition *b*). The decreasing distance between the triarylamine redox centers in **TAA1-4** goes along with an increase of electronic coupling between the associated diabatic states as obtained by analysis of the NIR spectra within a two-dimensional two-state model including an asymmetric as well as a symmetric ET coordinate (in cm^{-1}):^[20] $H_{\text{ab}} = 1790$ (**TAA1**), 2400 (**TAA2**), 2800 (**TAA3**) and 4300 (**TAA4**). In addition, the positive charge in localized systems is well shielded by the large 4-methoxyphenyl-moieties (condition *d*), which is an important advantage compared to the dinitroaromatic radical anions studied in chapter 6. Furthermore, condition *e* is fulfilled since **TAA1-4** are molecules of moderate size for DFT.



Scheme 3.1: Four bis-triarylamine (TAA) radical cations used for the derivation of the quantum chemical protocol.

The systematic validation of this molecular test set is performed by a threefold strategy.

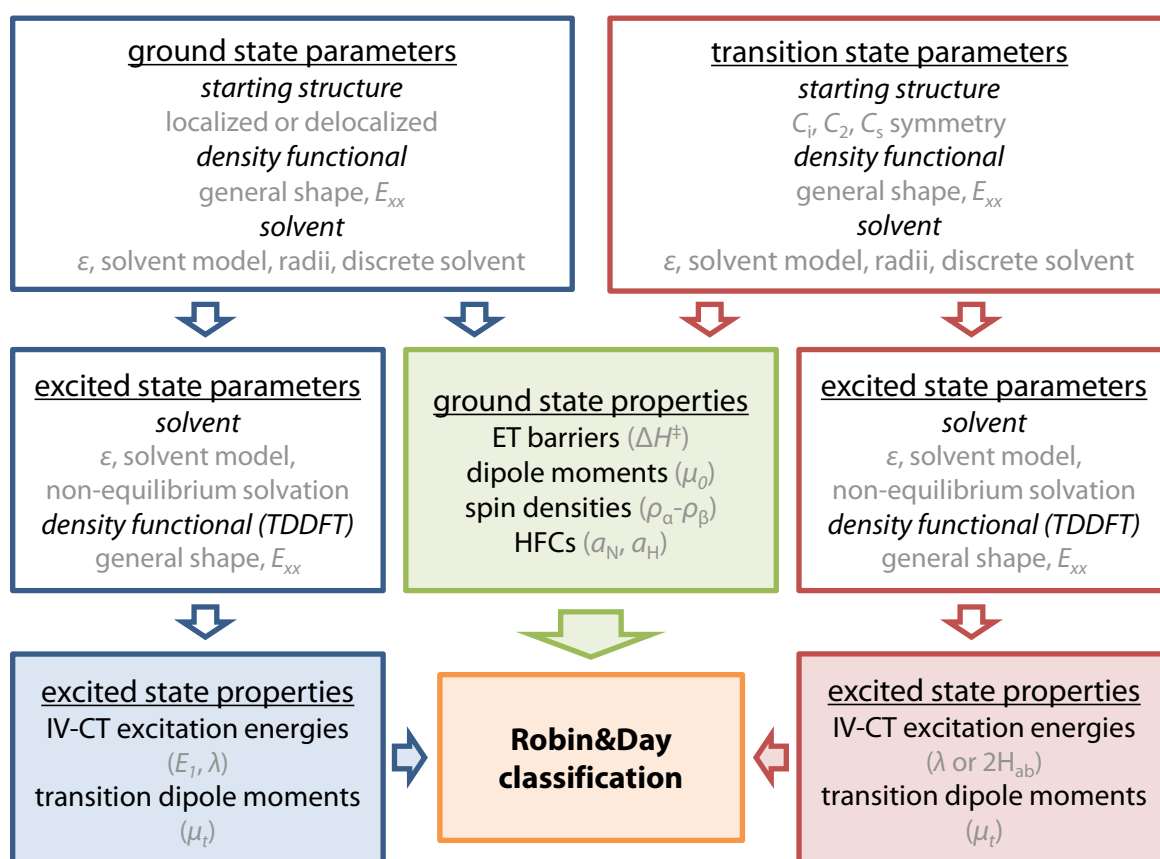
First, the amount of exact-exchange admixture a (see eq. (3.1) below) in a set of general global hybrid functionals will be varied systematically and the value of a at which charge localization occurs, will be examined. This will be done by scrutinizing in each case structure, dipole moment, spin-density distribution, and electron-transfer barrier.

Second, as most experiments on such systems are carried out in solution, gas-phase results will be compared with calculations including solvent effects via a conductor-like screening (COSMO)^[120] continuum solvent model for the nonpolar solvent hexane, the polar solvent acetonitrile, and to some extent the intermediate-polarity solvent dichloromethane (which is predominantly used for vis/NIR spectroscopy on these systems). This procedure allows not only to quantify the influence of dielectric solvent effects on the charge localization/delocalization preferences in organic MV radical cations but also to provide guidelines for a practical computational protocol (see below).

Third, IV-CT transition energies computed by time-dependent DFT (TDDFT) will be compared for both localized and delocalized structures to characterize the nature of the

system for a given solvent and to their corresponding, experimentally available IV-CT bands.

Finally, this computational protocol – based on customized hybrid functionals, continuum solvent models, and TDDFT computation of excitation energies – should allow a reliable positioning of such organic MV systems along the localized-delocalized coordinate.^[44] In addition, it should provide a basis to evaluate alternative, possibly more sophisticated methods, which will be described in the following chapters.



Scheme 3.2. Overview of the parameters used in this quantum chemical protocol (hollow boxes, parameters in *italics*, properties in grey) and ground as well as excited state properties derived from it (filled boxes).

Scheme 3.2 shows an overview of the scope of this protocol, including parameters which can be varied and potential properties. The focus in this chapter lies on the following parameters (cf. computational details): (i) for the ground as well as excited state, the

amount of exact-exchange admixture (E_{xx}) and the influence of the solvent (characterized by the dielectric constant ϵ) are investigated for unsymmetrical and C_i -symmetrical structures (which corresponds to the transition state for class II systems). (ii) The resulting properties are compared with available experimental data (especially IV-CT energies).

All other parameters will be evaluated in the following chapters. While the focus in chapter 4 and 5 lies on the extension of this protocol to further TAA-based molecules and new properties (e.g. hyperfine coupling constants, HFCs), chapter 6 and 7 will deal mainly with other density functionals and solvent models applied to dinitroaromatic or diquinone radical anions.

3.2 Available Experimental Information

The four organic mixed-valence radical cations studied (see Scheme 3.1) all feature two *N,N*-di(4-methoxyphenyl)-moieties with different bridges. Compound **TAA1**, *bis*-[4-[*N,N*-di(4-methoxyphenyl)amino]phenyl]-butadiyne, has the largest separation between the coupled redox centers. This distance is successively shortened by changing the bridge to a single diphenylacetylene in **TAA2**, *bis*-[4-[*N,N*-di(4-methoxyphenyl)amino]phenyl]-acetylene, to a biphenylene bridge in **TAA3**, 4,4'-*bis*[*N,N*-di(4-methoxyphenyl)amino]-biphenyl, and to a single phenylene bridge in **TAA4**, *N,N,N',N'*-tetra(4-methoxyphenyl)-1,4-phenylenediamine. Experimental evidence points to a class II character of **TAA1**, albeit with substantial electronic coupling. It shows an absorption maximum at 7550 cm⁻¹ in DCM with a transition dipole moment of 6.39 Debye^[15] and an electronic coupling of 3580 cm⁻¹ obtained from near-IR in DCM again.^[20] Compound **TAA2** is more strongly coupled but was indicated to be possibly still on the class II side, based on the shape of the IV-CT band (6190 cm⁻¹ in DCM ($\mu_t = 11.6$ Debye) and 7990 cm⁻¹ in MeCN)^[15, 191] and on the lack of inversion symmetry in the vibrational spectra in DCM (on the ESR time scale, no symmetry breaking has been detected, which suggests a small electron-transfer barrier, $2H_{ab} = 4800$ cm⁻¹).^[15, 20, 33, 191] Based on NIR spectra and vibrational data, compound **TAA3** is likely just on the class III side of the border,^[164] whereas **TAA4** can be considered to be a more clear-cut class III case (see also below).^[166] The absorption maximum of **TAA3** in

DCM is 6360 cm^{-1} ($\mu_t = 11.6$ Debye),^[15] while 2H_{ab} is estimated at 5600 cm^{-1} from near-IR spectra.^[20] These values are even higher for **TAA4**, $\lambda = 9530\text{ cm}^{-1}$ ($\mu_t = 9.17$ Debye),^[15] and an electronic coupling of 8600 cm^{-1} in DCM.^[20] X-ray structure determinations for salts of systems closely related to **TAA3** and **TAA4** (derivatives without the methoxy substituents) gave symmetrical structures which are also supported by Raman and IR spectroscopic measurements.^[166]

3.3 Computational Details

Structure optimizations as well as bonding analyses were performed with locally modified versions of TURBOMOLE 5.9 and 5.10,^[192] that allows the exact-exchange admixture in a global hybrid functional to be varied. The “custom hybrid” exchange-correlation functionals were constructed according to eq. (3.1), which is equal to eq. (2.29) in section 2.2.1, by varying the exact-exchange coefficient a , largely in steps of 0.1, between 0.0 and 1.0, i.e. between the “pure” gradient-corrected BLYP functional^[58, 60] ($a = 0.0$) via the BHLYP hybrid functional with 50% exact exchange ($a = 0.5$) to a functional made from 100% exact exchange ($a = 1.0$) with LYP correlation^[60] on top (the point $a = 0.1$ has been skipped, as it brings little further information). In some cases, pure HF calculations without correlation functional have been performed as well. SVP basis sets were employed on all atoms^[193] (test calculations with larger TZVP basis sets^[194] did not change the obtained results noticeably).

$$E_{\text{XC}} = (1 - a)(E_{\text{X}}^{\text{LSDA}} + \Delta E_{\text{X}}^{\text{B88}}) + a \cdot E_{\text{X}}^{\text{HF}} + E_{\text{C}}^{\text{LYP}} \quad (3.1)$$

In addition to gas-phase optimizations, calculations with the COSMO solvent model^[120] have been performed for *n*-hexane ($\epsilon = 1.89$), for dichloromethane (DCM, $\epsilon = 8.93$), and for acetonitrile (MeCN, $\epsilon = 36.64$). Near the critical values of a , where symmetry breaking occurs, the outcome of the structure optimizations sometimes depended on whether a symmetrical or unsymmetrical starting structure is used (see Scheme 3.2). In those cases, unsymmetrical starting structures (C_1) as well as symmetrical ones (C_i) have been employed. For unsymmetrical cases, this led to a lower energy of the symmetry-broken structure. For **TAA1**, different rotational conformers have been investigated. In some cases

(for **TAA1**, $a = 0.3$ in acetonitrile, $a = 0.4$ in the gas phase and in acetonitrile, $a = 0.6$ in hexane, and $a = 0.8$ in the gas phase and in acetonitrile), the stationary points on the potential energy surface have been characterized by harmonic vibrational frequency analysis. The electron transfer (ET) barrier $\Delta H^\ddagger$ was subsequently calculated as the energy difference between the C_i -symmetric transition state and the unsymmetric C_1 -optimized minimum, neglecting entropic contributions. Spin-density isosurface plots were obtained with the Molekel program.^[195]

Subsequent TDDFT-calculations of the lowest-energy electronic transitions (IV-CT bands) for both C_1 and C_i structures were done with the Gaussian 03 program (Go3),^[196] using the same type of custom hybrids and SVP basis sets^[193] as discussed above. In the Go3 calculations, solvent effects have been included by the CPCM keyword, which denotes the polarizable continuum model that is closest to the COSMO model used in the optimizations (see section 2.3).^[121] However, calculations with the more sophisticated IEF-PCM model^[197] gave almost identical data. The use of Go3 was initially motivated by the lack of custom hybrids in the local version of TURBOMOLE. During the course of this thesis, the custom hybrids were implemented, and test calculations with TURBOMOLE were done. While gas-phase calculations gave almost identical results as the Go3 data, the solvent-based calculations gave about 150-500 cm^{-1} larger excitation energies (depending on functional and system) for clearly localized, unsymmetrical structures, and about 800-1800 cm^{-1} larger values for symmetrical structures. As the Go3 results were consistently much closer to experiment, they are reported in the following sections. Obviously, the differences arise from technical details (van-der-Waals radii, solvent radii, number of tesserae per sphere, see also section 2.3) in the two solvent-model implementations, especially from the non-equilibrium solvation, which is only available in Go3. A more detailed investigation of these parameters is given in chapter 6. Test calculations with hybrid functionals constructed from other gradient-corrected exchange and correlation contributions (PBE) gave slightly shorter bonds but essentially the same behavior regarding the fraction of exact exchange at which charge localization occurs in a given environment (and similar IV-CT excitation energies).

3.4 Results and Discussion

3.4.1 Ground state calculations

The main results for the ground states of the radical cations **TAA1-4** are summarized in Table 3.1-3.4, which provide the C_{An} -N distances as indication for structural symmetry breaking (further structural data are available in Table S3.1-3.4 in the Appendix), the dipole moments, the electron transfer barriers, as well as the S^2 expectation values. Comparison of the latter has to be taken with some caution for hybrid DFT computations with different amounts of nonlocal Hartree-Fock-like exchange but should provide a reasonable measure of the quality of the spin-density distributions obtained. Figure 3.1 gives an illuminating overview over the most important trends by plotting the computed electron transfer barriers for compounds **TAA1-3** (**TAA4** remains delocalized – class III – at all DFT levels in the gas phase and in all solvent models; see below).

First of all, the general trends will be examined before looking at the individual MV radical cations in more detail. Taking the exact-exchange admixture a at which symmetry breaking occurs and an ET barrier develops in a given environment (gas phase *vs.* hexane *vs.* dichloromethane *vs.* acetonitrile solvent) as an indication for the localized *vs.* delocalized character, the expected trend from **TAA1** towards **TAA4** is found: the critical exact-exchange admixture at which a ET barrier is formed in a given environment moves from left to right (compare Table 3.1 and Figure 3.1). This is consistent with the weakest electronic coupling for the longest bridge in **TAA1** and the strongest coupling for the shortest bridge in **TAA4**. The influence of the COSMO continuum solvent is striking. All gas-phase calculations require exceedingly large exact-exchange admixtures for symmetry breaking even for compound **TAA1**, which should be most clearly on the localized class II side. A low-polarity solvent like hexane moves the point of symmetry breaking to a somewhat lower value of a . Yet, the effect of the more polar dichloromethane and acetonitrile solvents is much larger, indicating that solvent polarity may have a dramatic effect on the electron-transfer characteristics of a given MV radical cation^[37, 176] (in DCM, the point of symmetry breaking is at about 5-10% larger than in MeCN). Electrochemical and spectroscopic experiments on such radical ions are usually done in such solvents of moderate to apprecia-

ble polarity. Therefore, the MeCN results can be regarded as a reasonably realistic simulation of typical experimental conditions for electrochemistry, and the DCM results as particularly realistic for optical spectroscopy (see below).

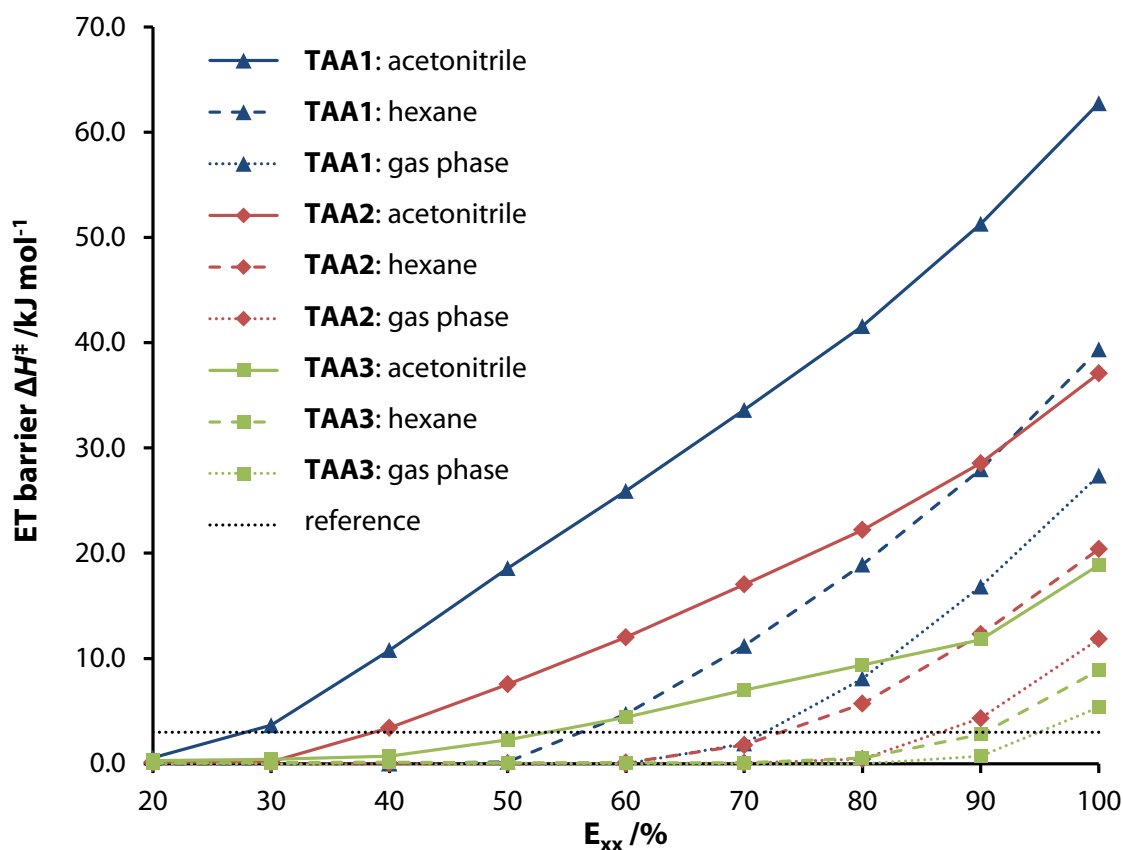


Figure 3.1. ET barriers of **TAA1-3** as a function of exact exchange admixture and solvent environment. For **TAA4** all functionals provide a zero ET barrier, see Table 3.4. A reference line for small ET barriers has arbitrarily been set at 3.0 kJ mol⁻¹.

Furthermore, it must be noted, that after the point of symmetry breaking the curves of the electron transfer barriers for the three cations **TAA1-3** increase slightly more than linearly with exact-exchange admixture (Figure 3.1). Dipole moments show a dramatic increase around the critical a values and a rather moderate one at even higher values of a (cf. Table 3.1-3.3).

Table 3.1. Calculated key ground state parameters for **TAA1** as a function of E_{xx} and solvent environment^a

%HF	BLYP	20	30	35	40	50	60	70	80	90	100
<i>gas phase</i>											
μ_o^b	0.02	0.14	0.01	0.03	0.03	0.03	0.04	22.09	25.38	27.30	28.37
$\Delta H^\ddagger$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.9	8.1	16.8	27.4
$\langle S^2 \rangle$	0.75	0.76	0.77	0.78	0.78	0.80	0.81	0.94	1.05	1.23	1.49
$d_1(\text{C}_{\text{An}}\text{-N})$	1.436	1.429	1.427	1.426	1.425	1.425	1.423	1.418	1.413	1.409	1.406
$d_2(\text{C}_{\text{An}}\text{-N})$	1.436	1.429	1.427	1.426	1.425	1.425	1.423	1.407	1.400	1.394	1.391
<i>hexane</i>											
μ_o^b	0.05	0.39	0.02	0.02	0.06	19.34	26.42	28.24	29.13	29.91	30.21
$\Delta H^\ddagger$	0.0	0.0	0.0	0.0	0.0	0.2	4.7	11.2	18.9	28.0	39.4
$\langle S^2 \rangle$	0.75	0.76	0.77	0.78	0.78	0.82	0.88	0.95	1.06	1.23	1.49
$d_1(\text{C}_{\text{An}}\text{-N})$	1.436	1.429	1.427	1.426	1.426	1.412	1.401	1.397	1.393	1.389	1.387
$d_2(\text{C}_{\text{An}}\text{-N})$	1.436	1.430	1.427	1.426	1.425	1.424	1.420	1.416	1.412	1.409	1.406
<i>dichloromethane</i>											
μ_o^b	0.02	0.39	5.03	26.82	29.33	31.24	31.89	32.17	32.23	32.22	32.32
$\Delta H^\ddagger$	0.3	0.2	0.2	3.2	6.1	13.3	20.9	28.5	36.9	45.9	57.5
$\langle S^2 \rangle$	0.75	0.76	0.77	0.79	0.80	0.82	0.87	0.94	1.05	1.23	1.50
$d_1(\text{C}_{\text{An}}\text{-N})$	1.435	1.428	1.424	1.408	1.404	1.422	1.393	1.429	1.412	1.409	1.405
$d_2(\text{C}_{\text{An}}\text{-N})$	1.435	1.428	1.428	1.428	1.426	1.398	1.419	1.426	1.389	1.386	1.385
<i>acetonitrile</i>											
μ_o^b	0.04	3.56	28.07	29.89	31.17	32.27	32.75	33.14	33.13	33.04	32.97
$\Delta H^\ddagger$	0.5	0.6	3.7	7.2	10.8	18.6	25.9	33.6	41.6	51.3	62.8
$\langle S^2 \rangle$	0.75	0.76	0.78	0.79	0.80	0.82	0.87	0.93	1.04	1.22	1.49
$d_1(\text{C}_{\text{An}}\text{-N})$	1.435	1.427	1.409	1.406	1.402	1.397	1.393	1.388	1.386	1.384	1.382
$d_2(\text{C}_{\text{An}}\text{-N})$	1.435	1.430	1.430	1.428	1.426	1.422	1.419	1.415	1.412	1.409	1.406

^a Dipole moments μ_o in Debye, ET barriers $\Delta H^\ddagger$ in kJ mol⁻¹ and C_{An}-N bond lengths (d_1 , d_2) in Å. ^b With the center of mass as the origin.

Having a closer look at the results for the individual cations, gas-phase calculations require about 70% exact-exchange admixture for symmetry breaking in the most clear-cut class II case **TAA1** (see Table 3.1 and Figure 3.1). This is accompanied by substantial spin contamination, which indicates unphysically large valence-shell spin polarization. A COSMO hexane model shifts the critical a value from 0.7 to 0.6, still with substantial spin contamination in the localized case (Table 3.1). Notably, both in the gas phase and in hexane, the critical step in a from a delocalized to a localized solution is accompanied by a dramatic enhancement of the S^2 expectation value. In contrast, in MeCN, charge localization starts to

occur at more reasonable exact-exchange admixtures of about 30%. In this case, the S^2 value increases only very little, from 0.76 at $a = 0.2$ to 0.78 to $a = 0.3$, indicating almost negligible spin contamination. A further moderate increase is found at $a = 0.4$ and $a = 0.5$ in this case. The ET barrier also increases in a continuous fashion in MeCN, whereas the changes are more abrupt at the high a values needed in the gas phase or in hexane. The DCM data indicate a slightly larger critical step at around 35% exact exchange.

Table 3.2. Calculated key ground state parameters for **TAAz** as a function of E_{xx} and solvent environment^d

%HF	BLYP	20	30	35	40	50	60	70	80	90	100
<i>gas phase</i>											
μ_o^b	0.02	0.14	0.09	0.03	0.04	0.01	0.12	0.18	13.92	17.52	21.40
$\Delta H^\ddagger$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.4	4.3	11.9
$\langle S^2 \rangle$	0.75	0.76	0.77	0.77	0.78	0.79	0.80	0.82	0.93	1.07	1.36
$d_1(\text{C}_{\text{An}}-\text{N})$	1.435	1.429	1.427	1.426	1.426	1.424	1.423	1.421	1.416	1.412	1.407
$d_2(\text{C}_{\text{An}}-\text{N})$	1.435	1.429	1.426	1.425	1.426	1.425	1.423	1.421	1.412	1.407	1.393
<i>hexane</i>											
μ_o^b	0.04	0.10	0.08	1.25	0.18	0.02	0.16	18.33	20.58	23.04	23.98
$\Delta H^\ddagger$	0.0	0.1	0.1	-0.2	0.0	0.0	0.1	1.8	5.7	12.3	20.4
$\langle S^2 \rangle$	0.75	0.76	0.77	0.77	0.78	0.79	0.80	0.91	1.01	1.17	1.41
$d_1(\text{C}_{\text{An}}-\text{N})$	1.435	1.428	1.427	1.428	1.426	1.425	1.423	1.419	1.416	1.410	1.405
$d_2(\text{C}_{\text{An}}-\text{N})$	1.435	1.428	1.427	1.425	1.426	1.425	1.423	1.407	1.401	1.392	1.389
<i>dichloromethane</i>											
μ_o^b	0.02	0.10	0.07	10.07	19.83	23.14	25.17	25.82	25.76	25.74	26.06
$\Delta H^\ddagger$	0.1	0.1	0.1	0.1	0.7	4.4	8.5	13.2	18.4	24.9	33.3
$\langle S^2 \rangle$	0.75	0.76	0.77	0.78	0.79	0.82	0.86	0.93	1.03	1.18	1.42
$d_1(\text{C}_{\text{An}}-\text{N})$	1.435	1.428	1.427	1.428	1.427	1.427	1.426	1.427	1.413	1.410	1.406
$d_2(\text{C}_{\text{An}}-\text{N})$	1.435	1.428	1.426	1.421	1.410	1.427	1.427	1.426	1.389	1.387	1.385
<i>acetonitrile</i>											
μ_o^b	0.03	1.39	0.27	20.09	23.30	25.48	26.22	26.35	26.67	26.73	26.84
$\Delta H^\ddagger$	0.1	0.2	0.2	1.5	3.4	7.5	12.0	17.0	22.2	28.6	37.1
$\langle S^2 \rangle$	0.75	0.76	0.77	0.78	0.79	0.82	0.86	0.93	1.03	1.19	1.43
$d_1(\text{C}_{\text{An}}-\text{N})$	1.435	1.428	1.427	1.428	1.426	1.422	1.418	1.416	1.412	1.408	1.405
$d_2(\text{C}_{\text{An}}-\text{N})$	1.435	1.429	1.427	1.412	1.406	1.399	1.394	1.392	1.388	1.387	1.384

^a Dipole moments μ_o in Debye, ET barriers $\Delta H^\ddagger$ in kJ mol^{-1} and $\text{C}_{\text{An}}-\text{N}$ bond lengths (d_1 , d_2) in Å. ^b With the center of mass as the origin.

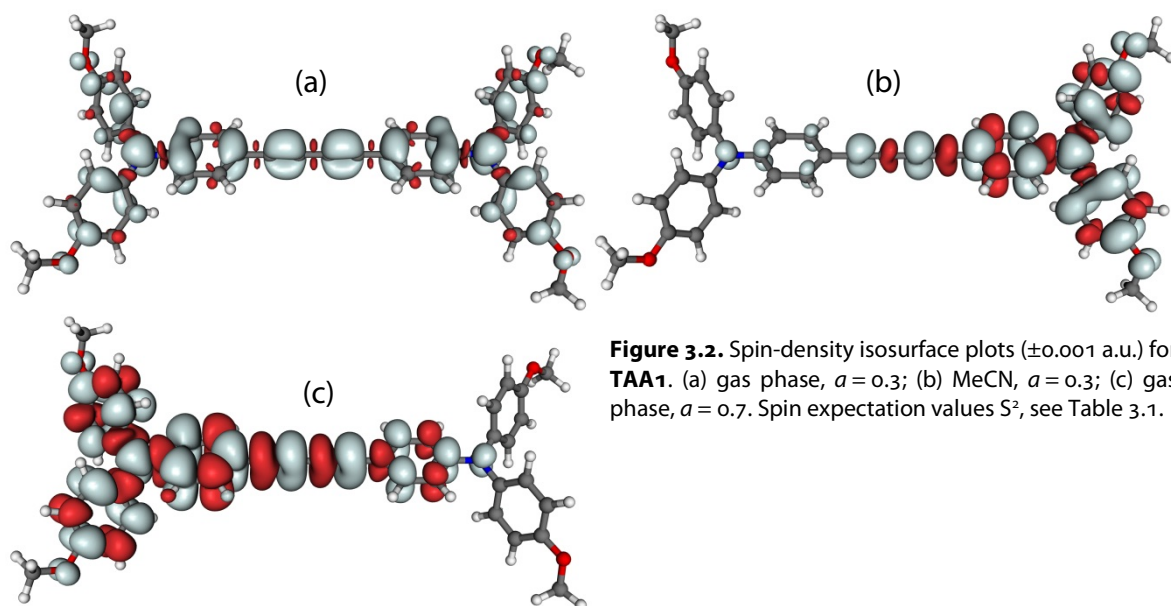


Figure 3.2. Spin-density isosurface plots (± 0.001 a.u.) for **TAA1**. (a) gas phase, $a = 0.3$; (b) MeCN, $a = 0.3$; (c) gas phase, $a = 0.7$. Spin expectation values S^2 , see Table 3.1.

Further confirmation for these conclusions comes from inspection of spin-density distributions (Figure 3.2): at 30% HF-like exchange in the gas phase (a), a perfectly symmetrical distribution with little spin polarization is seen. With the same exact-exchange admixture in MeCN, symmetry breaking occurs, and spin polarization becomes notable (b). The latter is largely restricted to the spin-carrying, oxidized half of the system. The situation at 70% HF-like exchange in the gas phase (c) looks substantially different: here the spin polarization is dramatic, consistent with the large spin contamination (cf. Table 3.1), and it extends also to the non-oxidized part of the system (see Figure 3.2).

Similar behavior was also found for spin-density distributions of unsymmetrical **TAA2** and **TAA3** in the gas phase or in hexane at large exact-exchange admixtures (see e.g. Figure 3.3 for **TAA2** and Table 3.2-3.3). Investigations of other rotational conformers give very similar results. Energy differences between the three conformers found (*P,P* and its enantiomer *M,M* as well as the meso compound *P,M*, all identified as minima on the potential energy surface) are below 1 kJ mol^{-1} , whereas dipole moments may differ by up to 4 Debye, depending on the arrangement of the methoxy groups. On one hand these results encourage that the symmetry breaking in MeCN solvent is not an artifact of an unsuitable functional, in contrast to the gas-phase or hexane calculations with large exact-exchange admixtures. On the other hand, at this point the MeCN and DCM results provide only a

limited bracketing of the preferred a value, as no quantitative experimental data on the ET barrier, the structural symmetry breaking or the dipole moment is available. So far, a HF-like exchange admixture around 35% looks reasonable, but 20% or 40% cannot be excluded. At least it can be already seen that a proper DFT description of the Robin-Day character of such systems may not be elusive.

Table 3.3. Calculated key ground state parameters for **TAA3** as a function of E_{xx} and solvent environment^a

%HF	BLYP	20	30	35	40	50	60	70	80	90	100
<i>gas phase</i>											
μ_o^b	0.02	0.10	0.02	0.03	0.19	0.04	0.04	0.02	0.05	12.73	15.45
$\Delta H^\ddagger$	0.0	0.0	0.0	0.0	-0.3	0.0	0.0	0.00	0.0	0.7	5.3
$\langle S^2 \rangle$	0.75	0.76	0.77	0.77	0.78	0.79	0.80	0.81	0.83	1.04	1.28
$d_1(\text{C}_{\text{An}}\text{-N})$	1.434	1.427	1.426	1.425	1.424	1.424	1.422	1.420	1.418	1.412	1.407
$d_2(\text{C}_{\text{An}}\text{-N})$	1.434	1.428	1.426	1.425	1.425	1.424	1.422	1.420	1.418	1.405	1.397
<i>hexane</i>											
μ_o^b	0.01	0.19	0.04	0.03	0.02	0.09	0.06	0.02	9.20	12.18	16.85
$\Delta H^\ddagger$	0.0	0.0	0.1	0.1	0.2	0.1	0.1	0.1	0.5	2.8	8.9
$\langle S^2 \rangle$	0.75	0.76	0.77	0.77	0.78	0.79	0.80	0.81	0.89	1.01	1.34
$d_1(\text{C}_{\text{An}}\text{-N})$	1.434	1.427	1.426	1.426	1.425	1.424	1.422	1.420	1.416	1.412	1.406
$d_2(\text{C}_{\text{An}}\text{-N})$	1.434	1.428	1.426	1.426	1.425	1.424	1.423	1.420	1.414	1.411	1.396
<i>dichloromethane</i>											
μ_o^b	0.01	0.36	0.27	0.05	0.17	0.12	18.19	18.33	18.88	19.66	19.87
$\Delta H^\ddagger$	0.2	0.2	0.3	0.3	0.8	0.7	2.1	4.4	7.0	11.6	17.8
$\langle S^2 \rangle$	0.75	0.76	0.77	0.77	0.78	0.79	0.85	0.91	1.00	1.15	1.38
$d_1(\text{C}_{\text{An}}\text{-N})$	1.434	1.427	1.426	1.426	1.425	1.425	1.420	1.416	1.412	1.409	1.405
$d_2(\text{C}_{\text{An}}\text{-N})$	1.434	1.428	1.426	1.426	1.425	1.425	1.401	1.399	1.396	1.391	1.390
<i>acetonitrile</i>											
μ_o^b	0.05	0.80	0.08	6.34	13.28	18.07	19.16	19.69	20.02	19.94	20.25
$\Delta H^\ddagger$	0.3	0.3	0.4	0.4	0.7	2.3	4.4	7.0	9.4	11.8	18.9
$\langle S^2 \rangle$	0.75	0.76	0.77	0.77	0.79	0.81	0.85	0.91	1.00	1.19	1.42
$d_1(\text{C}_{\text{An}}\text{-N})$	1.434	1.428	1.427	1.427	1.426	1.423	1.419	1.416	1.412	1.407	1.404
$d_2(\text{C}_{\text{An}}\text{-N})$	1.434	1.429	1.427	1.421	1.414	1.405	1.400	1.396	1.393	1.393	1.389

^a Dipole moments μ_o in Debye, ET barriers $\Delta H^\ddagger$ in kJ mol^{-1} and $\text{C}_{\text{An}}\text{-N}$ bond lengths (d_1 , d_2) in Å. ^b With the center of mass as the origin.

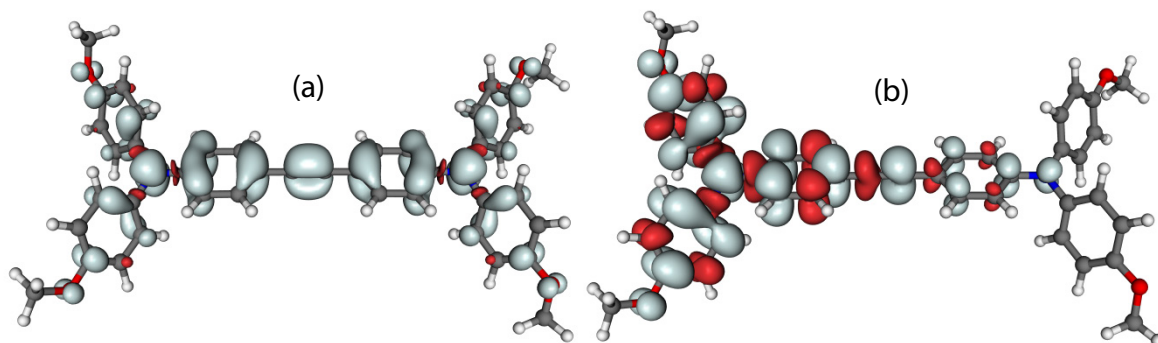


Figure 3.3. Spin-density isosurface plots (± 0.001 a.u.) of **TAA2**. (a) gas phase, $a = 0.4$; (b) MeCN, $a = 0.4$. Spin expectation values S^2 , see Table 3.2.

Table 3.4. Calculated key ground state parameters for **TAA4** as a function of E_{xx} and solvent environment^a

%HF	BLYP	20	30	35	40	50	60	80	100	HF
<i>gas phase</i>										
μ_o^b	0.03	0.02	0.06	0.03	0.16	0.01	0.04	0.04	0.09	8.43
$\Delta H^\ddagger$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.0
$\langle S^2 \rangle$	0.75	0.76	0.77	0.77	0.78	0.79	0.80	0.83	0.93	2.84
$d_1(\text{C}_{\text{An}}\text{-N})$	1.436	1.428	1.426	1.425	1.425	1.422	1.420	1.416	1.411	1.429
$d_2(\text{C}_{\text{An}}\text{-N})$	1.435	1.428	1.426	1.425	1.424	1.422	1.420	1.416	1.412	1.414
<i>hexane</i>										
μ_o^b	0.01	0.01	0.02	0.03	0.04	0.01	0.03	0.01	0.08	9.47
$\Delta H^\ddagger$	0.1	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	9.5
$\langle S^2 \rangle$	0.75	0.76	0.77	0.77	0.78	0.78	0.79	0.82	0.92	2.90
$d_1(\text{C}_{\text{An}}\text{-N})$	1.434	1.428	1.426	1.425	1.424	1.422	1.422	1.417	1.411	1.428
$d_2(\text{C}_{\text{An}}\text{-N})$	1.435	1.428	1.426	1.425	1.424	1.423	1.422	1.417	1.411	1.412
<i>dichloromethane</i>										
μ_o^b	0.04	0.02	0.13	0.03	0.33	0.08	0.09	0.05	0.06	11.07
$\Delta H^\ddagger$	0.4	0.2	0.2	0.2	0.1	0.2	0.2	0.5	0.7	14.3
$\langle S^2 \rangle$	0.75	0.76	0.77	0.77	0.77	0.78	0.79	0.82	0.92	2.99
$d_1(\text{C}_{\text{An}}\text{-N})$	1.435	1.428	1.427	1.425	1.425	1.422	1.421	1.416	1.411	1.424
$d_2(\text{C}_{\text{An}}\text{-N})$	1.435	1.428	1.426	1.425	1.423	1.422	1.420	1.416	1.411	1.409
<i>acetonitrile</i>										
μ_o^b	0.01	0.23	0.01	0.01	0.02	0.06	0.01	0.03	0.01	11.44
$\Delta H^\ddagger$	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.8	1.0	15.5
$\langle S^2 \rangle$	0.75	0.76	0.77	0.77	0.77	0.78	0.79	0.82	0.90	3.00
$d_1(\text{C}_{\text{An}}\text{-N})$	1.435	1.429	1.426	1.426	1.424	1.423	1.421	1.417	1.412	1.424
$d_2(\text{C}_{\text{An}}\text{-N})$	1.435	1.428	1.426	1.426	1.424	1.423	1.421	1.417	1.412	1.408

^a Dipole moments μ_o in Debye, ET barriers $\Delta H^\ddagger$ in kJ mol^{-1} and $\text{C}_{\text{An}}\text{-N}$ bond lengths (d_1 , d_2) in Å. ^b With the center of mass as the origin.

The classification of **TAA4** is most straightforward (Table 3.4): in none of the four environments and at no value of a , symmetry-broken structures are obtained. There can thus be no doubt from the computational point of view that **TAA4** is a class III system under all conceivable conditions. Therefore, the performance of pure HF calculations has been evaluated (Table 3.4): at HF level without a correlation functional added, unsymmetrical solutions are indeed obtained even in the gas-phase calculations when starting from an unsymmetrical structure. This is consistent with semi-empirical MO results, which also give unphysical symmetry breaking for such class III cases^[15, 167] (see also ref. [182] for an *ab initio* HF calculation).

3.4.2 Excited State Calculations

Table 3.5-3.8 provide TDDFT results for the IV-CT excitation energies of **TAA1-4** (more results for a wider variety of structure optimization levels and for further excitations are given in Table S3.5-S3.13 in the Appendix). In each case, data are given for full optimizations without symmetry (C_1) and for symmetrical C_i structures. In localized cases, the former are minima and the latter are the transition states for electron transfer. In delocalized situations, the C_1 optimizations should in principle give identical structures as the C_i optimizations. As discussed above, this is not fully the case due to numerical limitations, and thus for completeness both sets of data are given in such cases.

For **TAA1**, Table 3.6 gives only data for one level of structure optimization (at 35% exact-exchange admixture; as optical spectroscopy has been done in DCM, this is the preferred solvent here), but with different exact-exchange admixtures and solvent polarities in the subsequent TDDFT calculations (with 35% HF-like exchange, also gas-phase TDDFT results are provided to quantify the total solvent shifts, see also Figure 3.4). As **TAA2** is still delocalized at 35% HF-like exchange in DCM, data at 40% exact exchange in the structure optimization is also included (cf. Table 3.2), as this allows the comparison of a localized minimum and a delocalized transition state (Table 3.7). As symmetry breaking is difficult to achieve at moderate exact-exchange admixtures for **TAA3** in DCM, data for structures obtained at 50% HF-like exchange in MeCN have been included in this case to evaluate the effect of symmetry breaking on the excitation energies (Table 3.8). Only for **TAA4**, a

delocalized structure was obtained at all levels and focus is again on the structure obtained with 35% HF-like exchange in DCM (Table 3.5).

Table 3.5. TDDFT results for IV-CT excitation energies, E_i , and transition dipole moments, $\mu_{t,i}$, for **TAA4** as function of exact-exchange admixture and solvent

ground-state structure	% HF for TDDFT	solvent for TDDFT	C ₁ structure		C _i structure	
			<i>E_i</i> (λ) ^{<i>a</i>}	μ _{<i>t,i</i>} ^{<i>c</i>}	<i>E_i</i> (2H _{ab}) ^{<i>b</i>}	μ _{<i>t,i</i>} ^{<i>c</i>}
35% HF in DCM						
	0	DCM	9838	8.78	9819	8.75
	20	DCM	9950	11.03	9906	11.01
		MeCN	10125	10.83	10080	10.81
	30	DCM	10113	11.36	10054	11.35
		MeCN	10305	11.15	10244	11.14
	35	gas phase	10580	10.43	10526	10.41
		DCM	10145	11.55	10078	11.54
		MeCN	10345	11.33	10277	11.33
	40	DCM	10136	11.76	10060	11.75
		MeCN	10345	11.53	10269	11.53

^aThe experimental value for λ (absorption maximum) in DCM is 9530 cm⁻¹.^[15] ^bThe experimental estimate for $2H_{ab}$ from NIR spectra^[20] in DCM is 8600 cm⁻¹. ^cThe experimental transition dipole moment $\mu_{t,i}$ in DCM is 9.17 Debye.^[15]

Indeed, as a clear-cut class III case compound **TAA4** is ideally suited to validate first the quality of the TDDFT calculations at the different levels, as no structural ambiguities arise here. First of all, it has to be noted, that solvent shifts of the IV-CT excitation frequency are small, amounting only to a few hundred cm⁻¹ for this symmetrical system (cf. gas-phase and solvent data at 35% HF-like exchange in Table 3.5). The effect of changing exact-exchange admixture a is similarly small (see Figure 3.4). Selecting the value for 35% HF-like exchange in DCM, the experimental value of 9530 cm⁻¹ (this is the experimental absorption maximum in DCM) is overestimated by 615 cm⁻¹ or by about 6%. This may be within systematic errors of about 5-10% arising from ion pairing effects that might be present in the experiments, but which have been neglected in the computations. The result suggests that the exact-exchange admixture of about 35%, which was found to be particularly suitable to describe the symmetry breaking in some of these MV radical cations (see above), may also be used to properly compute the IV-CT excitation energy.

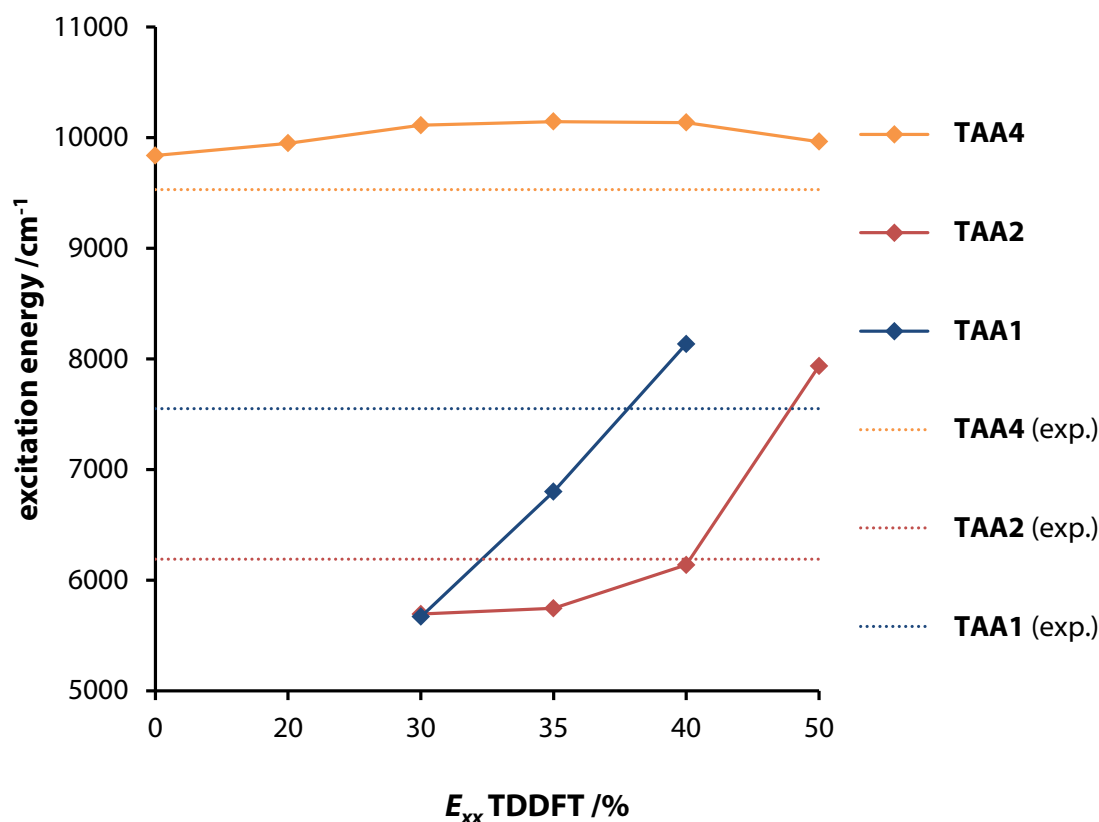


Figure 3.4. Calculated IV-CT excitation energies dependent on the amount of exact-exchange admixture in TDDFT in DCM, compared to experimental values (.....). Particular ground state structures calculated in BLYP35/DCM (**TAA1**, **TAA4**) or BLYP40/DCM (**TAA2**).

With these results for the class III system **TAA4** in mind, a detailed examination of **TAA1** is possible, which was found to be on the class II side based on ground-state properties (see section 3.4.1). In contrast to **TAA4**, one has to compare the excitations at the localized C_1 minima and at the C_i -symmetrical transition states (see Table 3.6). As already mentioned above a relatively small dependence of the excitation frequency on solvent and exact-exchange admixture for the C_i -symmetrical structure, consistent with the results for **TAA4**, has been found (yet total solvent shifts relative to the gas-phase result are larger than for **TAA4**). Much larger blue shifts with increasing solvent polarity are found for the localized MV structure. This is the expected behavior for a charge-localized system. Now the dependence on exact-exchange admixture is also much more pronounced (see Figure 3.4). For consistency, and based on the results for **TAA4**, the results with $a = 0.35$ (35% HF-like exchange) in DCM will be the reference point. The 6800 cm^{-1} obtained at this level for the

localized C_i minimum of **TAA1** is only about 750 cm^{-1} (about 10%) below the experimental value. In contrast, a much lower excitation energy of 4230 cm^{-1} is obtained for the C_i transition state. This is completely consistent with the scheme for a localized class II system (cf. Figure 1.2b), where the excitation at the localized minimum corresponds to the reorganization energy λ and the excitation energy at the symmetrical transition state corresponds to $2H_{ab}$, i.e. two times the electronic coupling matrix element H_{ab} . As $\lambda > 2H_{ab}$ for a class II system (see also section 2.4), the TDDFT results for **TAA1** agree nicely with the class II character inferred from the ground-state calculations (see section 3.4.1).

Table 3.6. TDDFT results for IV-CT excitation energies, E_i , and transition dipole moments, $\mu_{t,i}$, for **TAA1** as function of exact-exchange admixture and solvent

ground-state structure	% HF for TDDFT	solvent for TDDFT	C ₁ structure		C _i structure	
			<i>E_i</i> (λ) ^a	μ _{t,i} ^c	<i>E_i</i> (2H _{ab}) ^b	μ _{t,i} ^c
35% HF in DCM						
	30	DCM	5668	16.31	4655	24.45
		MeCN	6511	14.27	4843	23.77
	35	gas phase	4962	20.96	5865	20.85
		DCM	6800	14.39	4230	26.30
		MeCN	7752	12.83	4451	25.43
	40	DCM	8134	12.98	3646	29.03
		MeCN	9112	11.83	3920	27.79

^aThe experimental value for λ (absorption maximum) in DCM is 7550 cm^{-1} .^[15] ^bThe experimental estimate for $2H_{ab}$ from NIR spectra^[20] in DCM is 3580 cm^{-1} . ^cThe experimental transition dipole moment $\mu_{t,i}$ in DCM is 6.39 Debye.^[15]

Furthermore, it has to be noted, that the transition dipole moment is in all cases appreciable (larger for symmetrical, delocalized structures but still notable for localized ones, Table 3.6-3.8). Therefore, no systematic difficulties with TDDFT are expected regarding too low transition energies^[115] for small overlap between ground and excited state. This holds for delocalized as well as for localized structures. Notably, from an orbital point of view the principal nature of the IV-CT transition does not change when going from the delocalized to the localized case: in general, the IV-CT band is dominated by the HOMO-LUMO transition. Compared to the experimental transition dipole moments the computed values are too large for **TAA1-3** but agree well for **TAA4** (cf. footnotes to Table 3.6-3.8). For symmetrical structures the trend of previous gas-phase TD-B3LYP calculations is con-

firmed (see Table 2 in ref. [182]), but with slightly larger absolute values due to the inclusion of solvent effects (cf. also gas-phase data in Table 3.6-3.8).

Table 3.7. TDDFT results for IV-CT excitation energies, E_i , and transition dipole moments, $\mu_{t,i}$, for **TAA2** as function of exact-exchange admixture and solvent

ground-state structure	% HF for TDDFT	solvent for TDDFT	C ₁ structure		C _i structure	
			<i>E_i</i> (λ) ^a	μ _{t,i} ^c	<i>E_i</i> (2H _{ab}) ^b	μ _{t,i} ^c
35% HF in DCM						
	30	DCM	5693	19.84	5653	20.56
		MeCN	6048	18.84	5862	20.04
	35	gas phase	6440	18.18	6646	18.09
		DCM	5745	19.86	5356	21.61
		MeCN	6310	18.41	5593	20.99
	40	DCM	6137	19.13	4972	22.94
		MeCN	6925	17.42	5247	22.18
40% HF in DCM						
	30	DCM	5955	17.40	5807	20.33
		MeCN	6521	15.98	6014	19.83
	35	gas phase	5979	18.17	6791	17.92
		DCM	6561	16.31	5530	21.31
		MeCN	7289	14.89	5764	20.72
	40	DCM	7460	15.10	5171	22.54
		MeCN	8278	13.85	5440	21.82

^aThe experimental value for λ (absorption maximum) is 6190 cm⁻¹ in DCM^[15] and 7990 cm⁻¹ in MeCN.^[191] ^bThe experimental estimate for $2H_{ab}$ from NIR spectra^[20] in DCM is 4800 cm⁻¹. ^cThe experimental transition dipole moment $\mu_{t,i}$ in DCM is 11.6 Debye.^[15]

With this in mind the true borderline case **TAA2** (Table 3.7) can be evaluated. Here the optimizations at 35% HF-like exchange in DCM afforded a structure just on the verge of symmetry breaking, whereas the same DFT level gave clear symmetry breaking in MeCN. Hence, this compound seems to be so close to the class II/III borderline that even this moderate increase of solvent polarity may determine the character observed. From the ground-state data alone, a clear classification remains thus elusive. To be able to discuss results for a clearly symmetry-broken structure, Table 3.7 includes also data obtained at structures optimized with $a = 0.4$ (in DCM, cf. Table 3.2). For the C_1 minimum in the latter case, a substantial dependence of the excitation energy on solvent and exact-exchange

admixture has been seen as expected for a charge-localized state (see Figure 3.4). In contrast, the excitation energies at the C_i transition state (and at the symmetrical structure obtained upon optimization at 35% exact-exchange admixture) exhibit again little dependence on solvent or functional. Based on the excitation energies computed in DCM alone, no clear-cut answer is obtained for **TAA2**. At $a = 0.35$, a localized structure gives an excitation energy about 6% above experiment, and a delocalized structure provides excitation energies about 10% below the experimental absorption maximum. This does not allow a clear classification of **TAA2** as localized or delocalized. However, for **TAA2** an IV-CT frequency in MeCN is also available (footnote *a* to Table 3.7),^[191] and it is clearly blue-shifted by 1800 cm^{-1} compared to the DCM result. This is more in line with a localized ground state. The predicted blue shift for a symmetrical structure is only about 200 cm^{-1} , that for a localized structure up to about 800 cm^{-1} , depending on structure and functional used (Table 3.7). While this is still too small relative to the experimental shift (where ion-pairing effects may enhance charge localization and thus the blue shifts), the solvent dependence points clearly to a class II character for **TAA2**.

Finally, **TAA3**, which based on the ground-state calculations should be more on the class III side than **TAA2** (see above). In this case, the optimizations in DCM at 35% HF-like exchange gave clearly a delocalized structure (cf. Table 3.3), and much larger exact-exchange admixtures are needed to force localization. Thus, Table 3.8 includes in addition to results for the structure with 35% in DCM also those for the structure optimized at 50% in MeCN, providing charge localization (cf. Table 3.3). In this case, the excitation energies obtained with 35% HF-like exchange in DCM differ relatively little between C_i and C_i structures. They are larger for the structure obtained with 50% HF-like exchange in MeCN than for that computed with 35% HF-like exchange in DCM, probably reflecting the overall somewhat shorter bonds at the former level (cf. Table S3.3 and Table S3.9-3.10 in the Appendix). The results for the latter structure agree better with experiment. This alone does not allow a clear computational Robin-Day classification. However, together with the fact that rather large exact-exchange admixtures are needed to provoke symmetry breaking of the ground-state structure (Table 3.3) even in MeCN and even more so in DCM, it feels that **TAA3** may be assigned to the class III side, albeit close to the border.

Table 3.8. TDDFT results for IV-CT excitation energies, E_i , and transition dipole moments, $\mu_{t,i}$, for **TAA3** as function of exact-exchange admixture and solvent

ground-state structure	% HF for TDDFT	solvent for TDDFT	C ₁ structure		C _i structure	
			E_i (λ) ^a	$\mu_{t,i}$ ^c	E_i (2H _{ab}) ^b	$\mu_{t,i}$ ^c
35% HF in DCM						
	30	DCM	6843	16.87	6760	16.92
		MeCN	7065	16.47	6987	16.51
	35	gas phase	7544	17.48	7469	15.26
		DCM	6653	17.48	6561	17.55
		MeCN	6898	17.03	6811	17.09
	40	DCM	6405	18.19	6299	18.29
		MeCN	6678	17.68	6579	17.76
50% HF in MeCN						
	30	DCM	6790	14.57	7642	15.88
		MeCN	7264	13.73	7866	15.52
	35	gas phase	6583	14.99	8272	14.45
		DCM	7294	13.99	7541	16.33
		MeCN	7881	13.12	7785	15.94
	40	DCM	8033	13.28	7392	16.86
		MeCN	8699	12.47	7658	16.42

^aThe experimental value for λ (absorption maximum) in DCM is 6360 cm⁻¹.^[15] ^bThe experimental estimate for 2H_{ab} from NIR spectra^[20] in DCM is 5600 cm⁻¹. ^cThe experimental transition dipole moment $\mu_{t,i}$ in DCM is 11.6 D.^[15]

A graphical summary of the computed IV-CT excitation energies (with structure optimizations as well as TDDFT calculations using 35% HF-like exchange in DCM) in comparison with experiment is shown in Figure 3.5. In the case of **TAA3** and **TAA4**, differences between results obtained with C_i and C_i structures, respectively, reflect only slight numerical inaccuracies in the optimizations and have no diagnostic meaning. As shown above, these two systems should be regarded as class III (although **TAA3** is close to the border line). Incidentally, in both cases, the C_i results are indeed very slightly closer to experiment, but always higher, which is typical for a delocalized system. For **TAA1** the much larger excitation energy computed for the localized C_i structure agrees significantly better with experiment than the C_i result, consistent with the class II character found. For **TAA2**, the C_i structure at this computational level was found to be just on the way towards localization. The difference in excitation energies is not large, but the C_i result is closer to experiment, consistent with the class II character assigned above on the basis of solvent shifts. In

contrast to the class III systems, the excitation energies for the localized systems are underestimated – typical for class II systems (see also sections 4.4.1 or 6.4.5)

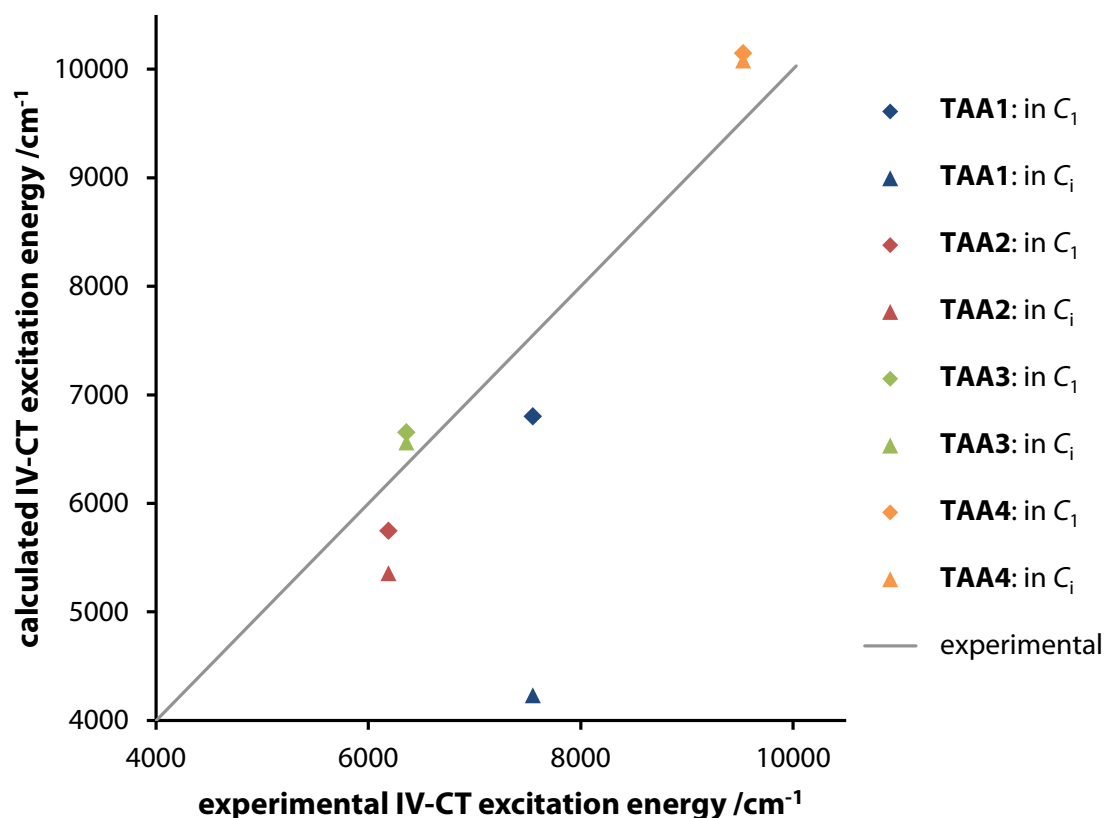


Figure 3.5. IV-CT excitation energies obtained for **TAA1-4** with 35% HF-like exchange in DCM in both structure optimization and TDDFT computation. Perfect agreement with experiment is indicated by the diagonal line. Data for unsymmetrical structures (C_1) and symmetrical structures (C_i) are provided.

It should be noted again (cf. Computational Details) that the quantitative agreement of the TDDFT excitation energies with experiment depends on the chosen solvent model, and more work will have to be invested in examining how the parameters of the solvent model affect the excitation energies (see section 6.4.1). Furthermore, the continuum solvent models used in this chapter involve only the static dielectric constant. It is conceivable that more detailed future evaluations might have to deal with the different time scales of solvent relaxation. This discussion is outside the scope of the present work (see, e.g. refs. [37, 176]). A last point should be noted regarding the computed IV-CT excitation energies. As shown above, it is not trivial to arrive at the correct localized or delocalized structure, and due to

the large solvent dependence of charge localization, gas-phase calculations are clearly inadequate in this context. In view of the appreciable dependence of the IV-CT excitation energies on the quality of the optimized input structure, the often-found short-cut methods that use gas-phase optimized ground-state structures and include solvent effects only in the TDDFT calculation are clearly inappropriate and discouraged.

3.5 Conclusions

The presented, systematic study of ground-state structures and properties, as well as IV-CT transition energies, of a series of organic MV radical cations close to the class II/III borderline has provided important insights that may bear on the computational description of organic (or even inorganic) MV systems in general. First of all, a strikingly large influence of solvent polarity on the positioning of such organic MV radical cations along the Robin-Day classification coordinate has been found. Indeed, such classifications should generally be provided with explicit indication of the solvent used for the experimental characterization. The results of the previous sections suggest that for systems close to the class II/III crossover, solvent polarity may indeed play the decisive role for the qualitative character of the MV radical cation. The importance of solvent polarity is even more significant due to the fact that these cations have to be studied in relatively polar solvents. So far, the influence of the counterions has not been considered yet, but there will be some investigations on this topic in chapter 6.^[38] Interionic interactions may also play a role, in particular regarding the crystal environment for solids. This has to be considered when interpreting X-ray structural results for such organic MV radical cations.

While the experimental evidence for the character of the title systems was partly contradictory and rather indirect, the combination of ground-state structure optimizations with the comparison of computed IV-CT excitation energies to experiment provided an unprecedentedly detailed classification and characterization. Among the four systems studied here, the phenylene-bridged, most strongly coupled example **TAA4** has been found computationally to be a clear-cut class III case, irrespective of whether this is in the gas phase, or in different dielectric continuum solvent environments. All four cations **TAA1-4** are class III

in the gas phase or in a nonpolar solvent like hexane. In a more polar solvent like MeCN or DCM, at least **TAA1** and **TAA2** exhibited symmetry breaking with hybrid functionals at moderate exact-exchange admixtures of about 35%. Analysis of ground- and excited-state data for the diphenylbutadiyne-bridged system **TAA1** indicates clearly that in this case the symmetry breaking is real, and the compound is on the class II side both in DCM and in MeCN. This contrasts to artificially induced charge localization observed at very high exact-exchange admixtures in the gas phase or in hexane solution. The diphenylethyne-bridged compound **TAA2** is closest to the class II/III border in MeCN and DCM, but could be characterized as class II based on the solvent dependence of the IV-CT excitation energy. Finally, the computations on the biphenylene-bridged cation **TAA3** suggest it to be on the class III side, but barely so.

In the end, the main result of this chapter is the proposal of a simple, practical protocol for reliable calculations on organic MV systems in general, based on hybrid functionals with about 35% exact-exchange admixture, together with suitable dielectric-continuum solvent models. The exact-exchange admixture of 35% is somewhat larger than in typical thermochemically optimized global hybrids like B3LYP. However, this does not seem to be a serious obstacle, as hybrid functionals with some dependence on local kinetic energy density may allow such elevated exact-exchange admixtures without sacrificing overall thermochemical accuracy (cf. chapter 6). Alternatively, more sophisticated approaches such as range-separated hybrids or local hybrids may provide further improved accuracy. Eventually, for even more detailed evaluations, it may become necessary to consider also ion pairing in case of ionic MV systems.

The presented results and data set provide now a basis against which further methods may be compared and validated. *First*, this protocol will be extended to further bis-triarylamine radical cations as well as neutral PCTM-triarylamine radicals (see chapter 4). *Second*, paracyclophane-bridged bis-triarylamine radical cations will be examined using this protocol (see chapter 5). *Third*, detailed studies on the computational methods, basis sets and solvent models will be performed for small dinitroaromatic and diquinone radical anions (see chapter 6 and 7).

Chapter 4

It is unworthy of excellent men to lose hours like slaves in the labor of calculation which could be safely relegated to anyone else if machines were used.

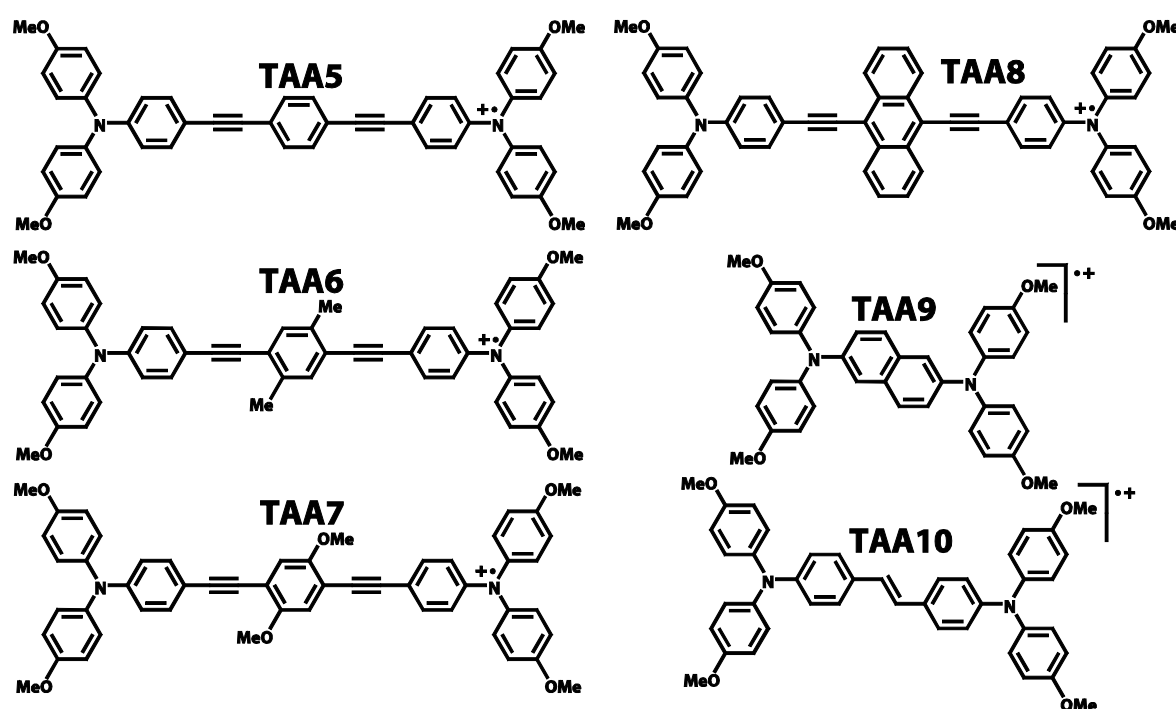
-- Gottfried Wilhelm Leibniz

4 Extension to further Radical Cations and Neutral Systems

4.1 Introduction

In this chapter further mixed-valence compounds are discussed, which should be classified and characterized in terms of their localized *vs.* delocalized character. This is done by using the quantum chemical protocol based on non-standard hybrid functionals and continuum solvent models suggested in the previous chapter.^[44] The extended set of six MV bis-triarylamine radical cations (**TAA5-10**, see Scheme 4.1) investigated in this chapter is augmented by seven unsymmetrical, neutral triarylamine-perchlorotriphenylmethyl radicals (**TAA11-17**, see Scheme 4.2). The systems **TAA5-8** may be derived from **TAA1** by introducing different aryl groups into the center of the bridge. Starting from **TAA5**, using an unsubstituted phenyl group, the bridging aryl group is replaced by more and more pronounced electron-rich units, namely by 2,5-dimethyl- (**TAA6**) and 2,5-dimethoxy-substituted phenyl moieties (**TAA7**) or by an anthracene group (**TAA8**) connected to the redox centers at the 9,10-position. As a consequence, the coupling between the two triarylamine units will be enhanced and move the localized/delocalized character succes-

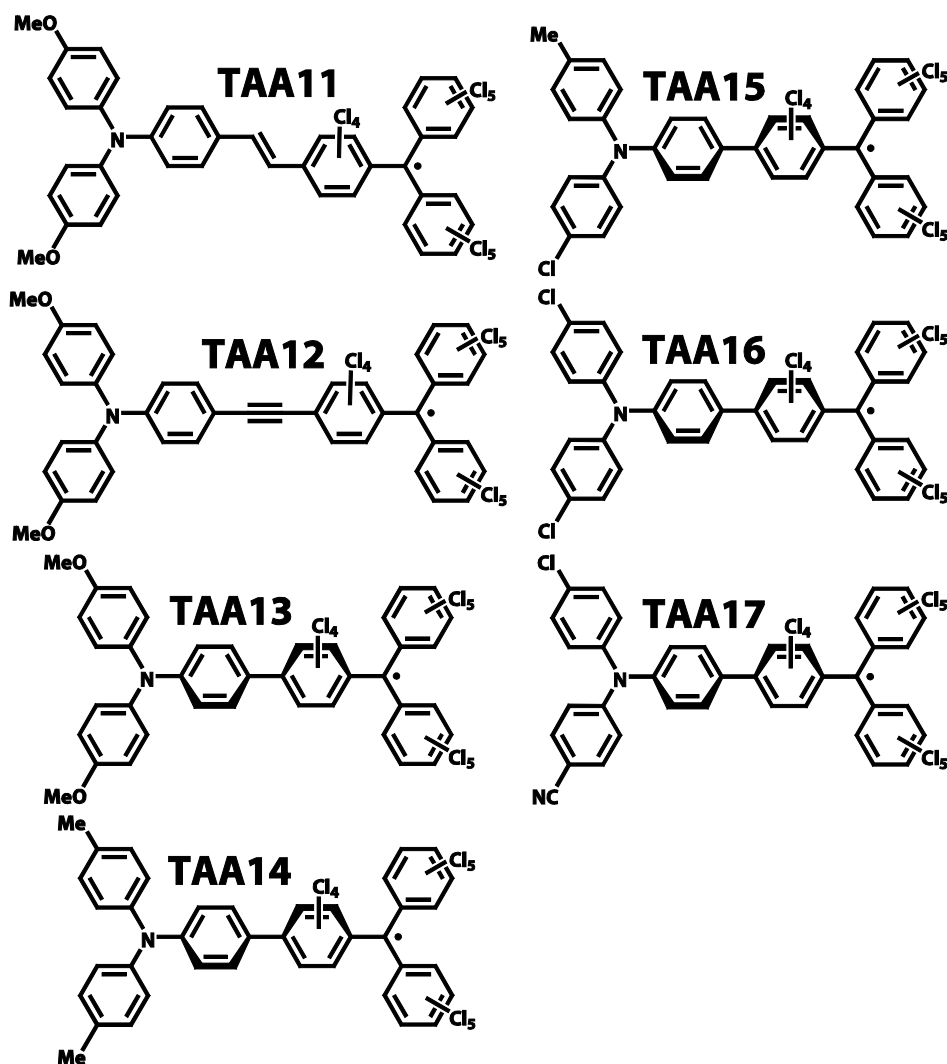
sively towards class III. This is confirmed by experimental observations (see section 4.2).^[15, 17, 18, 20, 31-33, 198-203] With **TAA8** bearing the rather large central anthracene group and thus representing a special case (see below),^[18] the protocol can be put to its limits because it is suspected that specific solute-solvent interactions are important and not covered by the continuum solvent model.



Scheme 4.1. Six additional bis-triarylamine radical cations studied, in addition to **TAA1-4** (see Scheme 3.1).

The radicals **TAA11-17** are asymmetric neutral MV systems with two non-degenerate redox centers. However, they have an electronic structure closely related to the bis-triarylamine radical cations and feature a number of interesting properties that make them suitable targets for further study. While **TAA11** and **TAA12** possess an ethylene and an acetylene moiety in the center of the bridge, compounds **TAA13-17** have a direct biphenyl connection, but different substitution patterns. They all feature a perchlorinated triphenylmethyl radical (PCTM) acceptor group, whereas the substituents in *para*-position of the two terminal aryl groups of the triarylamine donors change from two methoxy (**TAA13**) via two methyl (**TAA14**), methyl/chloro (**TAA15**), two chloro (**TAA16**) to chloro/cyano (**TAA17**) groups (Scheme 4.2). These small substituents influence the electron donor

strength of the triarylamine, that is, the triarylamine in **TAA13** is the strongest donor while that of **TAA17** is the weakest. Thus, this series allows for the investigation of subtle donor-acceptor strength variations. Due to their neutral character, it is expected that solvent effects may be less pronounced for radicals **TAA11-17** than for the cations **TAA1-10**.



Scheme 4.2. Neutral MV systems **TAA11-17**, all using one perchlorotriphenylmethyl moiety.

4.2 Available Experimental Information

The cations **TAA5-7** move towards the border from the class II side (indicated by the decreasing experimental ET barriers in DCM from 12.6 kJ mol⁻¹ for **TAA5**,^[18] towards

10.8 kJ mol⁻¹ (5.7 kJ mol⁻¹ in MeCN) for **TAA6**^[31, 32] to 6.9 kJ mol⁻¹ for **TAA7**,^[18] see also Table 4.1). Compound **TAA8** is particularly close to the class II/III borderline, as exemplified by the spectroscopic observation of a class II behavior in MeCN and a class III behavior in DCM.^[18] Finally, **TAA9** and **TAA10** have relatively short bridges and are expected to be on the class III side as described by optical spectroscopy.^[15, 33, 163, 198, 201, 204-206] Detailed experimental excitation energies and transition dipole moments for **TAA5-10** will be discussed in Table 4.2. For **TAA5** and **TAA6**, also ¹⁴N-hyperfine coupling constants (HFCs) are available in DCM, 23.5 MHz for **TAA5** and 23.1 MHz for **TAA6**. The first experimental studies on the unsymmetrical compounds **TAA11-17** have been carried out recently,^[184, 207] with particular emphasis on **TAA11**, **TAA12** and **TAA13**. As the donor is clearly on the triarylamine side, these systems are best represented as localized class II cases, possibly with only one minimum along the ET coordinate. In contrast to the symmetrical compounds, experimental ground state dipole moments by electro-optical absorption (EOA) spectroscopy are available in cyclohexane, representing the decreasing donor strength of the triarylamine unit from **TAA13-17**: 4.6±0.6 Debye for **TAA13** over 4.6±0.2, 3.2±0.2 and 2.5±0.2 Debye for **TAA14-16** to 0.3±0.4 Debye for **TAA17**.^{[45][208]} Furthermore, IV-CT energies are available in hexane. For some systems additional data in other solvents is also reported. They will be discussed in detail in Table 4.3. In addition, electron coupling values 2H_{ab} are available, but it is challenging to obtain these computationally, due to the unsymmetrical structure. Hence, computed ET barriers will not be available for these compounds.

4.3 Computational Details

Structure optimizations as well as bonding analyses were performed with locally modified versions of TURBOMOLE (TBM) 5.9 and 5.10,^[192] that allow the exact-exchange admixture in a global hybrid functional to be varied. The “custom hybrid” exchange-correlation functionals were constructed according to Eq. (4.1). As specified in chapter 3 and ref. [44], a systematic variation of the exact-exchange coefficient *a* has been performed, to interpolate between the “pure” gradient-corrected BLYP functional^[58, 60] (*a* = 0.0) via the BHLYP hybrid functional with 50% exact exchange (*a* = 0.5) to a functional made from 100% exact exchange (*a* = 1.0) with LYP correlation^[60] on top. In this chapter, the focus concentrates

largely on the optimal value of $a = 0.35$ found in chapter 3 and ref. [44]. However, also larger values of a will be occasionally scanned, where necessary. In some cases, pure HF calculations without correlation functional have been performed as well. SVP basis sets were employed on all atoms.^[193]

$$E_{XC} = (1 - a)(E_X^{LSDA} + \Delta E_X^{B88}) + a \cdot E_X^{HF} + E_C^{LYP} \quad (4.1)$$

In addition to gas-phase optimizations, in all cases optimizations with the COSMO solvent model^[120] have been used for hexane ($\epsilon = 1.89$), for dichloromethane (DCM, $\epsilon = 8.93$), and for acetonitrile (MeCN, $\epsilon = 36.64$). Near the critical values of a , where symmetry breaking occurs, the outcome of the structure optimizations depended sometimes on whether a symmetrical or unsymmetrical starting structure is used. In those cases, unsymmetrical starting structures (C_1) as well as symmetrical ones (C_i) have been tried, as explained in the previous chapter. For unsymmetrical cases, this led to a lower energy of the symmetry-broken structure. The ET barrier was subsequently calculated as the energy difference between the C_i -symmetric transition state and the unsymmetric C_1 -optimized minimum. Due to the asymmetry of **TAA11-17**, no ET barriers have been calculated. Spin-density isosurface plots and plots of dipole moments were obtained with the Molekel program.^[195]

Subsequent TDDFT-calculations of the lowest-energy electronic transitions (IV-CT bands) for both C_1 and C_i structures were done with the Gaussian 03 program (Go3),^[196] using the same type of custom hybrids and SVP basis sets^[193] as discussed above. In the Go3 calculations, solvent effects have been included by the CPCM keyword, which denotes the polarizable continuum model that is closest to the COSMO model used in the optimizations.^[121] The Go3 TDDFT results have been found to agree better with experiment than the TBM data (particularly for symmetrical structures, see chapter 3 and ref. [44]) as soon as a polarizable continuum solvent was included. The differences arise from technical details (van-der-Waals radii, solvent radii, number of tesserae per sphere, see also section 2.3) in the two solvent-model implementations. In part, the fact that Go3 but not TBM (5.9 or 5.10) includes non-equilibrium solvation in the TDDFT implementation may be responsi-

ble. The dipole moments of the first excited states have been calculated by Go9,^[209] using the Go3 CPCM defaults to reproduce the data of Go3 calculations.

Hyperfine coupling constants (HFCs) have been calculated by generating the Kohn-Sham orbitals using TBM, with IGLO-II basis sets (H (3s1p)/[5s1p], C N O (5s4p1d)/[9s5p1d])^[210] and the hybrid functional including 35% ($a = 0.35$) exact exchange admixture. The orbitals were then transferred to the MAG-ReSpect program package^[211] for computation of the HFCs.

4.4 Results and Discussion

4.4.1 Bis-triarylamine radical cations – ground state properties

Table 4.1 summarizes the key ground-state parameters of **TAA5-10** computed using 35% HF exchange admixture, for DCM and MeCN solvent models (results in hexane or in the gas phase place **TAA1-10** generally on the delocalized class III side; see Table S4.1-10 in the Appendix). This allows an evaluation whether quantum chemical protocol established successfully for **TAA1-4** (see chapter 3) is useful also for the remaining six cations. In agreement with experimental observation – as already described in section 4.2, **TAA5-7** are localized (class II) in both solvents.^[15, 17, 18, 20, 31-33, 198-203] This is indicated by the ET barriers, the dipole moments, and the asymmetry of the C_{Ar}-N distances. As expected from the increasing donor capacity of the substituents on the central phenyl ring (H for **TAA5**, CH₃ for **TAA6**, and OCH₃ for **TAA7**), the amount of symmetry breaking tends to decrease from **TAA5** to **TAA7** in a given solvent (albeit **TAA5** and **TAA6** behave very similarly and only **TAA7** is notably less localized in DCM). The more polar MeCN is moreover expected to give rise to a more pronounced symmetry breaking compared to DCM. The slightly lower ET barrier of **TAA6** compared to **TAA5** in DCM is consistent with the barriers estimated experimentally (by temperature-dependent ESR, see below).^[31] The fact that **TAA7** has the lowest ET barrier (as well as dipole moment and structural asymmetry, Table 4.1), is also consistent with the lower end of the range of measured ET barriers, but the experimental uncertainty is higher in this case.^[18] The ET barriers for **TAA5-8** in MeCN and DCM are graphically compared in Figure 4.1. The increase of the donor capacity of the substituents

from **TAA5** to **TAA8** leads to a decrease of the ET barriers. The ET barriers in DCM are about 5 kJ mol⁻¹ lower than the barriers in MeCN, as expected. Compared to experimental results in DCM, the ET barriers computed in the same solvent are underestimated. Curiously, the values computed for MeCN tend to be closer to the experimental DCM data.

Table 4.1. Calculated key ground state parameters for **TAA5-10** in different solvents. Computed dipole moments μ_0 in Debye, ET barrier $\Delta H^\ddagger$ in kJ mol⁻¹, spin expectation values $\langle S^2 \rangle$ (theoretical value would be 0.75), C-N bond lengths d_1 and d_2 in Å as well as the ¹⁴N-HFCs a_{N1} and a_{N2} in MHz at the two nitrogen atoms^a

molecule in solvent	μ_0^b	$\Delta H^\ddagger$	$\langle S^2 \rangle$	$d_1(\text{C}_{\text{Ar}}-\text{N})$ $d_2(\text{C}_{\text{Ar}}-\text{N})$	$a_{N1}(\text{C}_1)$ $a_{N2}(\text{C}_1)$	$a_{N1}(\text{C}_i)$ $a_{N2}(\text{C}_i)$
TAA5 in DCM	40.2	10.0	0.79	1.406	24.4 (23.5) ^c	10.6
		(12.6 ^e /13.9 ^e)		1.426	0.3	10.6
TAA5 in MeCN	42.1	15.6	0.79	1.405	24.6	10.7
				1.426	0.2	10.7
TAA6 in DCM	38.9	4.8	0.79	1.407	24.0 (23.1) ^c	10.1
		(10.8) ^c		1.426	0.4	10.1
TAA6 in MeCN	41.2	10.3	0.79	1.405	24.6	10.2
		(5.7) ^d		1.426	0.2	10.2
TAA7 in DCM	35.2	3.1	0.79	1.412	22.4	7.9
		(6.9) ^e		1.425	0.8	7.9
TAA7 in MeCN	40.0	8.4	0.79	1.408	24.2	7.8
				1.425	0.3	7.8
TAA8 in DCM	0.0	0.3	0.78	1.430	5.9	5.9
		(0.0) ^e		1.429	5.9	5.9
TAA8 in MeCN	0.0	0.5	0.78	1.430	5.7	5.7
				1.430	5.7	5.7
TAA9 in DCM	0.8	0.0	0.77	1.426	14.6	14.1
				1.425	13.6	14.1
TAA9 in MeCN	0.7	0.1	0.77	1.426	14.5	14.1
				1.425	13.7	14.1
TAA10 in DCM	0.1	0.3	0.77	1.429	10.4	10.6
				1.429	10.5	10.6
TAA10 in MeCN	0.1	0.3	0.77	1.429	10.2	10.3
				1.429	10.3	10.3

^a With 35% HF exchange and COSMO. Experimental values in parentheses. Further computational data are available in Table S4.5-10 in the Appendix. ^b With the center of mass as the origin. ^c $\Delta H^\ddagger$ by EPR spectroscopy.^[31] ^d Ref. [202]. ^e Free energy barrier ΔG^* from a fit of the potential energy surface to the experimental absorption spectra.^[18]

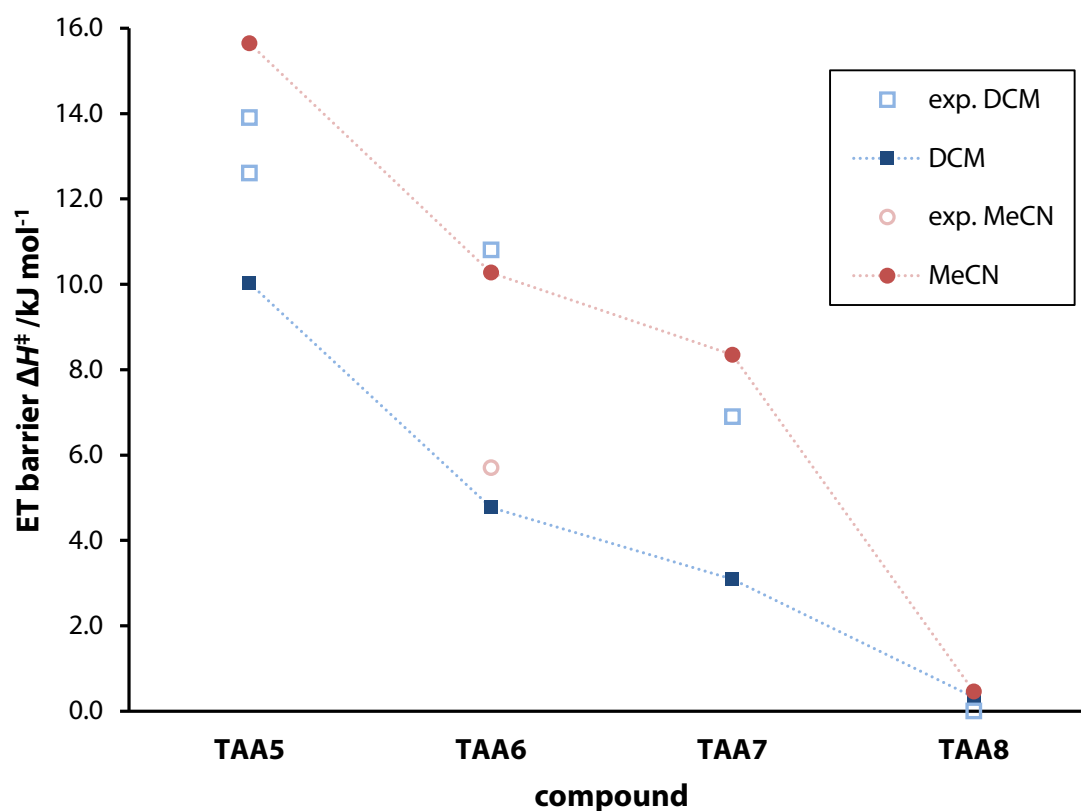


Figure 4.1. Computed ET barriers $\Delta H^\ddagger$ of **TAA5-8** in DCM (dark blue, ■) and MeCN (dark red, ●) compared to experimental values according to Table 4.1 (light colored, □ and ○). Two different experimental results for **TAA5** in DCM are obtained either by EPR spectroscopy (larger value, ref. [31]), or from a fit of the potential energy surface to the experimental absorption spectra (lower value, ref. [18]).

The ^{14}N -HFC for **TAA5** in DCM is found to be 23.5 MHz (0.839 mT) experimentally^[31] and 24.4 and 0.3 MHz respectively using BLYP35 (see Table 4.1). The computed HFC for **TAA6** (about 24.0 MHz in DCM) agrees also well with the measured one (23.1 MHz) and confirms the class II character.^[31] This suggests the computed HFCs (22.4 MHz in DCM) for the related **TAA7**, where no experimental data is available, to be reliable as well. The somewhat lower HFC points to increased delocalization in **TAA7**, comparable to trends in the class II systems with HFCs of 23.3 MHz for **TAA1** in DCM (see Table S4.1 in the Appendix) and 17.0 MHz for **TAA2** (Table S4.2). The calculated values indicate **TAA2** to be a system very close to the class II/III borderline: in the localized case, one expects one HFC near 20 MHz, the other vanishing. Two identical HFCs of about 10 MHz are expected for true class III systems. The decisive evidence for **TAA2** being class II was, however, the

comparison of the coupling matrix element $2H_{ab} = E_i(C_i)$ with the calculated excitation energy of the transition state (see section 3.4.2 and ref. [44]).

Cation **TAA8** may be viewed as a further extension of the series **TAA5-7**, as it exhibits the most electron-rich aryl moiety in the middle of the bridge, an anthracene unit (Scheme 4.1). As mentioned above, **TAA8** is particularly close to the class II/III border and appears to switch from class II to class III simply by changing the solvent from MeCN to a solution of 5% MeCN in DCM, as indicated by UV/vis data.^[18] Optimization with 35% HF exchange-admixture in COSMO solvent models for MeCN and DCM gives generally a delocalized class III situation (negligible dipole moment, ET barrier, structural distortion and nonequivalence of the HFCs). This indicates that this compound may probe the limits of the suggested quantum chemical protocol. Symmetry breaking may be induced by either a) increasing exact-exchange admixture to 40% in MeCN, or alternatively by b) increasing the dielectric constant of the model solvent from $\epsilon = 36.64$ for MeCN to $\epsilon = 50$. But even then no noticeable ET barrier has developed (indeed, the delocalized structure remains slightly more stable). Only a pure HF calculation without correlation functional provides a sizeable ET barrier ($156.9 \text{ kJ mol}^{-1}$) and a clearly localized description (but with sizeable spin contamination). Apart from the fact, that this compound is probably the one closest to the class II/III borderline of all compounds studied so far, its large aromatic anthracene unit in the center of the bridge may also represent a challenge to the continuum solvent model used. It is conceivable that direct solvent coordination to the electron-rich aromatic ring may be involved, which is not covered by the model (Figure 4.2 clearly shows the substantial spin delocalization onto the anthracene moiety which also leads to comparatively small ^{14}N -HFCs). A treatment that includes the actual solvent dynamics explicitly is outside the scope of this work. Compound **TAA8** remains thus a veritable challenge. However, it has to be noted that direct COSMO-RS (see section 2.3 and 6.4.6) can somewhat improve the description, yielding dipole moments of about 19 Debye in both, MeCN and DCM, and a rather small ET barrier ($< 1 \text{ kJ mol}^{-1}$) for MeCN and even smaller for DCM.

On the other hand, compounds **TAA9** and **TAA10**, with their rather short bridges, exhibit large coupling of the two redox centers, as almost found for **TAA4** (see section 3.4.1).

Consequently, they are both classified as delocalized, symmetrical class III systems by the suggested protocol (cf. data in Table 4.1, Table S4.9-4.10 in the Appendix), consistent with experimental evidence from IV-CT line shape and solvatochromism, crystallography and vibrational spectra.^[33, 198]

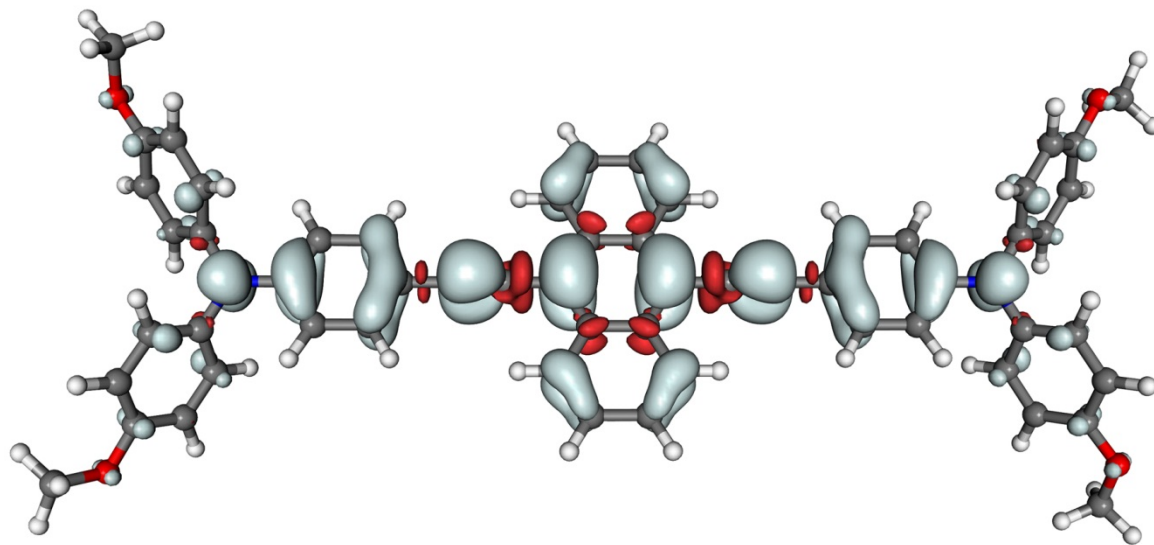


Figure 4.2. Spin-density isosurface plot (± 0.001 a.u.) for **TAA8** in BLYP35/MeCN showing substantial spin delocalization onto the anthracene bridge.

4.4.2 Bis-triarylamine radical cations – excited state properties

Table 4.2 summarizes the excitation energies and transition moments computed by TDDFT methods for **TAA5-10**, in comparison with the available experimental data.

For **TAA5**, the computed excitation energy of 6969 cm^{-1} in DCM deviates by about 1000 cm^{-1} from the recently obtained experimental data.^[18, 31, 198] The computed electronic coupling $2H_{ab} = E_i(C_i)$ in DCM agrees within 400 cm^{-1} to experimental estimates within a two-state model.^[18, 31] For **TAA6**, the computed IV-CT excitation energy in DCM model solvent lies within 700 cm^{-1} from experiment^[20, 31] and the computed electronic coupling $2H_{ab}$ agrees excellently (within better than 200 cm^{-1}) to the experimentally obtained value.^[20] Similar agreement with experiment is found for **TAA7**, with a deviation of only about 520 cm^{-1} for the IV-CT band and of about 150 cm^{-1} for the electronic coupling.^[18]

Table 4.2. Computed IV-CT transition energies E_i (in cm^{-1}) and transition dipole moments $\mu_{t,i}$ (in Debye) for **TAA5-10** in DCM and MeCN compared to available experimental data (in parentheses)

molecule in solvent	E_i (C_i) ^a	$E_i (= 2H_{ab})^b$ (C_i) ^c	$\mu_{t,i}$ (C_i)	$\mu_{t,i}$ (C_i)	Ref.
TAA5 in DCM	6969 (8060) (7780)	2421 [1896] ^d (2087) ^f (2000) ^e	10.62 (6.2) (5.85)	35.46	[17, 18] [33, 198]
TAA5 in MeCN	8351 (9910)	2654 [2003] ^d (2282) ^f	9.15	33.49	[33]
TAA6 in DCM	6828 (7500)	2537 [2068] ^d (2280) ^f (2440) ^e	11.60 (7.6±0.3)	34.74	[20]
TAA6 in MeCN	8150	2847 [2125] ^d (2439) ^f	9.81	32.78	
TAA7 in DCM	6000 (6520)	3969 [2543] ^d (3260) ^f (3820) ^e	15.66 (9.7)	28.82	[17, 18]
TAA7 in MeCN	7436	4184 [2428] ^d (3214) ^f	12.04	27.86	
TAA8 in DCM	5881	5844 [5881] ^d (5857) ^f (4640)	22.27	22.36 (14.1)	[18]
TAA8 in MeCN	6127 (6770)	6054 [6127] ^d (6079) ^f	21.40	21.57	[18]
TAA9 in DCM	7891	7874 [7866] ^d (7869) ^f (7620)	14.19	14.23 (11.1)	[15]
TAA9 in MeCN	8065	8166 [8043] ^d (8112) ^f	13.90	13.82	
TAA10 in DCM	7211	6959 [7211] ^d (7086) ^f (6150) (6080)	18.18	18.50 (13.0) (13.5)	[163] [33]
TAA10 in MeCN	7661	7390 [7661] ^d (7523) ^f (7010)	17.40	17.72	[33]

^a Computed excitation energies in C_i -symmetry compared to maximum absorption in UV/vis spectra in parentheses, where available. ^b This equivalence holds only within the two-state model. ^c Computed excitation energies in C_i -symmetry compared to “experimental” $2H_{ab}$ from the two-state model in parentheses, where available. ^d $2H_{ab}$ in italics and brackets obtained alternatively from computed dipole moments and excitation energies *via* eqs. (2.52) and (2.54). ^e Experimental coupling $2H_{ab}$ evaluated by a three-state Mulliken-Hush-analysis. ^f Evaluated by eq. (2.52) and $\Delta\mu_{ab} = 2\mu_{t,i}(C_i)$.

In case of **TAA8**, the computations underestimate the excitation energy in MeCN by 650 cm^{-1} , that in DCM by 1200 cm^{-1} .^[18] For all these comparisons one has to keep in mind that twice the computed electronic coupling refers to the energy difference of ground and excited state at C_i geometry (which is exact in a two-state one-mode model with harmonic potentials as given in Figure 2.2) while the experimental couplings were estimated by a

three-state generalized Mulliken-Hush model. In cases where the third state plays a minor role, this comparison is reasonable. However, for **TAA8** in DCM, a class III system with strong mixing of states, this comparison is no longer useful. In this case one can simply take the IV-CT energy as twice the coupling as given in Table 4.2.

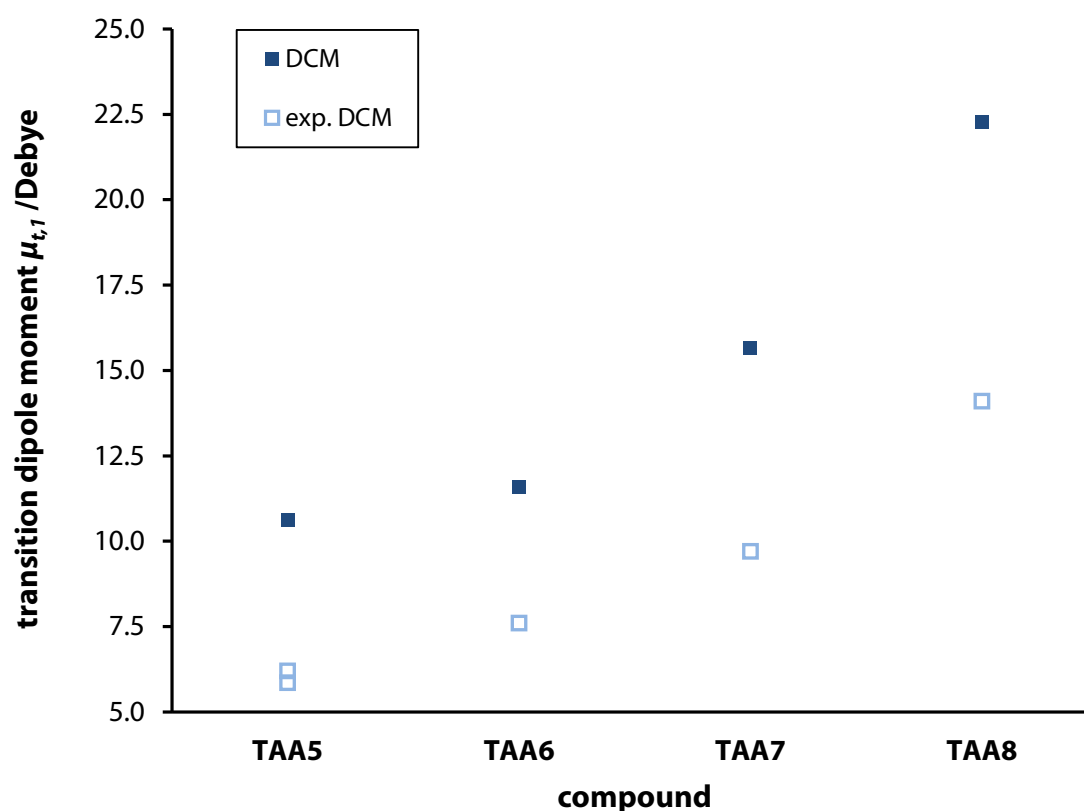


Figure 4.3. Computed transition dipole moments of **TAA5-8** in DCM (dark blue, ■) compared to experimental values (light blue, □) according to Table 4.2.

Turning to the more clear-cut class III cases **TAA9** and **TAA10**, very good agreement with experiment of excitation energy and transition moment computed for **TAA9** in DCM is found.^[15] For **TAA10**, the measured IV-CT excitation energy^[33] is overestimated by 1100 cm⁻¹ in DCM and by 650 cm⁻¹ in MeCN. The computed transition and dipole moments of ground and excited state also allow calculating $2H_{ab}$ by eqs. (2.52) and (2.54) by using purely DFT computed properties as input. As can be viewed from Table 4.2 the agreement with DFT computed E_t is generally reasonable for localized **TAA5-7** and excellent for delocalized **TAA8-10** in both solvents.

An alternative way to compute $2H_{ab}$ by eq. (2.52) follows an idea of Matyushov and Voth^[212] and of Coropceanu *et al.*^[34] who showed that the diabatic transition dipole moment difference is equal to twice the adiabatic transition dipole moment $\Delta\mu_{ab} = 2\mu_{t,1}(C_i)$ at the transition state of the thermal ET within the two-level model. The $2H_{ab}$ values computed in this way proved to be in better agreement with the computed $E_t = 2H_{ab}$ for the localized set of compound while they are equally excellent for the delocalized set. Overall, it appears that the computed transition moments correlate well with the experimental ones but overestimate the latter consistently. As seen in Figure 4.3, the transition dipole moments increase when moving towards class III character, due to the better overlap of the ground and excited state wave functions in delocalized systems.

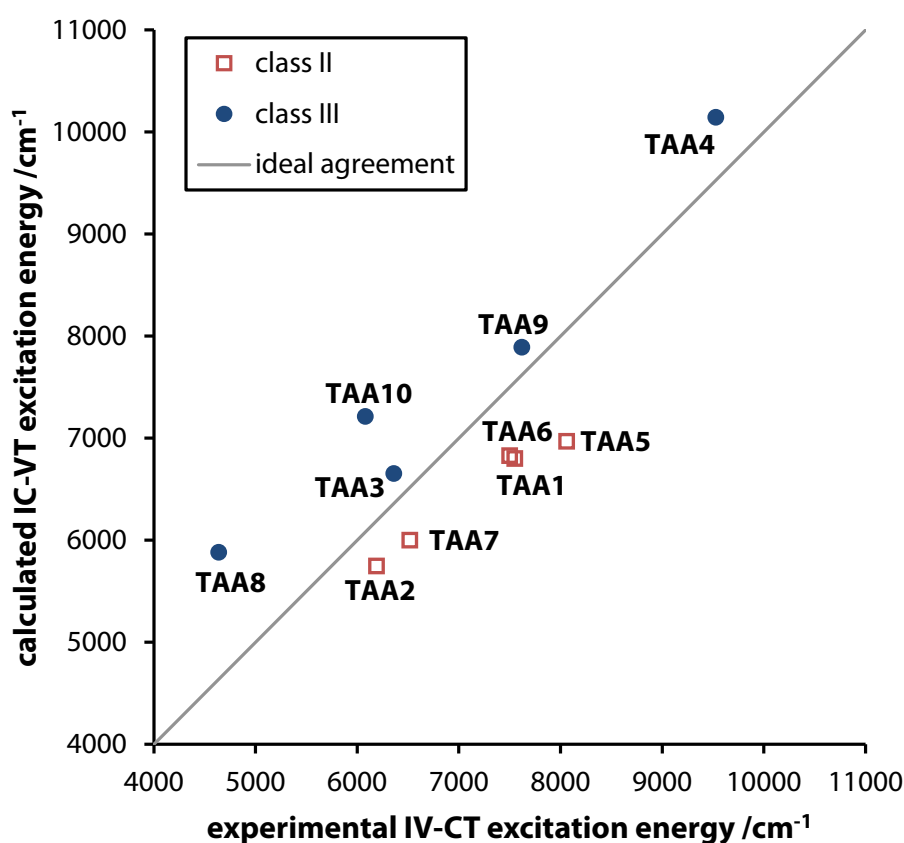


Figure 4.4. Comparison of IV-CT excitation energies computed for **TAA1-10** with experimental data (computations with 35% HF-like exchange in DCM for structure and TDDFT calculation, experimental data in DCM).

Figure 4.4 displays graphically the agreement with experiment of IV-CT excitation energies for **TAA1-10** in DCM computed using the present quantum chemical protocol. Apart from the overall very satisfactory agreement, it seems that the excitation energies for the class II systems (**TAA1**, **TAA2**, **TAA5**, **TAA6**, **TAA7**) are systematically underestimated, whereas they are overestimated for the clear-cut class III systems (**TAA4**, **TAA9**, **TAA10**), particularly for **TAA10**. The borderline class III case **TAA3** is well described,^[44] whereas the difficulties in describing the extremely subtle situation for the extreme borderline case **TAA8** are reflected by a relatively large overestimate.

4.4.3 Neutral perchlorotriphenylmethyl-triarylamine radicals

Turning now to the application of the computational protocol to the unsymmetrical, neutral radicals **TAA11-17** (Scheme 4.2), the focus will be on the comparison of the computed IV-CT band and dipole moments with experiment.^[45] First, it has to be noted that the optimized ground-state structures, which have been computed with the usual protocol (35% HF exchange-admixture in DCM COSMO solvent), reflect the localized electronic structure of the radicals, which have their spin density predominantly on the perchlorotriphenylmethyl (PCTM) radical center, as expected (e.g. for **TAA14**, Figure 4.5c).

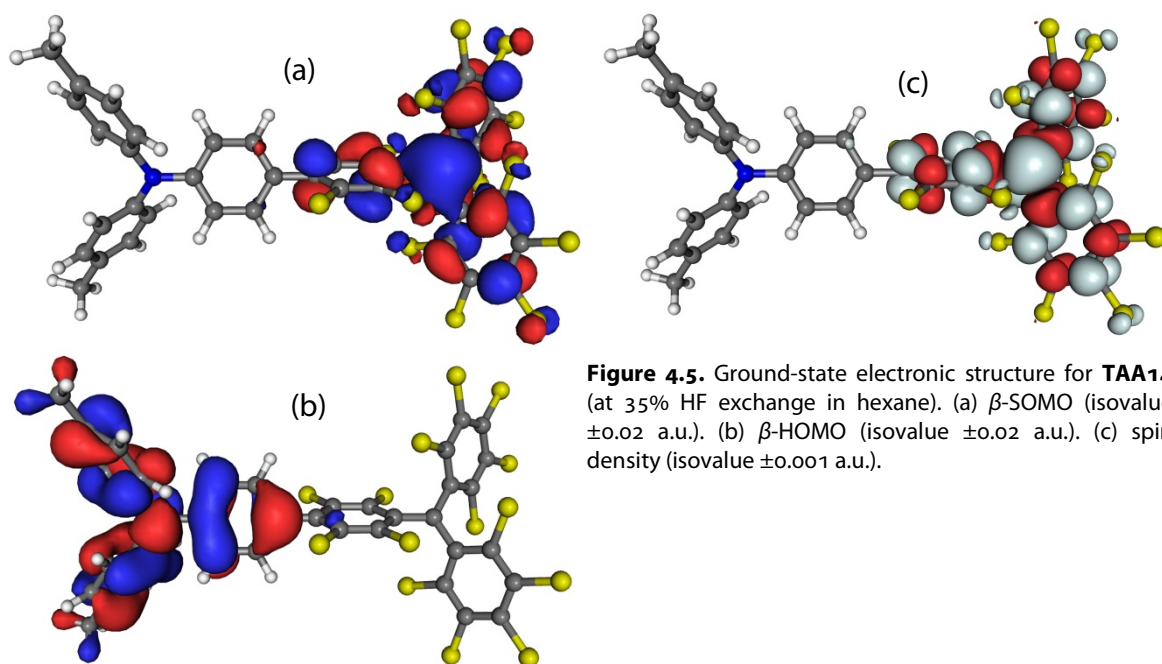


Figure 4.5. Ground-state electronic structure for **TAA14** (at 35% HF exchange in hexane). (a) β -SOMO (isovalue ± 0.02 a.u.). (b) β -HOMO (isovalue ± 0.02 a.u.). (c) spin density (isovalue ± 0.001 a.u.).

This is also indicated by the ^{13}C -HFCs, which are calculated (35% HF exchange in MeCN, DCM and hexane) to be 96-97 MHz for **TAA11** and **TAA12** (with a weak dependence on exact-exchange admixture), consistent with experimental values of about 84 MHz for the PCTM radical (obtained by EPR spectra in THF and tetrachloroethylene).^[213] Consequently, the IV-CT band is expected to correspond to an excitation from the triarylamine to the PCTM radical moiety, as confirmed by the character of the HOMO and SOMO (e.g. for **TAA14**, Figure 4.5) and by the analysis of the TDDFT data. Calculations on different diastereomers of **TAA14** and **TAA17** do not change the results noticeably. The calculations confirm the doublet character of the ground state and of the first excited state (the “IV-CT” state). Computations in DCM place the first quartet state at 16436 cm^{-1} , 18547 cm^{-1} and 22439 cm^{-1} above the ground state for **TAA11**, **TAA12**, and **TAA17** respectively.

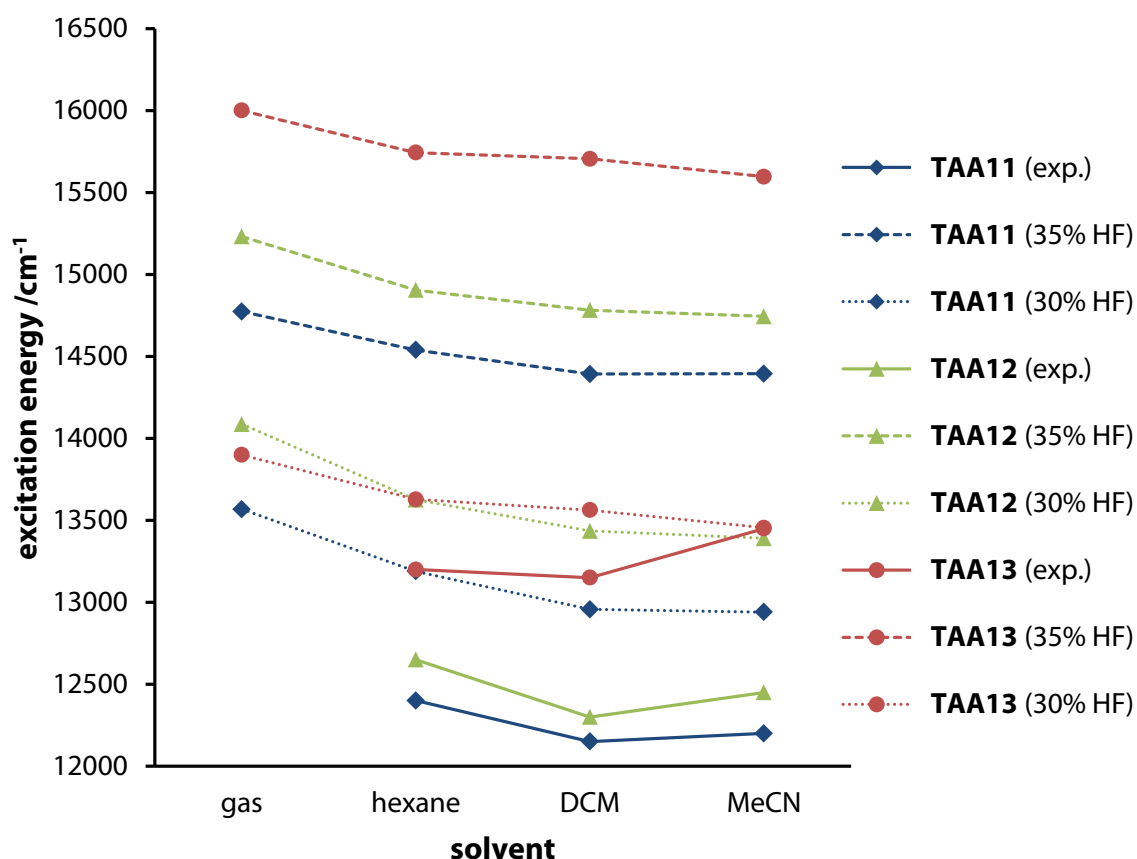


Figure 4.6. Excitation energies for **TAA11**, **TAA12**, and **TAA13**, computed by TDDFT for different exact-exchange admixtures and for different solvents. Experimental data are connected by solid lines, computational ones by dashed (35% HF exchange) or dotted (30% HF exchange) lines.

Table 4.3. Computed and experimental lowest excitation energies E_i (in cm^{-1}) and transition moments $\mu_{i,1}$ (in Debye) for **TAA11-17**, depending on solvent and on exact exchange admixture in TDDFT functional

compound	E_{xx} (TDDFT)	E_i			$\mu_{i,1}$		
		hexane	DCM	MeCN	hexane	DCM	MeCN
TAA11 (<i>stilbene</i>)	<i>exp.</i> ^a	12400	12150	12200	3.6		3.6
	30%	13189	12956	12940	5.1	5.2	5.2
	35%	14539	14392	14394	4.2	4.4	4.4
TAA12 (<i>acetylene</i>)	<i>exp.</i> ^a	12650	12300	12450	4.1		4.1
	30%	13626	13435	13390	6.0	6.1	6.1
	35%	14904	14782	14745	5.2	5.3	5.3
TAA13 (<i>OMe/OMe</i>)	<i>exp.</i>	12700 ^b	13150 ^a	13450 ^a	1.21 ^b		
		13200 ^a					
	30%	13715	13618	13669	2.5	2.5	2.4
	35%	15812	15731	15796	2.4	2.4	2.3
TAA14 (<i>Me/Me</i>)	<i>exp.</i> ^b	13150			1.23		
	30%	14674	14463	14457	2.2	2.3	2.2
	35%	16735	16534	16545	2.2	2.3	2.1
TAA15 (<i>Me/Cl</i>)	<i>exp.</i> ^b	14400			1.31		
	30%	15646	15351	15288	2.0	1.9	2.0
	35%	17743	17471	17407	1.9	1.9	1.9
TAA16 (<i>Cl/Cl</i>)	<i>exp.</i> ^b	15100			1.16		
	30%	16568	16167	16092	1.8	1.8	1.7
	35%	18674	18304	18244	1.9	1.8	1.7
TAA17 (<i>Cl/CN</i>)	<i>exp.</i> ^b	17400			1.17		
	30%	18348	18031	18118	2.1	1.7	1.1
	35%	20274	20095	20281	2.1	1.8	1.2

^a Experimental values from ref. [184]. ^b Experimental values in cyclohexane from ref. [207].

Straightforward application of the TDDFT protocol with 35% HF exchange to the IV-CT excitation energies provides a systematic overestimate compared to experiment^[184] of about 2000-2500 cm^{-1} for **TAA11-13**, and of about 2700-3500 cm^{-1} for **TAA14-17** (Table 4.3, Figure 4.6). The same types of calculations produced much closer agreement with experiment for the cationic bis-triarylamines (see refs. [44, 45] and Table 4.2). This overestimation can be reduced notably by scaling down the HF exchange-admixture to 30% (Table 4.3): now deviations are about 700-1500 cm^{-1} (test calculations indicate that at 25% the computed energies are already underestimated somewhat). But why is less exact-

exchange admixture required for the neutral radicals **TAA11-17** than for the cations **TAA1-10**?

It appears possible, that the HF exchange-admixture of 35% found to be optimum for both ground- and excited-state calculations on the cationic species may have compensated for some counter-ion effects neglected in the computational protocol. As these are absent for the neutral radicals, less exact exchange is required. Due to the unsymmetric, localized character of **TAA11-17**, it could not been probed at which exact-exchange admixture a delocalized ground-state situation would occur for these systems. While UV/vis data for **TAA14-17** are available only in cyclohexane (computations were done with $\epsilon = 1.89$ for hexane, which is only a minor difference to $\epsilon = 2.02$ of cyclohexane), data for cyclohexane, MeCN, and DCM are available for **TAA11-13** (see above). The calculations confirm essentially the slightly larger excitation energy in (cyclo-)hexane compared to DCM. But they would essentially suggest no differences between DCM and MeCN, whereas experimentally there is a somewhat larger difference for **TAA13** (Table 4.3, Figure 4.6). Transition dipole moments $\mu_{t,1}$ for **TAA11-17** were systematically overestimated by the computations (Table 4.3). But they are strongly dependent on rotations around the biphenyl axis. With the two phenyl groups orthogonal, the transition dipole moment almost vanishes (see Table S4.14), due to the small overlap of the π -orbitals. The computed potential energy surface for this rotation is extremely flat, and a dynamical situation is likely, rendering the computed transition dipole moments less well defined.

Table 4.4. Experimental ground-state dipole moment μ_o and dipole moment difference $\Delta\mu_{0,1}$ (in Debye) as well as electronic coupling H_{ab} in cm^{-1} for **TAA13-17** from EOA spectroscopy in cyclohexane at 298 K.

	TAA13 (OMe/OMe)	TAA14 (Me/Me)	TAA15 (Me/Cl)	TAA16 (Cl/Cl)	TAA17 (Cl/CN)
μ_o^a	4.6 ± 0.6 (3.2 ^d)	4.6 ± 0.2 (3.8)	3.2 ± 0.2 (3.1)	2.5 ± 0.2 (0.5)	0.3 ± 0.4 (-4.4 ^e)
$\Delta\mu_{0,1}^b$	30.7 ± 6.9	28.4 ± 1.6	28.5 ± 1.4	28.8 ± 1.7	26.5 ± 2.7
H_{ab}^c	500	570	660	620	770

^a Experimental data from ref. [45], calculated values in parentheses. ^b Calculated as difference between ground and Franck-Condon excited state by $\Delta\mu_{0,1} = \mu_o - \mu_i$. ^c Evaluated by eqs. (2.52) and (2.54) ^d This is the dipole moment of the C_2 -symmetric structure. It is 5.2 Debye for the isoenergetic non-symmetric structure (rotated methoxy-groups). ^e The change in sign indicates that the direction of the dipole moment vector has reversed. This cannot be probed by EOA spectroscopy.

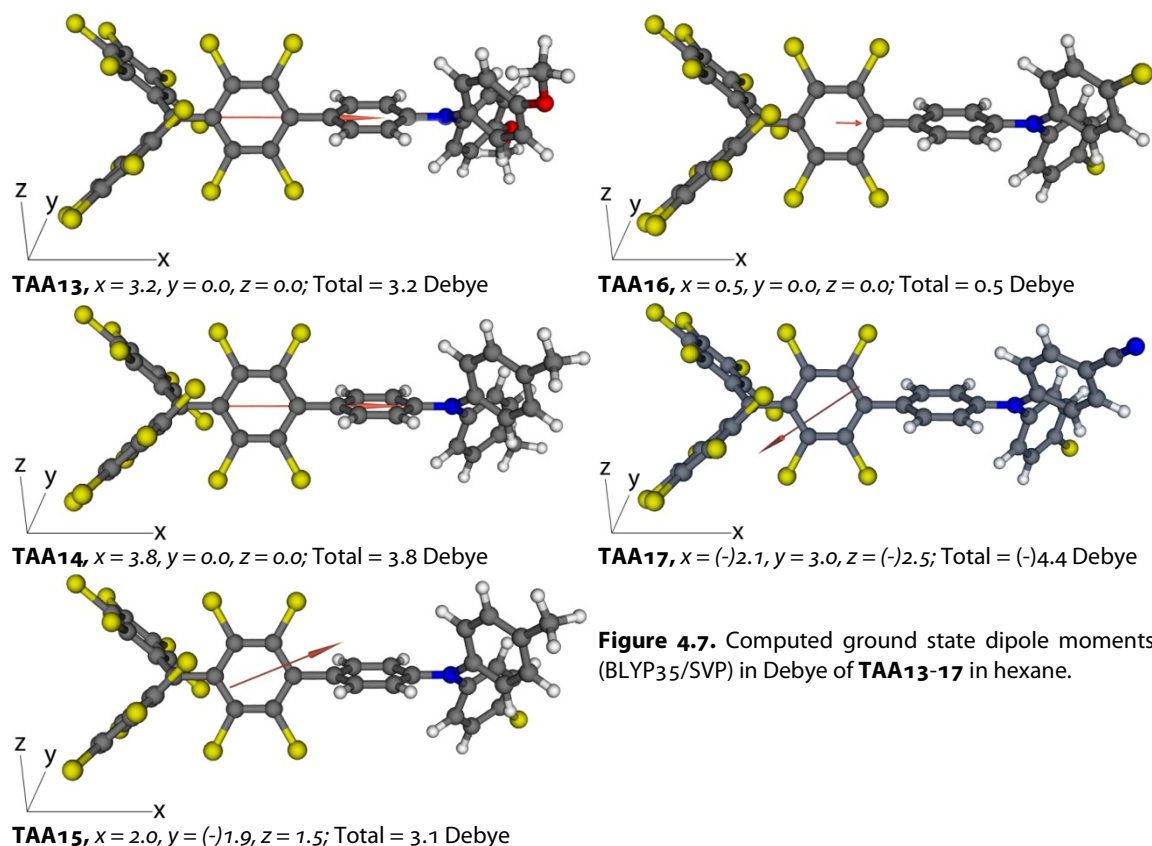


Figure 4.7. Computed ground state dipole moments μ_o (BLYP35/SVP) in Debye of **TAA13-17** in hexane.

Ground-state dipole moments μ_o as well as dipole moment differences between ground- and excited state $\Delta\mu_{o,1}$ for **TAA13-17** have been determined by electro-optical absorption (EOA) spectroscopy in cyclohexane at 298 K.^[45] They decrease along the series **TAA13-17** as the substituents attached to the triarylamine are less electron donating/more electron withdrawing. For **TAA17** the ground-state dipole moment almost vanishes. Agreement between computation and experiment is qualitatively reasonable for these neutral systems, where dipole moments are well defined, in contrast to the radical cations **TAA1-10** studied. However, the decrease of computed values from **TAA13** to **TAA17** is more pronounced than the experimental decrease, leading to a vanishing dipole moment already for **TAA16** and to an inversion of the direction for **TAA17**. The direction is essentially towards the PCTM side for **TAA13-15** and to the opposite side for **TAA17** (Figure 4.7). While for the species with C_2 symmetry the computed ground-state dipole moments point exactly along the long molecular axis between the nitrogen atom and the carbon atom (see **TAA13**, **TAA14** and **TAA16** in Figure 4.7 and Table 4.4), those with C_1 symmetry (**TAA15**, **TAA17**) display stronger deviations. This is particularly the case for **TAA17** where the local dipole

moment of the aminobenzonitrile chromophore within the triarylamine breaks the symmetry and reverses the overall ground-state dipole moment. The torsion angle around the biphenyl axis is around 70° for **TAA13-17**, depending only slightly on the polarity of the solvent. This twisting contributes to a partial decoupling of the two redox centers and affects the excitation energies and transition moments substantially (see e.g. Table S4.14 for **TAA14** in the Appendix). The dynamics of this rotation should thus be kept in mind regarding the agreement of the TDDFT results with experiment. On the other hand, the electronic coupling H_{ab} evaluated by eqs. (2.52) and (2.54) depends only moderately on the substituents.

4.5 Conclusions

The validation of the quantum chemical protocol for the computational description of organic MV compounds, based on non-standard hybrid functionals and continuum solvent models, introduced in chapter 3, has been extended to a larger number of compounds, including ten cationic bis-triarylamine radical cations and seven neutral triarylamine-triarylmethyl radicals.

Performance of the protocol for the newly included cationic radicals **TAA5-10** is comparable to the previously obtained results for the cations **TAA1-4**. This holds for the ground-state properties as well as for the IV-CT bands. That is, the localized class II *vs.* delocalized class III character of these MV systems is reproduced well by the protocol, provided that the polar solvent (DCM and MeCN) is included by a continuum model. Rather accurate IV-CT excitation energies and transition dipole moments may also be obtained computationally. The limits of the suggested protocol are probed by compound **TAA8**. This cation is so close to the class II/III borderline, that experimentally a change of solvent from MeCN to DCM switches the situation from class II to class III. The protocol with 35% HF exchange admixture does not recover this switchover and predicts the system as class III in both solvents. It appears possible that the presence of a large anthracene aromatic ring system at the center of the bridge in **TAA8** gives rise to specific solvent effects not being covered by the current model.

In case of the neutral radicals **TAA11-17** the protocol does seem to provide a good description of the ground-state properties (e.g. dipole moments). However, the lowest excitation energies are overestimated by about 2000-3500 cm⁻¹ when using 35% HF exchange admixture. A reduction to 30% brings computations into better agreement with experiment. One might speculate that the larger exact-exchange admixture needed to give sufficient symmetry breaking for class II cationic systems may compensate to some extent for counter-ion effects not present in the model. As these are absent in the neutral radicals, slightly less exact-exchange admixture is adequate for their description.

It thus seems that the greatest remaining challenge in the computational evaluation of organic mixed-valence systems is the proper description of environmental effects, which will be examined in detail in chapter 6. However, even at the present stage, the model allows a considerably more realistic computational study of such MV systems than hitherto possible.

Chapter 5

The more accurate the calculations become, the more the concepts tend to vanish into thin air.

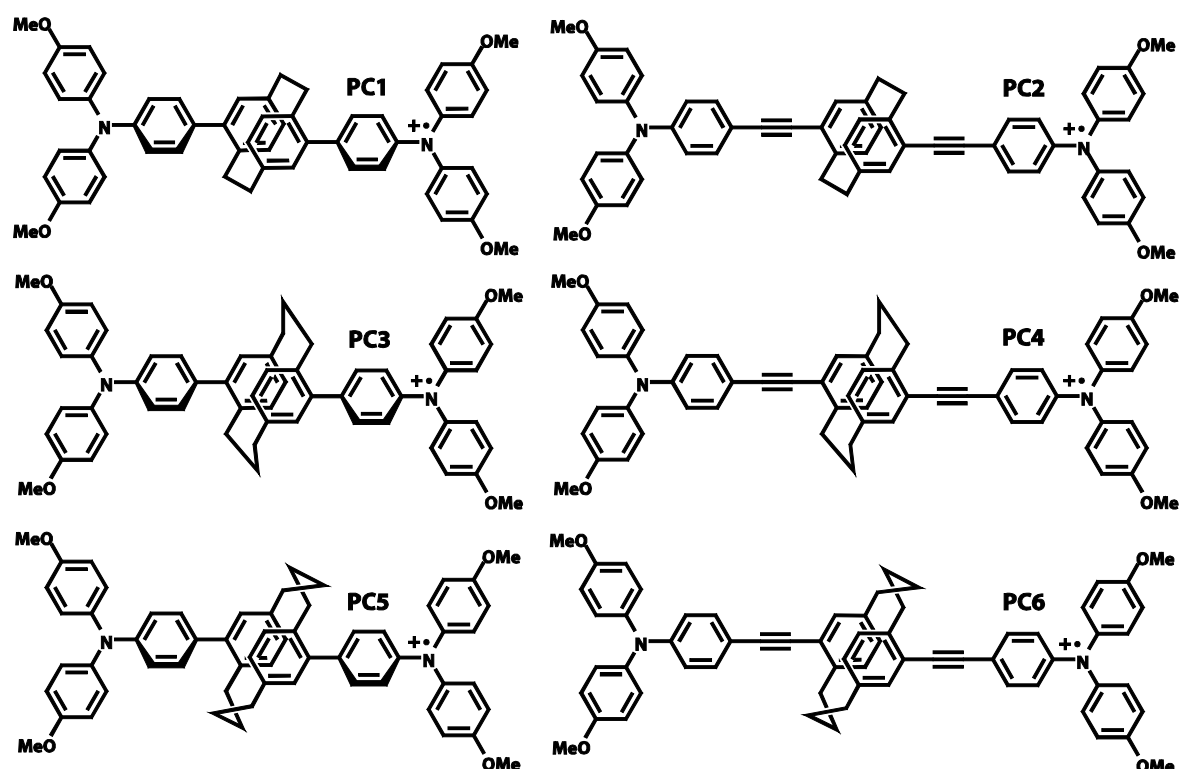
-- Robert S. Mulliken

5 Paracyclophane-bridged bis-triarylamine radical cations

5.1 Introduction

The triarylamine-based MV systems **TAA1-10** discussed in the two previous chapters had essentially fully conjugated bridges, and the ET clearly was sustained by the framework of the covalent bonds. For practical applications in organic molecular electronics, however, intermolecular ET between separated units, e.g. in π -stacked molecular aggregates, is also of substantial interest. While the geometries of such aggregates may be ill-defined and strongly dependent on intermolecular dynamics, paracyclophanes offer better-defined π -stacked interactions within an intramolecular situation. TAA-based MV systems with paracyclophane units as part of the bridge are thus of particular interest to probe the importance of ET via π - π interactions, and both experimental and computational studies have been initiated. The paracyclophane units are internally connected by saturated σ -bonded hydrocarbon linkers. Hence the question arises to what extent the coupling between the redox centers proceeds via the π - π interactions (through space) or via the linkers (through bond). Early studies of simple paracyclophanes by photoelectron spectroscopy suggested that both pathways may be important.^[214] The conclusions drawn from

spectroscopic studies of the present target systems are less clear-cut regarding the detailed situation.^[20, 31] Computational studies are ideally suited to answer this question, provided the computational protocol captures well the molecular and electronic structure of such systems. Given the importance of non-covalent π - π interactions, the DFT-based protocol presented above will be investigated in particular by additional dispersion corrections during the structure optimization step.



Scheme 5.1. Six mixed-valence bis-triarylamine radical cations with paracyclophane bridges. *Upper:* **PC1** and **PC2** with [2.2]paracyclophane. *Middle:* **PC3** and **PC4** with [3.3]paracyclophane. *Bottom:* **PC5** and **PC6** with [4.4]paracyclophane. The right-side structures include additional acetylene spacers on both sides.

A series of paracyclophane-bridged bis-triarylamine radical cations **PC1-6** (Scheme 5.1) is thus studied in this chapter. The paracyclophane units within the bridge feature π -stacked benzene rings, linked by two alkyl chains (ethyl, propyl or butyl) in 1,4-position. The distance between the π -systems is typically about 3 Å. It has to be noted that investigations of MV dinitroaromatic radical anions (related to the systems **DN1-6** studied in chapter 6 below) with paracyclophane bridges have provided indications that the electronic coupling

may also depend appreciably on the relative position (*ortho* vs. *para*) of the linkers on the benzene rings.^[215]

Half of the molecules in the present systematic test set features [2.2], [3.3] and [4.4]paracyclophanes as spacers, connected directly to one of the aryl rings of the triarylamine redox centers (**PC1**, **PC3** and **PC5**, respectively). The systems **PC2**, **PC4** and **PC6** have additional acetylene groups in between on each side. It is thought, that the extra acetylene spacers may prevent a twisting of the biphenyl units. Only a part of these systems (particularly **PC1** and **PC2**, partly **PC4**) so far has been studied also experimentally,^[20, 31, 32, 202] and thus only a limited amount of experimental reference data for comparison is available. However, due to the reduced coupling provided by the paracyclophane linkers compared to fully conjugated bridges in **TAA1-10** (chapters 3 and 4), it is clearly expected that all six systems will be class II cases.

5.2 Computational Details

Structure optimizations as well as bonding analyses were performed with TURBOMOLE (TBM) 5.9 and 5.10^[192] both locally modified to allow variation of the exact-exchange admixture in a global hybrid functional. The “custom hybrid” exchange-correlation functionals were constructed according to eq. (3.1). As specified in chapter 3 and 4,^[44, 45] the optimal value for the description of mixed-valence systems is $a = 0.35$. If not stated otherwise SVP basis sets were used.^[193] Optimizations with the COSMO solvent model^[120] have been performed for hexane ($\epsilon = 1.89$), dichloromethane (DCM, $\epsilon = 8.93$), and acetonitrile (MeCN, $\epsilon = 36.64$) in addition to gas phase calculations. In all cases unsymmetrical starting structures (C_i) as well as symmetrical starting structures (C_i) have been investigated. As all systems turned out to be unsymmetrical class II systems (see below), the C_i -symmetric transition-state structures were also optimized to provide the adiabatic ET barriers. Spin-density isosurface plots were plotted with the Molekel program.^[195]

Subsequent TDDFT-calculations of the lowest-energy electronic transitions (IV-CT bands) for both C_i - and C_i -symmetric structures were done with the Gaussian 03 program

(Go3),^[196] using the same type of hybrid functionals and SVP basis sets^[193] as discussed above. Solvent effects in Go3 calculations have been included by the CPCM keyword, which denotes the polarizable continuum model that is closest to the COSMO model used in the optimizations.^[121] The Go3 TDDFT results have been found to agree better with experiment than the TBM5.9 or TBM5.10 data (particularly for symmetrical structures, see chapter 3 and ref. [44]) as soon as a polarizable continuum solvent was included. The differences arise from technical details (van-der-Waals radii, solvent radii, number of tesserae per sphere) in the two solvent-model implementations and especially from the fact that Go3 but not TBM (5.9 or 5.10) includes non-equilibrium solvation in the TDDFT implementation.

Hyperfine coupling constants (HFCs) have been calculated by generating the Kohn-Sham orbitals using TURBOMOLE, with IGLO-II basis sets (H (3s1p)/[5s1p], C N O (5s4p1d)/[9s5p1d])^[210] and the previously proposed hybrid functional including 35% ($a = 0.35$) exact exchange admixture. The orbitals were then transferred to the MAG-ReSpect program package^[211] for computation of the HFCs.

It is well-known that van-der-Waals-type correlation effects are crucial for the correct description of π -stacking interactions. While standard DFT functionals like the one used here do not account for such dispersion effects, semi-empirical dispersion correction terms within DFT-D approaches are well suited to incorporate these contributions.^[216, 217]

These dispersion effects are included by Grimme's DFT-D2 approach, as implemented in TBM5.10.^[218, 219] The empirical dispersion correction is simply added to the Kohn-Sham-energy

$$E_{DFT-D} = E_{KS-DFT} + E_{disp} . \quad (5.1)$$

Several forms of corrections E_{disp} are known. They consist of diatomic interaction terms with the R^{-6} dependence known since London^[220] and Pauling,^[221] obtained from atomic terms with empirical C_6 -coefficients in the form^[218, 222-226]

$$E_{disp} = -\frac{C_6}{R^6}. \quad (5.2)$$

The DFT-D2 *ansatz* available in TBM5.10 exhibits furthermore a damping function and a semi-empirical scaling parameter s_6 to adjust for the attractive/repulsive behavior of the underlying density functional.^[218] The dispersion energy for a system with N atoms and the interatomic distance R_{ij} is thus defined as

$$E_{disp} = -s_6 \sum_{i=1}^{N-1} \sum_{j=1}^N \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij}), \quad (5.3)$$

with a damping function

$$f_{dmp}(R_{ij}) = \left[1 + \exp \left\{ -d \left(\frac{R_{ij}}{R_r} - 1 \right) \right\} \right]^{-1}, \quad (5.4)$$

where R_r is the sum of the van-der-Waals radii in the ground state and d a constant damping factor. The diatomic C_6^{ij} -coefficients are calculated as geometric mean from atomic values.^[219] The global s_6 -parameter was adjusted to 1.0 for the BLYP35 functional using the S22 test set by Hobza.^[227] The use of this DFT-D2 implementation was motivated by the availability in TBM5.10. Meanwhile, more refined DFT-D3 variants are also available, featuring a number of improvements.^[228]

5.3 Results and Discussion

As mentioned above, the experimental data are so far limited to the radical cations of **PC1**, **PC2** and **PC4**,^[20, 31] and to two studies of corresponding neutral and dicationic states.^[32, 202] All of them agree that the coupling between the redox centers is still appreciable but weaker than in corresponding fully conjugated cases, leading to a class II behavior in all cases. The ET barriers determined both by ESR and by optical measurements (via a Generalized-Mulliken-Hush (GMH) analysis) in solvents like DCM agree well and are in the range between 9 kJ mol⁻¹ and 17 kJ mol⁻¹ (see below). Computed ground state properties for **PC1**, **PC2**, and **PC3** at BLYP35/SVP level in a range of environments are shown in Table 5.1

(corresponding predictions for **PC3**, **PC5**, and **PC6** are given in Table S5.1 in the Appendix). As expected from previous calculations (see chapters 3 and 4), all molecules are delocalized class III cases in the gas phase and in the non-polar solvent hexane, as indicated by negligible dipole moments and ET barriers, and symmetric spin-density distributions (cf. Figure 5.1, left). Unsurprisingly, BLYP35/SVP/COSMO calculations in DCM and MeCN provide charge localized structures (cf. Figure 5.1, right). The dipole moment is about 32 Debye for **PC1**, consistent with recent AM1-CISD calculations by Lambert *et al.*, who obtained values of 33.4 and 34.1 Debye.^[20] The latter also include solvent effects (COSMO, $\epsilon = 2.0$). In that work, slightly larger values have been obtained for **PC2**. This is confirmed here: the dipole moments of **PC2** are about 9 Debye larger than those of **PC1**. The same holds true for comparisons of **PC3** vs. **PC4** or **PC5** vs. **PC6** (see Table 5.1 and Table S5.1).

Table 5.1. Ground state properties (dipole moments μ_o in Debye, ET barriers $\Delta H^\ddagger$ in kJ mol^{-1} , distance $d_{\pi-\pi}$ and vertical displacement d_{dis} of the benzene rings as well as C-N bond lengths d and d' in Å, and torsion angle of the biphenyl axis α in degrees)^a in different environments for **PC1**, **PC2** and **PC4**

	environment	μ_o^b	$\Delta H^\ddagger$	$d_{\pi-\pi}$	d_{dis}	$d(\text{C}_{\text{Ar}}-\text{N})$	$d'(\text{C}_{\text{Ar}}-\text{N})$	α
PC1^c	gas phase	0.01	0.3	2.97	0.47	1.412	1.412	32.2±0.0
	hexane	0.02	-0.3	2.96	0.46	1.411	1.411	32.2±0.0
	DCM	32.33	14.7 ^d	2.96	0.45	1.417	1.403	32.2±0.3
		(33.91)	(19.9)	(3.04)	(0.16)	(1.422)	(1.405)	(38.6±2.4)
	MeCN	33.27	20.4	2.97	0.41	1.417	1.402	32.5±0.6
PC2^c	gas phase	0.13	0.0	2.94	0.40	1.415	1.416	
	hexane	0.34	-0.1	2.94	0.39	1.415	1.416	
	DCM	41.28	16.2 ^d	2.95	0.30	1.420	1.403	
		(42.52)	(19.0)	(3.02)	(0.00)	(1.425)	(1.406)	
	MeCN	42.46	22.1	2.95	0.30	1.420	1.402	
		(43.76)	(24.8)	(3.02)	(0.00)	(1.425)	(1.405)	
PC4	gas phase	0.00	0.0	3.08	0.70	1.416	1.416	
	hexane	0.01	0.1	3.08	0.70	1.416	1.416	
	DCM	43.68	15.5 ^d	3.11	0.65	1.420	1.403	
	MeCN	44.97	21.9	3.11	0.64	1.420	1.402	

^a Mean values of centroid and plane distances/displacements are given. The systematic errors in distance are <0.03 Å and in displacement <0.15 Å. ^b With the center of mass as the origin. ^c Values in parentheses calculated without dispersion corrections. ^d Experimental adiabatic ET barriers ΔG^* derived from GMH analysis and PES fits are 13.0±1.2 kJ mol^{-1} for **PC1** and 14.1±1.2 kJ mol^{-1} for **PC2**.^[20] Experimental enthalpies of activation, $\Delta H^\ddagger$, from ESR spectroscopy are 9.3±0.3 kJ mol^{-1} for **PC1**, 13.8±1.0 kJ mol^{-1} for **PC2** and 16.9±0.7 kJ mol^{-1} for **PC4**.^[31]

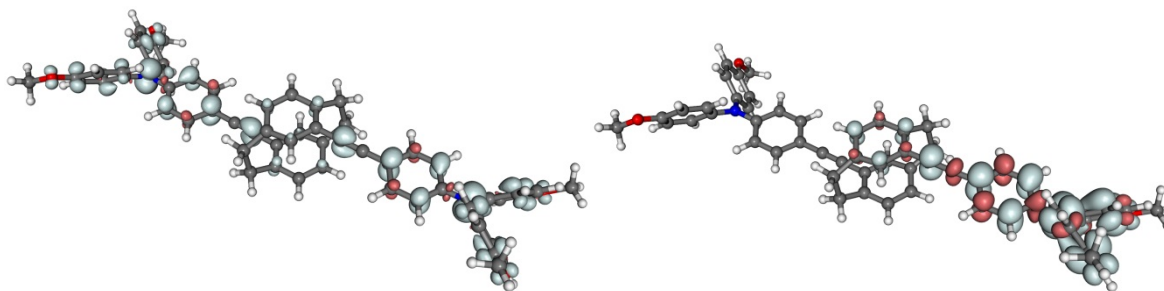
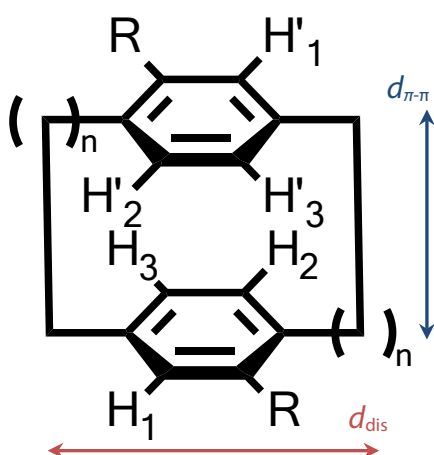


Figure 5.1. Spin-density distributions (BLYP35/SVP, isovalue ± 0.002 a.u.) of **PC2** in hexane (left) and DCM (right).



Scheme 5.2. Assignments of $[n.n]$ paracyclophane ($n = 1-3$), benzene distance $d_{\pi-\pi}$ and vertical displacement d_{dis} .

The calculated ET barriers agree well with experimental barriers in DCM obtained from GMH analysis and potential-energy-surface (PES) fits^[20] or with experimental enthalpies of activation derived from ESR spectroscopy.^[31] The π - π -distance between the two benzene-rings of the paracyclophanes $d_{\pi-\pi}$ (see Scheme 5.2) is around 2.94-2.97 Å for the [2.2]paracyclophanes, somewhat larger (3.08-3.20 Å) for the [3.3]paracyclophanes **PC3** and **PC4**. (see Table 5.1 and Table S5.1) and still somewhat larger in the [4.4]paracyclophane **PC5** (3.25 Å). Surprisingly, the π - π -distance for the [4.4]paracyclophane **PC6** is much

larger (about 3.8 Å) for the localized structures in DCM and MeCN (Table S5.1). The computed π - π -distances $d_{\pi-\pi}$ for **PC1** and **PC3** agree well with crystal structure data ($d_{\pi-\pi}(\mathbf{PC1}) = 2.98$ Å, $d_{\pi-\pi}(\mathbf{PC3}) = 3.23$ Å) for the neutral systems.^[229] They are also consistent with experimental π - π -distances for other substituted paracyclophanes, where values of about 3.05-3.07 Å are typical for [2.2]paracyclophanes and 3.25-3.32 Å for [3.3]paracyclophanes.^[230, 231] Both sets of values are smaller than expected from the sum of the van-der-Waals radii (3.4 Å). The π - π -distance in a [4.4]paracyclophane is about 4 Å,^[232, 233] which is larger than the calculated values for **PC5** and **PC6**. However, due to the different substituents and charge, they cannot be compared directly. The computed values appear to be reasonable, and they exhibit the same trend as measured distances. This is also in the range of typical π - π -interactions, e.g. in stacked benzene or larger chromophores.^[234-236] The effect of the dispersion energy correction is negligible for the [2.2]paracyclophanes, where

the distances are apparently determined by the short ethylene-bridge. Effects are larger for the [3.3] and [4.4]paracyclophanes (see Table 5.1 and Table S5.1). This is also consistent with results from a recent DFT study (using B97-D and ω B97X-D compared to HF, B3LYP and Mo6-2X) on neutral and unsubstituted paracyclophanes, where the dispersion corrections play an important role for the longer and more flexible linkers.^[217] A second effect of the dispersion correction is a vertical displacement (d_{dis}) of the benzene rings of about 0.3-1.4 Å (see Scheme 5.2) which is absent when dispersion corrections are neglected. The displacement is particularly large for **PC5** and **PC6** as a result of the longer linkers. The rotational angle of the biphenyl axis of **PC1**, **PC3** and **PC4** is increases with system size, from about 30° for **PC1** to about 50° for **PC5**. (Table S5.1).

Table 5.2. Computational result for the first three excitation energies, for electronic couplings (E_i and $2H_{ab}$ in cm^{-1}), and for transition dipole moments $\mu_{t,i}$ in Debye as well as ^{14}N - and ^1H -HFCs a in MHz compared to experimental values in DCM where available

	E_i (C_i)	$2H_{ab}$ (C_i)	$\mu_{t,i}$ (C_i)	$\mu_{t,i}$ (C_i)	a ($\text{N}^{(i)}$)	a ($\text{H}^{(i)}_1$)	a ($\text{H}^{(i)}_2$)	a ($\text{H}^{(i)}_3$)
PC1	5916	516	2.04	26.96	0.24	-0.07	0.09	0.00
	12714		6.56		26.33	-2.64	2.09	-2.63
	14102		3.45					
<i>exp.</i>	6230 ^{a,b}	1410 ^{a,c}	7.6±0.3 ^a		24.66 ^b		-1.88 ^f	
	11870 ^{a,b}	1940 ^{a,d}	5.4±0.3 ^a					
	13480 ^{a,b}		-					
PC2	6560	635	2.13	33.41	0.15	-0.11	0.10	0.23
	11826		9.54		24.73	-2.91	1.98	-3.64
	14497		1.92					
<i>exp.</i>	6600 ^a /5870 ^b	680 ^{a,c}	3.4±0.1 ^a /3.5±0.2 ^b		23.65 ^b		-1.88 ^f	
	10700 ^a /10730 ^b	1140 ^{a,d}	5.9±0.3 ^a /6.2±0.3 ^b					
	13480 ^a /13460 ^b		-/-					
PC4	6491	789	3.70	34.11	0.22	-0.09	0.22	-0.50
	11039		8.63		24.21	-2.92	1.99	-4.18
	14059		4.07					
<i>exp.</i>	8500 ^b	640 ^{b,c,e}	2.3 ^b		23.12 ^b		-	
	10610 ^b	220 ^{b,d,e}	5.8 ^b					
	13500 ^b		- ^b					

^a Experimental value from ref. [20]. ^b Experimental value from ref. [31]. ^c Experimental coupling obtained by a two-level model. ^d Experimental coupling obtained by a three-level model. ^e Uncertain value, see ref. [31]. ^f Experimental ^1H -HFCs for methoxy-substituted [2.2]paracyclophanes.^[231]

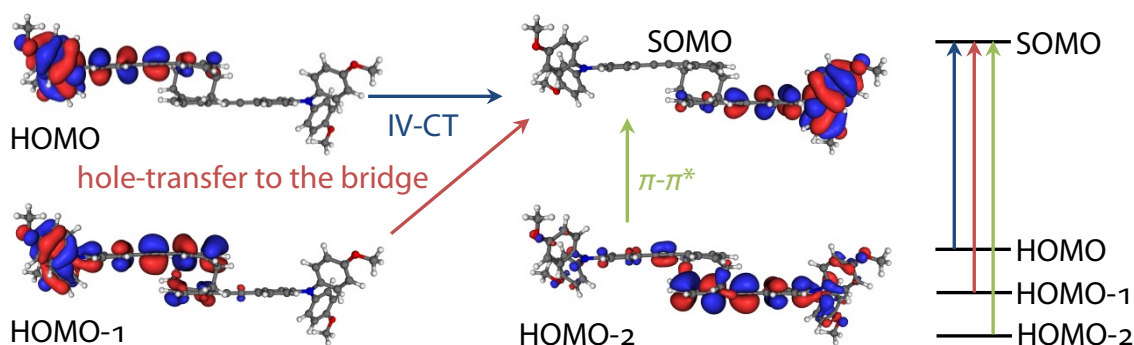


Figure 5.2. Molecular orbitals (β , isovalue ± 0.01) of **PC2** in DCM and corresponding transitions. The HOMO→SOMO transition corresponds clearly to IV-CT excitation. The main contribution of the hole-transfer to the bridge is the HOMO-1→SOMO transition, yet other orbitals with lower energy are part of this charge transfer. The π - π^* -transition is mainly composed of the HOMO-2→SOMO transition. Again, orbitals with lower energy contribute to this transition.

Computations of spectroscopic properties (optical transitions and HFCs, see Table 5.2, corresponding data for **PC3**, **PC5**, and **PC6** are given in Table S5.4, Table S5.6, and Table S5.7 in the Appendix) are fully consistent with the ground state characteristics. In general, the first excitation energy is somewhat underestimated compared to experimental values, as expected for class II systems. Both the second and third excitation energies are slightly overestimated, consistent with expectations at this computational level. The large deviation (2000 cm^{-1}) of the first excitation energy of **PC4** might be due to ambiguous Gaussian-fitting of this weak transition (fitting was easier for **PC1** and **PC2**).^[31] The lowest transition corresponds to the IV-CT transition (see involved orbitals in Figure 5.2). It is rather similar for the different paracyclophanes, about 6500 cm^{-1} in DCM. The value in MeCN is blue shifted by about 1300 cm^{-1} . Calculations without dispersion corrections during the structure optimization increase the transition energy by about 200 cm^{-1} . The second transition corresponds to the hole-transfer to the bridge, and the third to a π - π^* -transition, even though both transitions exhibit mixing of different molecular orbitals to these transitions (orbitals with the highest contribution to these transitions are given in Figure 5.2). Both are overestimated by about 400 - 1000 cm^{-1} in the TDDFT calculations, whereas the transition dipole moments are well reproduced. It is clear that the predictive value of these TDDFT calculations is superior to that of prior AM1-CISD calculations,^[20, 31] which overestimate both excitation energies and transition dipole moments. Use of erroneous delocalized structures obtained in hexane or gas phase calculations give very poor agreement with experiment for all transitions (see Table S5.2-5.7). The calculated electronic coupling $2H_{ab}$ is

around 200-1000 cm^{-1} at BYLP35/SVP/CPCM level (Table 5.2 and Table S5.2-5.7). The only exception is **PC6**, for which $2H_{ab} > 1200 \text{ cm}^{-1}$ is predicted. This contradicts expectations that the coupling should decrease with increasing $d_{\pi-\pi}$ distance, as also suggested by the trend in the experimental electron couplings (see Table 5.2) even if a two-level or three-level model is applied.

The class II character of the compounds in polar solvents is also confirmed by calculations of ^{14}N -HFCs. The asymmetrical spin-density distribution (see Figure 5.1) gives rise to only one sizeable coupling of about 25 MHz, which agrees quite well with experimental data (Table 5.2). Both calculated and experimental values exhibit the trend: $a_N(\text{PC1}) > a_N(\text{PC2}) > a_N(\text{PC4})$, with slightly higher values in the DFT calculations. As expected, two identical ^{14}N -HFCs ($a_N \approx 12 \text{ MHz}$) have been found for all symmetrical ground-state structures obtained in the gas phase and in hexane.

The asymmetric spin-density distribution in more polar environments are also reflected in the computed six aromatic ^1H -HFCs a_H of the paracyclophane (see Scheme 5.2 as well as Table 5.2 and Table S5.2-5.7), with negligible values on one of the benzene rings and $a_H \approx (\pm)1\text{-}4 \text{ MHz}$ on the other benzene ring. The delocalized character in the gas phase and in hexane produces generally three pairs of identical HFCs $a_H \approx (\pm)0.5\text{-}2 \text{ MHz}$. Due to the lack of experimental data for **PC1-6**, the computed values are compared to experimental data for radical cations of di- or tetramethoxy-substituted [2.2]paracyclophanes (Table 5.2).^[231] These are of course not MV systems but should correspond well to the situation for the present class II cases. One of the three calculated ^1H -HFCs are always negative (H_1 and H_3) and one is positive (H_2), consistent with the spin-density distributions (see Figure 5.1). Interestingly, for the analogous pairs (**PC1** and **PC2**, **PC3** and **PC4**, **PC5** and **PC6**) the additional acetylene-bridge incases a_H , particularly for the [3.3]- and [4.4]paracyclophanes, in fact consistent with the larger electronic couplings $2H_{ab}$ for these systems (Table S5.2-5.7). While this contradicts the intuition that larger spacers reduce the coupling, it can be rationalized by the twisting angle of the biphenyl axis in **PC1**, **PC3** and **PC5**. This reduces the overlap between the π -orbitals of different phenyl rings and thus reduces the coupling.

Table 5.3. Calculated ground state properties^a and excited state properties^b for **PC2a** (without ethyl-bridges at the paracyclophane) and the corresponding **PC2** in DCM

	μ_o	$\Delta H^\ddagger$	$d_{\pi-\pi}$	d_{dis}	d	d'	$E_i (C_1)$	$2H_{\text{ab}} (C_i)$	$\mu_{i,1} (C_1)$	$\mu_{t,1} (C_i)$
PC2a^c	38.93	12.9	3.31	1.47	1.420	1.404	6339	1252	5.03	32.02
							11985	8861	8.91	0.00
	(54.47)	(24.2)	(3.27)	(5.10)	(1.425)	(1.404)	(7485)	(405)	(0.11)	(25.83)
							(13258)	(10126)	(8.65)	(0.00)
PC2	41.28	16.2	2.96	0.30	1.420	1.403	6560	635	2.13	33.41
							11826	9678	9.54	10.53

^a Dipole moments μ_o in Debye (with the center of mass as the origin), ET barrier $\Delta H^\ddagger$ in kJ mol⁻¹, distances $d_{\pi-\pi}$, d_{dis} , d and d' in Å. ^b Excitation energies E_i and electronic coupling $2H_{\text{ab}}$ in cm⁻¹ and the corresponding transition dipole moments $\mu_{t,1}$ in Debye. ^c Values in parentheses without including dispersion corrections in DFT calculations.

Finally, the question of the through-space (π - π) vs. through-bond (σ) mechanism for the electron transfer is investigated. In analogy to a previous AM1-CISD study,^[20] a modified model compound **PC2a**, where the ethylene-bridges in **PC2** have been removed (replaced by hydrogen atoms), is explored. Optimization of this model obviously requires inclusion of dispersion corrections, as otherwise the system will dissociate into two separate fragments at large distance (cf. vertical displacement of >5 Å in calculations without dispersion terms, see Table 5.3). Even in the presence of dispersion corrections, $d_{\pi-\pi}$ and d_{dis} for **PC2a** are somewhat larger than for **PC2** (3.31 Å and 1.47 Å respectively). Yet, the influence on dipole moment and ET barrier is small. The ET barrier is actually lowered, and thus a larger electron coupling is obtained, contrasting the larger $d_{\pi-\pi}$. The excitation energies are also influenced only little by removal of the ethylene linkers, and the transition dipole moment for the IV-CT transition is increased. These observations point to a dominant through-space (π - π) mechanism for the electron transfer. This is further supported by the lack of spin density on the linker in **PC2** (Figure 5.1) and by the marginal contribution of the linker to the MOs involved in the IV-CT transition (Figure 5.2). This contrasts somewhat with the previous AM1-CISD+COSMO study,^[20] where both mechanisms were assumed to contribute to electronic coupling. This may be related to incomplete structure optimizations in the AM1-CISD calculations. Notably, however, detailed spectroscopic analyses by the same authors favored the through-space mechanism, consistent with the present results.^[31] It should be noted in any case, that “through space” in the case of π -stacked interactions refers to a space with high electron density throughout. This may be related to arguments

that have been put forward for through-space mechanisms for indirect nuclear spin-spin couplings.^[237]

5.4 Conclusions

With only one modification, namely the inclusion of dispersion corrections during DFT structure optimization, the BLYP₃₅/SVP/COSMO protocol introduced in the previous two chapters has also been extended successfully to the detailed analysis of electron transfer in the MV paracyclophane-bridged bis-triarylamine radical cations **PC1-6**. All systems belong to the Robin-Day class II in polar solvents (DCM and MeCN), consistent with experimental evidence for **PC1**, **PC2**, and **PC4**, but to class III in the gas phase or in hexane. Experimental ET barriers, optical transitions and hyperfine couplings are well reproduced by the computations. The π - π -distances are in good agreement with experimental structures for the corresponding neutral systems. The much larger distance for localized structures of **PC6** (in DCM and MeCN) indicates such an effect of charge-separation on the benzene-distance.

Computations on a model **PC2a** in which the ethylene linkers have been removed from **PC2** give very similar ET parameters as calculations on the full system. This supports clearly a dominance of a through-space mechanism for the electron transfer.

Chapter 6

Almost all the chemical processes which occur in nature, whether in animal or vegetable organisms, or in the non-living surface of the earth – take place between substances in solution.

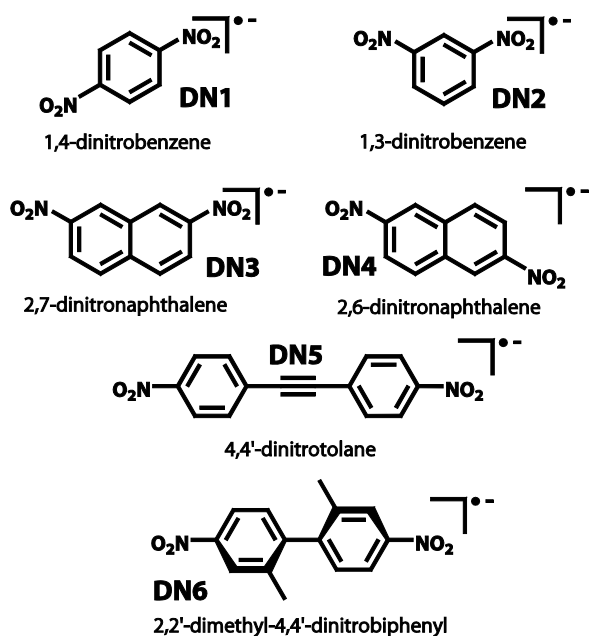
-- Wilhelm Ostwald

6 Extension to Dinitroaromatic Radical Anions

6.1 Introduction

The proposed quantum chemical protocol for the description of the character of organic mixed-valence (MV) compounds (see chapter 3-5)^[44, 45] will be evaluated and extended in this chapter for a series of dinitroaromatic radical anions **DN1-6** (Scheme 6.1). In addition to the previous chapter, the focus of this part of the work concentrates on the evaluation of solvent model implementations and basis set effects as well as on the influence of common density functionals on the properties (i.e. ET barriers and IV-CT energies) of these MV systems. For these surveys, **DN1-6** are much more suitable than the bis-triarylamines radical cations **TAA1-10**, because they are much smaller and they exhibit an exposed negative charge at the nitro moieties. The latter point is highly challenging, since this is more difficult to describe by a continuum solvent model – in contrast to the more shielded positive charge in the bis-triarylamine radical cations. Therefore, specific solvent-solute interactions will play an important role, especially for protic solvents. This is demonstrated by the transition of the 1,4-dinitrobenzene radical anion **DN1** from a class III behavior in

aprotic solvents to a class II behavior in alcohols, that is not recovered by the continuum solvent models applied so far. One possibility to deal with this problem is the novel direct conductor-like screening model for real solvents (D-COSMO-RS),^[123-125, 238] which can distinguish at least qualitatively between different solvents with identical or similar dielectric constants (see section 2.3). This approach might allow accurate estimates from the gas phase to aprotic and protic solvent environments, without the need for explicit *ab initio* molecular dynamics simulations, and without artificial constraints as sometimes used for the description of class II MV systems^[174, 239]



Scheme 6.1. Six dinitroaromatic radical anions studied.

In addition, the basis-set requirements to describe the negative charge at the nitro groups are more pronounced than by the protocol proposed in the previous chapters, where the relatively small SVP basis sets^[193] have been sufficient. Due to the system size of DN1-6, a much wider range of popular hybrid density functionals can be evaluated, for example the highly parameterized hyper-GGA hybrid functionals (Mo5, Mo6, Mo5-2X, Mo6-2X, BMK),^[240-243] the range-separated hybrids (CAM-B3LYP, ω B97X, LC-BLYP)^[64, 69, 244] and the double hybrids (B2PLYP/B2PLYPD).^[245]

Furthermore, the peculiar EPR spectroscopic behavior of dinitroaromatic radical anions DN1-6 has been studied in detail since the early 1960's, even before the very notion of mixed-valency had been discussed.^[141-152] Finally, they have been widely used as model systems in quantum chemical studies.^[42, 43, 170-172, 174, 239, 246]

6.2 Available Experimental Information

The six dinitroaromatic radical anions **DN1-6** studied in this chapter (see Scheme 6.1) feature two nitro substituents as redox centers which are all connected by aromatic bridges. Some of these anions are among the earliest MV systems studied in the 1960s,^[141-152] in particular by ESR spectroscopy. They cover the range from class II to class III of the Robin-Day scheme (see Figure 1.2) while remaining sufficiently close to the borderline to be a challenge for standard quantum chemical treatments.

The radical anion of 1,4-dinitrobenzene, **DN1**, is a class III system in aprotic solvents, consistent with strong electronic coupling for a Kekulé substitution pattern, i.e. for an odd number of bonds between the two nitrogen atoms. **DN1** does not exhibit alternating line-broadening effects in ESR in aprotic solvents and has narrow, intense low-energy optical bands with vibrational structure with maxima at 10820 cm⁻¹ and 11000 cm⁻¹ in dimethylformamide (DMF) and in acetonitrile (MeCN), respectively.^[190, 247] Lü *et al.* showed by X-ray crystallography, and by spectroscopy in solution, that strong ion pairing can lead to an asymmetrical structure of **DN1**, whereas use of cryptands to prevent ion pairing keeps the system delocalized even in the solid state.^[248] Preliminary calculations confirm that close ion pairing can distort the symmetry of **DN1** when the counter-ion (sodium) is placed near one of the nitro groups, both in gas phase and solvents, while it remains symmetric if the sodium atom is placed above the ring (see Figure S6.1 in the Appendix). This holds also true for the other compounds **DN2-6**, even if discrete solvent molecules are included into the calculations. But the results are unreliable and mainly dependent on the starting structure used, i.e. where the counter ion or solvent molecule is placed. Therefore, full molecular dynamic treatment would be required for a proper description of this issue. Given that the abovementioned spectroscopic data in aprotic solution all suggest class III character, strong ion pairing under these conditions is unlikely. However, due to hydrogen bonding (see below), the system becomes class II on the ESR time scale in alcoholic solvents even up to near room temperature, with estimated thermal electron transfer (ET) barriers ($\Delta H^\ddagger$) between 22 kJ mol⁻¹ and 36 kJ mol⁻¹, depending on the specific alcoholic solvent.^[156] The 2,6-dinitronaphthalene radical anion **DN4** is also a class III system in aprotic solvents,^[42, 190] with a narrow, intense IV-CT band in DMF.

In contrast, the radical anion of 1,3-dinitrobenzene, **DN2**, has a non-Kekulé substitution pattern, with an even number of bonds between the nitrogen atoms. It exhibits class II character already in polar aprotic solvents like acetonitrile or DMF, with alternating ESR line-broadening, broad inter-valence charge transfer (IV-CT) bands, and ESR-derived thermal ET barriers of about 22 kJ mol⁻¹ in MeCN or DMF.^[42, 247] These values have been obtained after electrochemical reduction. Measurements in the presence of cryptand to suppress ion pairing gave ET barriers (at 298 K) of ca. 26 kJ mol⁻¹ in MeCN and of ca. 16 kJ mol⁻¹ in DMF.^[249] This suggests again that ion pairing, while overall non-negligible, does not affect the ET barriers in these environments to an extent that would invalidate the present calculations that neglect the influence of counterions. Within the general accuracy of the approach, this holds also largely for the other systems studied here. In alcoholic solvents, barriers of about 43 kJ mol⁻¹ have been measured for **DN2**, enhanced by hydrogen bonding (here ion pairing is expected to play an even smaller role).^[153, 154, 156]

Similarly, the radical anion of 2,7-dinitronaphthalene, **DN3**, is on the class II side already in aprotic solvents (in fact, **DN3** is the clearest class II case in this study, see below), with broad IV-CT bands in MeCN and in DMF.^[42] According to ESR studies, ET barriers are about 18 kJ mol⁻¹ in MeCN and of ca. 12-13 kJ mol⁻¹ in DMF and in hexamethylphosphoramide (HMPA).^[185] The corresponding barriers in alcoholic solvents like methanol are around 50 kJ mol⁻¹.^[155]

The radical anion of the 4,4'-dinitrotolane-bridged system **DN5** is of particular interest by being extremely close to the class II/III transition in aprotic solvents.^[176] Optical spectra and resonance Raman spectra suggest that delocalized and localized forms of the radical anion coexist, with the predominance of one over the other depending on the solvent.^[183] In solvents with presumably low solvent reorganization energies, λ_s , such as tetrahydrofuran (THF) or HMPA,^[250, 251] typical charge-delocalized spectra dominate. A small fraction of localized spectra persists, however, even when an excess of cryptand^[2.2.2] is added during reduction to minimize ion pairing. In these solvents, the maximum in the absorption band of the delocalized species is at 5860 cm⁻¹. In higher λ_s -solvents typical charge-localized spectra with broad IV-CT bands dominate. The band maxima range from 9560 cm⁻¹ in

DMF and 10800 cm⁻¹ in dichloromethane (DCM) to 11300 cm⁻¹ in MeCN. ESR-based ET barriers $\Delta H^\ddagger$ for the localized species are 11.3(±1.7) kJ mol⁻¹ in MeCN, 13.8(±1.9) kJ mol⁻¹ in DMF, and 11.5(±0.9) kJ mol⁻¹ in DCM.^[185]

In the radical anion of 2,2'-dimethyl-4,4'-dinitrobiphenyl, **DN6**, the presence of two methyl groups leads to a twisting of the two phenyl rings relative to each other.^[185] The resulting reduced overlap of the π -orbitals is expected to decrease electronic coupling and to favor a class II situation. This was confirmed by optical and ESR spectra in several aprotic solvents (e.g. MeCN, DMF or DCM). Broad IV-CT bands are observed in DMF, DCM, and MeCN, whereas the spectra in HMPA are consistent with both class III and class II species being present.^[185] The ESR-based electron transfer barriers $\Delta H^\ddagger$ are 8.8(±1.3) kJ mol⁻¹ in MeCN, 13.8(±1.7) kJ mol⁻¹ in DMF, and 4.2(±0.8) kJ mol⁻¹ in DCM.^[185]

6.3 Computational Details

6.3.1 Program versions, continuum solvent models and basis sets

In the previous chapters (see sections 3.3, 4.3 and 5.2) a version of the TURBOMOLE 5.10 (TBM5.10)^[192] code has been mainly employed for the ground-state structure optimizations, and the Gaussian 03 (Go3)^[196] code for subsequent TDDFT calculations of excitation energies and transition dipole moments. This use of two codes was mainly due to differences in computational efficiency and in the solvent models implemented (see sections 3.3, 4.3 and 5.2). Meanwhile, newer versions of both codes have appeared, TURBOMOLE 6.3 (TBM6.3)^[252] (also locally modified), and Gaussian 09 (Go9),^[209] with updates to the solvent models. In particular, a separation of fast and slow solvent modes in TDDFT is now also available in TBM6.3. In contrast to the derivation of the quantum chemical protocol (chapter 3), these more recent versions of the codes have been applied to the six dinitroaromatic radical anions. The differences to the previous versions have been primarily evaluated in detailed test calculations (mainly described in the Appendix, Table S6.1-S6.8). The relatively small sizes of the present MV systems will allow extensive structure optimizations with both codes and various approaches. The calculations with the modified TBM6.3

are mainly done in context of D-COSMO-RS^[123] approach and with G09 mainly for evaluating a wider range of density functionals (see below).

In the G09 and G03 calculations, the CPCM version^[121, 253] of the polarizable continuum (PCM) solvent model has been employed, as this is closest to the COSMO *ansatz* used in TURBOMOLE (previous tests using the IEFPCM model led to negligible changes, see section 3.3).^[44] One main change from G03 to G09 is the use of the continuous surface charge formalism.^[254, 255] Furthermore, in the construction of the cavity the United Atom Topological Model (UAo) has been replaced by UFF radii, which treat the hydrogen atoms explicitly (this makes the G09 and TURBOMOLE implementations more similar, even if there are still some deviations in the atomic radii used for the cavity construction, see Table S6.1). In the subsequent TDDFT calculations, Gaussian uses non-equilibrium solvation, where only the fast solvent modes are included in the linear response part. In TBM6.3, a similar division is now employed.^[128, 129] The relevant dielectric constants for the solvents used in this chapter are provided in Table 2.1.

Near the critical values of exact-exchange (E_{xx}) admixture a (see eq. (3.1)), where symmetry breaking occurs, the outcome of the ground-state structure optimizations depend sometimes on whether a symmetrical or unsymmetrical starting structure is used, as already known from previous chapters. In this case, different unsymmetrical (C_1) and symmetrical (typically C_{2v} , C_s or C_i) starting structures have been investigated, and the validity of a given structure has been evaluated energetically. Reported computational thermal ET barriers, $\Delta H^\ddagger$, have been obtained again as difference between the ground state energies of the symmetrical and the unsymmetrical structures, neglecting both zero-point vibrational and thermal corrections. Note, however, that the various solvent models do include solvent thermal effects (and even some entropic contributions), but these approximations cause uncertainties in the computed activation enthalpies and can be estimated of at least 5 kJ mol⁻¹. This should be kept in mind when comparing to the ESR-based values (which exhibit their own intrinsic errors, see below). In selected cases, the character of the optimized stationary points has been evaluated by harmonic vibrational frequency analysis, partly to compare with resonance Raman data. In some other cases, frequencies turned out

to be unreliable due to numerical aspects of the solvent models; therefore, utilizing zero-point vibrational corrections will be refrained. Subsequent TDDFT calculations of the lowest-energy electronic transitions (IV-CT bands) for both minima and transition-state structures have been done with either Gaussian or TURBOMOLE, using the same type of functional and basis sets and corresponding solvent models (see above).

While calculations on MV bis-triarylamine radical cation systems (see section 3.3) could rely mostly on moderate-sized SVP basis sets,^[193] as basis-set augmentation had only a small influence on the results (see also ref. [44]), it is well known that diffuse basis functions are more important for the proper description of anions. Thus, different basis sets have been evaluated for the present systems. Augmentation by a set of diffuse s- and p-functions led to SVP+ basis sets (the exponents of the additional diffuse functions for the non-hydrogen atoms were obtained by dividing the smallest s- and p-exponents of the SVP basis by a factor of 3). When diffuse augmentation was restricted to only the oxygen atoms of the nitro groups, the basis is termed SVP+(O). The largest basis set used, and the one employed finally in all further calculations, was TZVP.^[194]

6.3.2 Density Functionals

As already introduced in chapter 3, non-standard global hybrid functionals based on eq. (3.1), where the exact-exchange admixture a was taken as a semi-empirical parameter, have been used. The value $a = 0.35$ (BLYP35 functional) turned out to be near the optimum for ground-state properties, ET barriers, and IV-CT excitation energies of the previously studied organic MV systems.^[44, 45] The value $a = 0.0$ corresponds to the BLYP GGA functional,^[58, 60] $a = 0.5$ to the BHLYP hybrid functional.^[61] The “one-parameter” functional BLYP35 is not a thermochemically optimized functional and may thus be criticized. By introducing a dependence on local kinetic energy density in highly parameterized, so-called meta-GGA global hybrids, it is possible to combine, e.g., good classical barriers and thermochemistry in main group chemistry. Some examples of such optimized functionals will be evaluated in the present chapter. These are the BMK functional ($a = 0.42$),^[243] Truhlar’s Mo5 ($a = 0.28$)^[240] and Mo6 ($a = 0.27$),^[242] as well as their “double exact-exchange variants” Mo5-2X ($a = 0.56$)^[241] and Mo6-2X ($a = 0.54$).^[242] Additionally, a number of

range-separated hybrids (where exact-exchange admixture depends on the interelectronic distance) available in Gaussian 09 will be evaluated as well. These are CAM-B3LYP,^[64] ω B97X,^[244] and LC-BLYP.^[69] Furthermore, the double-hybrid functional B2PLYP and its dispersion corrected version, B2PLYP(D), were applied.^[245] Double hybrids include an MP2-like term as part of the correlation functional, and B2PLYP includes 53% exact-exchange admixture ($a = 0.53$). Structures were optimized in G09 with all functionals, in particular in MeCN and in DCM solvent, where necessary with both localized and delocalized starting structures, and IV-CT excitation energies were computed again by G09 at TDDFT level with the same functional and solvent.

6.3.3 Direct COSMO-RS

To go beyond the limitations of continuum solvent models, the COSMO-RS approach^[123] has been applied, which has been pioneered in self-consistent DFT implementations (called “direct-COSMO-RS”) by Neese, Klamt and coworkers within the ORCA code^[256]. A similar direct-COSMO-RS implementation is now also available in TBM6.3, which thus has been used in the calculations to reduce code-based disparities. For the relevant solvents, BP86/TZVP pre-generated σ -potentials have been obtained from the COSMOtherm program package^[257, 258] and have been used for structure optimizations and TDDFT calculations in the same manner as described above. All D-COSMO-RS results are reported at the BLYP35/TZVP level.

6.4 Results and Discussion

6.4.1 Differences between program versions

Before dealing with other aspects of the computational protocol, it has to be assured that changes in the continuum solvent models in more recent program versions (see section 6.3.1) do not affect the results. Test calculations, in particular for **DN2** (Table S6.2), indicate that the changes in the COSMO solvent implementation in TBM6.3 compared to TBM5.10 affect ground-state properties only weakly (dipole moments slightly increase, whereas ET barriers decrease somewhat, but which is mainly due to different solvent radii

used – Bondi *vs.* optimized radii). While the ground-state optimizations using Go9 give very similar results as those obtained with TBM6.3 (see Table S6.4 and Table S6.5), the IV-CT excitation energies computed with TDDFT and COSMO in TBM5.10 are systematically higher than those obtained with Go3 and Go9 (with CPCM) as well as TBM6.3 (see Table S6.2). This is due to the neglect of non-equilibrium solvation as already discussed in the previous chapters. Due to the focus on merely the fast solvent terms in TBM6.3, the TDDFT results with COSMO are now much closer to the Go3 TDDFT/CPCM data (see Table S6.2; the Gaussian 09 results are still slightly lower, up to 700 cm⁻¹ in MeCN; Table S6.4 and Table S6.5 provide further comparisons between different codes). This facilitates a comparison of results obtained with both program packages.

6.4.2 Basis set effects

As described in chapter 3-5, calculations on bis-triarylamine systems have been performed mainly with moderate-sized SVP basis sets, as test calculations with larger basis sets (TZVP) gave only relatively small modifications, both on ground-state properties and IV-CT excitation energies. Given the negative charge of the present test systems and the charge concentration on highly electronegative nitro groups, basis-set effects have to be reevaluated. Basis-set effects on the ground-state structures tend to be small but non-negligible. Test calculations on the class II system **DN2** indicate a slightly more asymmetrical structure when going from SVP to SVP+(O) and very little change upon further augmentation (Table S6.3 in the Appendix). Consequently, the dipole moment is somewhat enhanced. The ET barrier $\Delta H^\ddagger$ increases from 6.4 kJ mol⁻¹ [SVP] to 18.6 kJ mol⁻¹ [SVP+(O)] and remains close to the latter value for still larger basis sets. Probably as a consequence of the slightly more distorted ground-state structure, addition of diffuse functions on oxygen increases the IV-CT excitation energy and thus improves agreement with experiment, when using the previously validated BLYP35 functional and suitable continuum solvent models for MeCN (Figure 6.1, cf. Table S6.3). Again, changes from SVP+(O) to SVP+ or TZVP are minor. It is thus clear that the description of negative charge on the nitro oxygen atoms is the decisive point. Given the moderate size of the systems of the present study, TZVP basis sets have been used throughout. Efficiency considerations for larger systems may neverthe-

less render a mixed basis with addition of diffuse functions to selected atoms an attractive alternative.

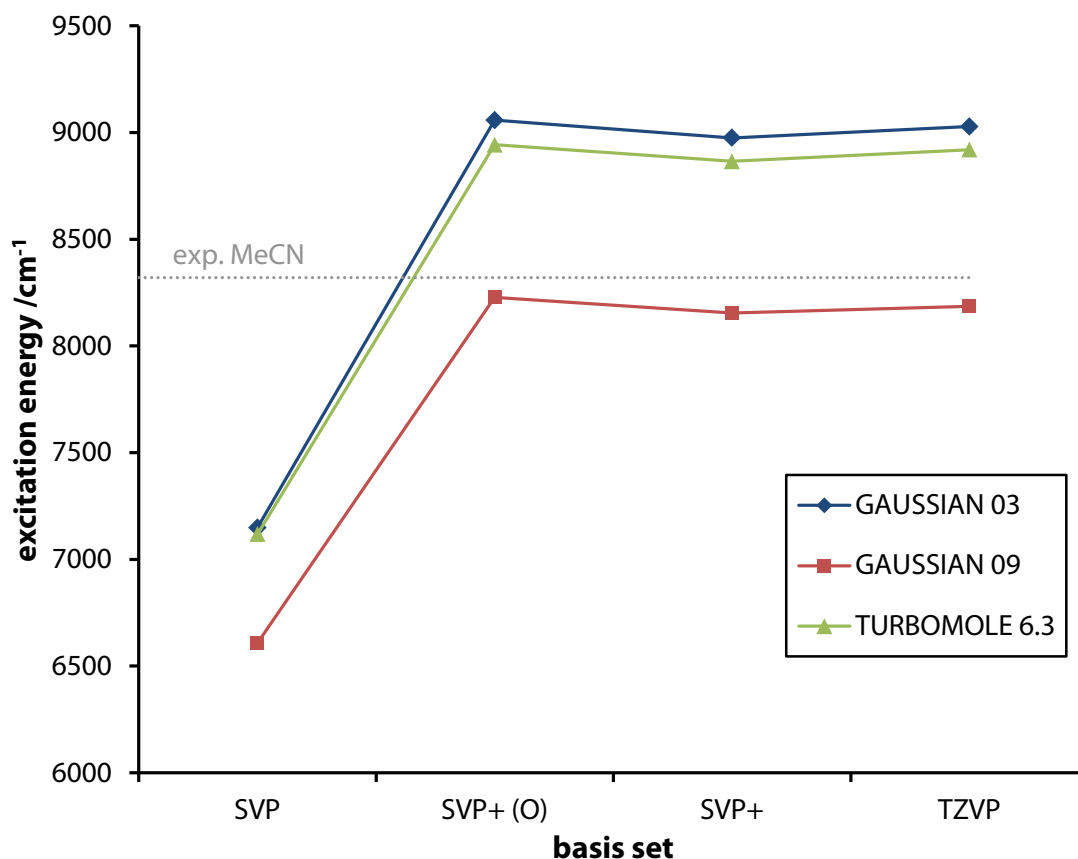


Figure 6.1. Basis-set dependence of TDDFT-BLYP35 results for IV-CT excitation energies of **DN2**, with different programs and COSMO/CPCM solvent model implementations in MeCN, compared to experiment.

Nevertheless, it has to be noted, that the Go9/CPCM implementation gives a slightly (about 500-700 cm^{-1}) lower excitation energy, and thus somewhat better agreement with experiment for **DN2**, than that in Go3/CPCM or the TBM6.3/COSMO implementation. This picture changes in other cases, regarding the other dinitroaromatic radical anions (see further below). Therefore, both codes provide a rather good description of the MV radical anions at a specific computational level, where sometimes TBM6.3 gives better results and sometimes Go9.

6.4.3 Performance of BLYP35/TZVP in gas phase

A number of previous computational studies have addressed the gas-phase molecular and electronic structures of some of the dinitroaromatic MV systems, with somewhat uncertain conclusions: UHF/6-31+G* and UMP2/6-31+G* gas-phase calculations on **DN2** gave a localized structure and a substantial ET barrier of ca. 28 kJ mol⁻¹ at UHF level.^[42] The UHF calculations were, however, plagued by the usual over-polarization and thus by substantial spin contamination, and therefore also the UMP2 results are doubtful. Subsequently, a number of computational studies on **DN2** employed CASSCF and multi-reference perturbation methods (MR-MP2, MCQDPT2, CASPT2),^[170-172, 174] as well as single-point CCSD(T)^[170] and CDFT calculations,^[174] with widely differing results: while CASSCF calculations lack dynamical electron correlation and provide a certainly still too large ET barrier (ca. 17 kJ mol⁻¹),^[170, 171] very shallow potential curves (obtained in single-point calculations along the ET coordinate) with multiple minima and ET barriers between ca. 4 kJ mol⁻¹ and ca. 10 kJ mol⁻¹ are obtained at, e.g., CASPT2, MR-MP2 or CCSD(T) levels (CDFT calculations reproduced the MR-MP2 data).^[174] Based on some of these results, a complicated four-level scheme for ET was proposed.^[174] However, given that dynamical correlation favors delocalized structures and only very moderate basis sets had been used (from 6-31G* to aug-cc-pVDZ), it is very likely that the extra minima are artifacts of the too small basis sets. They should vanish in more refined post-HF calculations. Consequently, BLYP35/TZVP gives a delocalized single-minimum class III description for **DN2**, and in fact for all radical anions of the present study in the gas phase (only for the borderline-case **DN3** a slight tendency of symmetry breaking is observed, Table S6.6, rendering this system the one most prone to localization within the present test set). Given the generally excellent performance of the BLYP35/TZVP level in the presence of a solvent model (see below), one could believe that it provides a more realistic description of the gas-phase potential energy surfaces than obtained in previous studies. 1,3-dinitrobenzene radical anion **DN2** is thus very likely a delocalized class III case in the gas phase, and the same holds for the five other radical anions.

6.4.4 Performance of the BLYP₃₅/TZVP/CPCM approach in solution

In chapter 3, where the quantum chemical protocol has been derived, the exact-exchange admixture a of a BLYP-based global hybrid (see eq. (3.1)) had been optimized as an empirical parameter to $a = 0.35$ (BLYP₃₅).^[44] Before going into a detailed comparison of different functionals, the (continuum-model) solution results for **DN1-6** obtained at the BLYP₃₅ level have been evaluated (Table 6.1). For comparability with the larger set of functionals discussed below, TZVP calculations obtained with Go9 and the corresponding CPCM implementation (see section 6.3.1; results obtained with other codes are provided in Table S6.4 and Table S6.5 in the Appendix) are reported here. BLYP₃₅/TZVP ground-state structure optimizations in MeCN (see Table 6.1, results for the less polar DCM are found in Table S6.7 in the Appendix) provide still essentially delocalized (class III) structures for **DN1** and **DN4**, as indicated by negligible structural distortions (independent of the starting point of the optimization), dipole moments and thermal ET barriers. These results are consistent with experimental observation in the same solvent (see above).

In contrast, the optimizations for radical anions **DN2**, **DN3**, and **DN6** in MeCN (Table 6.1) give clearly localized structures with double-well potentials and ET barriers between 12 kJ mol⁻¹ and 18 kJ mol⁻¹ (the optimizations with TBM6.3 give somewhat larger barriers in this solvent, see Table S6.8 in the Appendix). These three radicals are thus characterized as class II in MeCN at this level, again consistent with experimental evidence. The computed ET barriers are in the right range, but do not exhibit the same trend **DN3** > **DN2** > **DN6** as the ESR-based values for $\Delta H^\ddagger$ in MeCN (Table 6.1), as the latter two are flipping. Nevertheless, this trend is found in DCM (Table S6.7), however, experimental values are missing. It should be noted again that the ESR-based barriers come with non-negligible error bars, due to limited accuracy of the underlying Eyring plots for limited temperature ranges (barriers derived more indirectly from optical spectra differ).^[185, 247] Various approximations involved in the computational determination (cf. section 6.3.1) also limit the achievable accuracy.

The tolane-bridged radical anion **DN5** is closest to the class II/III borderline in the calculations in MeCN. The optimized structure is distorted, but the ET barrier is only

5.5 kJ mol⁻¹ in the G09 calculations. The switch to TBM6.3 and its COSMO solvation model increases the barrier to 10.2 kJ mol⁻¹, close to the ESR-based estimate (Table S6.8). Obviously, fine details of the implementation (solvent model, possibly SCF and structure optimization convergence) do already cause non-negligible changes in this borderline case. Yet, the borderline character of **DN5** is in line with the observation of a change to a class III situation when moving to lower- λ_s solvents like HMPA.^[250, 251] Overall, one can see that the BLYP35/TZVP/CPCM (or COSMO) based approach recovers very well the ground-state characteristics of these six dinitroaromatic MV radical anions in aprotic polar solvents like MeCN, thus extending the previous validation (chapter 3-5) on bis-triarylamine radical cations.

Table 6.1. Comparison of computed dipole moments (μ_o) in Debye, ET barriers ($\Delta H^\ddagger$) in kJ mol⁻¹, C-N bond lengths (d_1 , d_2) in Å, IV-CT excitation energies (E_1) as well as electronic coupling matrix elements ($2H_{ab}$) in cm⁻¹ and transition dipole moments ($\mu_{t,i}$) in Debye^a

	μ_o^b	$\Delta H^\ddagger$	$\Delta H^\ddagger_{exp.}^c$	d_1 (C-N)	d_2 (C-N)	E_1	$E_1_{exp.}^c$	$2H_{ab}^e$	$\mu_{t,i}^f$
DN1	0.05	0.0	^{-d}	1.398	1.398	12864	11000	12846	7.28 (7.29)
DN2	11.79	12.5	12.0	1.387	1.467	8140	8320	3420	1.68 (5.72)
DN3	15.09	18.1	18.4	1.386	1.462	8365	9360	2249	1.26 (7.98)
DN4	0.40	0.0	^{-d}	1.401	1.404	9750	8500	9742	9.68 (0.69)
DN5	19.06	5.5	11.3	1.384	1.450	10207	11300	6640	9.65 (15.89)
DN6	18.76	13.6	8.8	1.389	1.461	11143	12800	5435	3.79 (13.38)

^a BLYP35/TZVP/CPCM results in MeCN using Gaussian 09. Results in DCM are provided in Table S6.7. ^b With the center of mass as the origin. ^c ESR-based ET barriers and IV-CT excitation energies from the following refs. [42, 156, 176, 183, 185, 190, 247]. ^d Class III system. ^e Excitation energies obtained exactly at the symmetrical structure. ^f Transition dipole moments in parentheses obtained exactly at the symmetrical structure.

Turning to the IV-CT excitation energies in MeCN (Table 6.1), the performance of the BLYP35 calculations resembles again that obtained previously for MV bis-triarylamine radical cations: for the class III systems **DN1** and **DN4**, the excitation energies are overestimated by about 1800 cm⁻¹ and 1250 cm⁻¹, respectively, and the transition dipole moments are also overestimated (cf. Table S6.9 and Table S6.14). In case of the broad bands of class II systems, the experimental band maximum is more difficult to identify. Taking the reported data in Table 6.1, one nevertheless might conclude, that the BLYP35 calculations tend to underestimate these values by about 1000 cm⁻¹, again consistent with the previous results

for MV bis-triarylamine radical cations.^[44, 45] Only in case of **DN2**, the computed value is within 200 cm⁻¹ of the experimental band maximum. As the excitation energies computed with TBM6.3 (Table S6.8 in the Appendix) are about 1000 cm⁻¹ larger than the Gaussian values, they tend to agree better with experiment, of course except for **DN2**. Systematic differences between the solvent models account for most of the discrepancies between the Go9 and TBM6.3 results.

6.4.5 Evaluation of different density functionals

Despite its excellent performance above and in the previous studies,^[44, 45] BLYP35 is not a functional that is optimal for general main-group thermochemistry, as the exact-exchange admixture is too high for the simple form of the hybrid. It is known, however, that the inclusion of local kinetic energy density in so-called meta-GGA global hybrids allows high exact-exchange admixtures while maintaining accurate main-group thermochemistry.^[242, 259] The smaller size of the present test systems compared to the previous chapters has also allowed a systematic evaluation of such more highly parameterized meta-GGA hybrids, as implemented in Go9 (but not yet in TURBOMOLE), together with range hybrids and a double hybrid (cf. section 6.3.2).

Given that the E_{xx} admixture to the functional is known to diminish self-interaction errors, the amount of exact exchange is expected to be decisive for the performance of a given functional on the question of localization/delocalization.^[44] This is borne out by the following results. For global hybrids like BLYP35 ($a = 0.35$), and for meta-GGA global hybrids like BMK ($a = 0.42$), Mo5 ($a = 0.27$), Mo6 ($a = 0.28$), Mo5-2X ($a = 0.54$), and Mo6-2X ($a = 0.56$), parameter a from eq. (3.1) clearly controls the E_{xx} admixture. The same holds for the double hybrid B2PLYP ($a = 0.53$), albeit the MP2-like correlation term is expected to have a larger effect on the performance than the other correlation functionals in the comparison. The range hybrids are more difficult to compare to, as the E_{xx} admixture is not a constant but depends on interelectronic distance.

Structure optimizations for the class III system **DN1** gave delocalized structures with negligible structural distortions, dipole moments or ET barriers in both DCM and MeCN

solvents for all meta-GGA global hybrids, the B2PLYP double hybrid, and the CAM-B3LYP range hybrid (Table S6.9 in the Appendix). Only the range hybrids LC-BLYP and ω B97X provide some indications of incipient (unphysical) symmetry breaking. For ω B97X, the ET barriers are negligible, however, and the values for LC-BLYP are also still small. In any case, these observations suggest already that the overall exact-exchange admixture and thus the tendency towards symmetry breaking for these two range hybrids is particularly large compared to the other functionals in the present study.

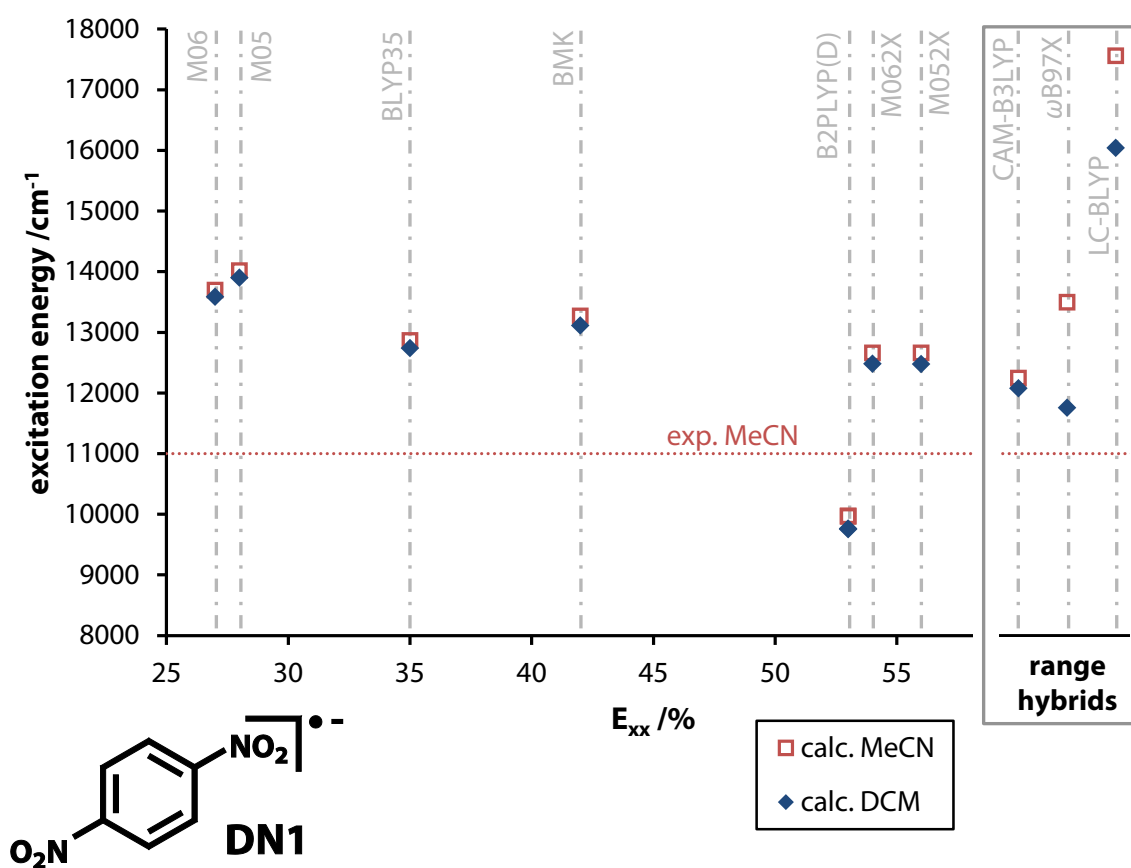


Figure 6.2. Computed excitation energies for the class III system **DN1** in MeCN and DCM depending on E_{xx} admixture of the density functional, compared to the experimental value in MeCN (11000 cm^{-1}).^[247]

Figure 6.2 compares the IV-CT excitation energies for **DN1** with the whole set of functionals in both solvents. In agreement with previous experience from section 3.4.2 and 4.4.2 (see also Figure 3.4),^[44, 45] the dependence on exact-exchange admixture for this class III system is only moderate. This is indicated by the fact that, e.g., the M05 and M06 functionals and their “double-exchange” analogues M05-2X and M06-2X all overestimate the

excitation energy by similar amounts, as do BLYP₃₅ and BMK. Only the B2PLYP double hybrid gives a lower value (the TDDFT treatment in this case involves a CIS(D) formalism for the MP2 term, in contrast to the CIS-type treatment for all other functionals). Among the range hybrids, CAM-B3LYP gives a similar value as the global hybrids. The fact that ω B97X in MeCN and LC-BLYP in both solvents give even much larger excitation energies, and thus larger deviations from experiment, is due to the incipient, erroneous ground-state symmetry breaking at these levels (see above). Transition dipole moments are overestimated systematically, increasing with E_{xx} admixture (Table S6.9).

Table 6.2. Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹, bond lengths d_1 , d_2 in Å) with different functionals for **DN2** in MeCN^a

functional/exp.	$E_{\text{xx}} = a$	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$
Mo6	0.27	9.99	1.6	1.391	1.463
Mo5	0.28	8.25	0.1	1.407	1.453
BLYP ₃₅	0.35	11.79	12.5	1.387	1.467
BMK	0.42	11.88	14.2	1.385	1.464
B2PLYP	0.53	12.78	0.9	1.393	1.475
B2PLYPD	0.53	12.78	0.9	1.393	1.476
Mo6-2X	0.54	11.97	23.5	1.388	1.475
Mo5-2X	0.56	12.09	23.1	1.385	1.469
CAM-B3LYP	-	11.93	19.4	1.387	1.470
ω B97X	-	12.10	28.5	1.388	1.476
LC-BLYP	-	12.62	39.9	1.380	1.464
ESR ^[247]			11.97±0.29		

^a TZVP/CPCM results obtained with Go9. Results in DCM are provided in Table S6.10. ^b With the center of mass as the origin.

Table 6.2 summarizes some of the most relevant computed ground-state characteristics for the class II radical anion **DN2** (in MeCN). Here the dependence on exact-exchange admixture is obvious: the Mo5 and Mo6 functionals with less than 30% exact-exchange admixture give a slight structural distortion but negligible energy lowering relative to the symmetrical transition-state structure (and thus negligible ET barriers). In this case the dipole moments are no perfect indicators of symmetry breaking, as even the symmetrical structure (C_2) has a dipole moment of about 5.74 Debye (symmetry breaking enhances it by about 6 Debye). All global hybrids with $a > 0.3$, and all three range hybrids give localized

structures, albeit with quite different ET barriers. BLYP₃₅ and BMK provide barriers closest to the ESR-based estimate of about 12 kJ mol⁻¹. The Mo5-2X and Mo6-2X functionals overestimate the barrier, probably indicating somewhat too large E_{xx} admixture. Among the range hybrids, CAM-B₃LYP appears to perform best, falling between the BLYP₃₅, BMK values and the Mo5-2X and Mo6-2X data, whereas the very large barriers obtained with ω B97X and LC-BLYP confirm the notion of over-localization and excessive E_{xx} admixture. It has to be noted, that recent TDDFT studies with ω B97X came to similar conclusions.^[260] Recent B₃LYP/6-311++G(d,p)/PCM calculations on **DN2** gave structural symmetry breaking in DMSO,^[43] which is confirmed by own calculations at B₃LYP/TZVP. However, a negligible ET barrier of 0.7 kJ mol⁻¹ is found (0.6 kJ mol⁻¹ in MeCN).

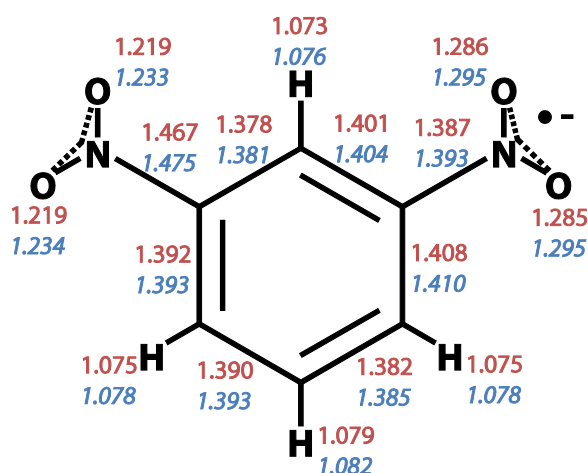


Figure 6.3. Computed ground-state bond lengths in Å for **DN2** in MeCN (CPCM) at BLYP₃₅ (upper values, red) and B2PLYP (lower values, blue) levels.

Interestingly, the double hybrid B2PLYP also gives a structural distortion and a dipole moment for **DN2** close to the results of the better-performing functionals (e.g. BLYP₃₅, cf. Figure 6.3 and Table 6.2), independent of the presence or absence of a dispersion correction. But the computed ET barrier is negligible, in spite of the relatively large exact-exchange admixture of 53%.

Closer inspection reveals that in the absence of the MP2 correlation term, the ET barrier would be 32 kJ mol⁻¹. The MP2 term (over-)stabilizes the symmetrical transition state by almost the same amount and thus creates a much too shallow double-minimum potential.

As expected for the class II system **DN2**, the dependence of the IV-CT excitation energy on the functional is much more pronounced than for the class III system **DN1** above. Figure 6.4 shows that Mo5 and Mo6 underestimate the excitation energy dramatically, due to the erroneously delocalized ground-state structures. The BLYP₃₅ and BMK functionals, with their “intermediate” a -values, perform best, whereas exact-exchange admixtures above

50%, as in Mo5-2X, Mo6-2X or in the double hybrid B2PLYP, cause an overestimate on the order of 4000 cm^{-1} . In the latter case it has been ascertained by B2PLYP TDDFT calculations at the BLYP35-optimized structure and vice versa, that this is not a problem of the ground-state structure (Table S6.11 in the Appendix). Completely unrealistic excitation energies are obtained with the ω B97X and LC-BLYP range hybrids, whereas CAM-B3LYP results are too high only by about 2000 cm^{-1} (in MeCN).

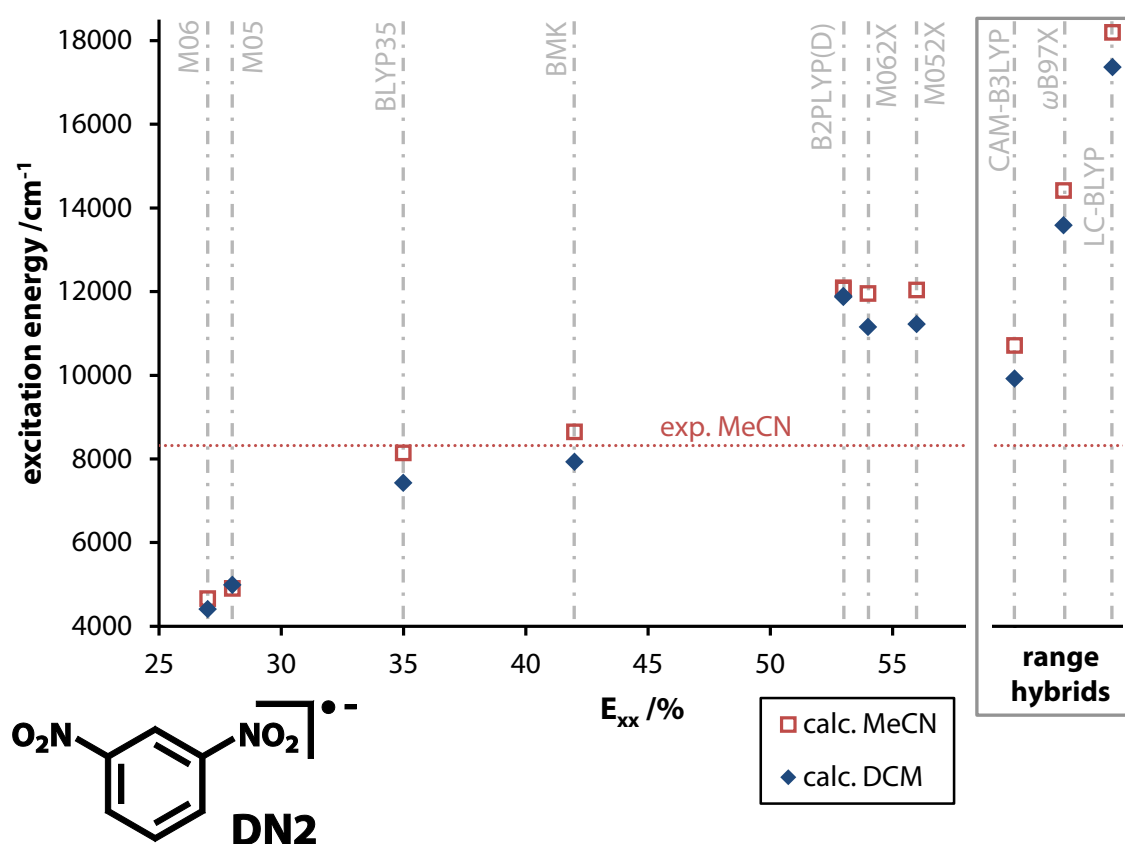


Figure 6.4. Computed excitation energies for the class II system **DN2** in MeCN and DCM depending on E_{xx} admixture of the density functional, compared to the experimental value in MeCN (8320 cm^{-1}).^[42, 247]

The dependences of thermal ET barriers and IV-CT excitation energies on the density functional for such a class II system thus go in parallel, and the previously evaluated BLYP35 functional performs quite well for both properties (this holds also for the other class II systems). As indicated above, however, BLYP35 is not a functional optimized for general main-group thermochemistry. In contrast, the more highly parameterized meta-GGA hybrid BMK^[243] is rather successful on this score, in spite of its 42% exact-exchange

admixture, and it performs also very well for the current set of MV compounds (see also below). It may thus be an interesting alternative, albeit it is not yet available in quite as many efficient codes. A potentially interesting global hybrid functional without meta-GGA part and with similar exact-exchange admixture ($a = 0.428$) is MPW1K,^[261] which has already been used in a few cases for transition-metal MV systems.^[262, 263] It does indeed give very similar (slightly inferior) results for **DN2** as BMK: in MeCN, a class II system is obtained with an ET barrier of 16.4 kJ mol⁻¹ and an IV-CT excitation energy of 10407 cm⁻¹ (for **DN1**, a class III structure was found with an excitation energy of 12952 cm⁻¹). Given the similarity to the BMK results, a more detailed discussion of MPW1K is refrained. Previous RISM-MCSCF calculations^[246] for **DN2** are discussed further below in the context of the D-COSMO-RS results (see section 6.4.6).

Given the above results for **DN1** and **DN2**, a somewhat narrower comparison of functionals for **DN3-6** can be provided, looking at global hybrids and meta-GGA global hybrids only. Table 6.3 shows computed ground-state parameters for **DN3** in MeCN. As this is the most clear-cut class II system of the six dinitroaromatic radical anions of the present test set (cf. Table 6.1), even the Mo5 and Mo6 functionals provide notable charge localization, albeit with insufficient asymmetry, too small ET barriers and a lower dipole moment than expected for a localized structure (even B3LYP with $a = 0.20$ gives already a partly localized class III situation for **DN3** in MeCN). Compared to the ESR-based ET barrier in MeCN, the BLYP35 and BMK functionals again perform best, whereas the Mo5-2X and Mo6-2X functionals give too large barriers at the given level of solvent model, just as found for **DN2** above. The experimental barrier is ca. 5 kJ mol⁻¹ lower in DMF than in MeCN (Table 6.3). This can clearly not be modeled at the continuum-solvent level, as both solvents have essentially identical dielectric constants (Table 2.1). But this question will be returned in section 6.4.6. The same holds for the IV-CT excitation energy, which is about 1200 cm⁻¹ lower in DMF than in MeCN (Figure 6.5). Focusing on the MeCN computational results, again the typical behavior of class II systems can be found (cf. Figure 6.5 and Figure 3.4), i.e. a strong dependence on exact-exchange admixture and best performance for BLYP35 and BMK. Measured transition dipole moments $\mu_{t,1}$ are 1.04-1.12 Debye, depending on the method of determination.^[42] They are reasonably well reproduced by BLYP35, BMK,

Mo5-2X, and Mo6-2X but overestimated by the Mo5 and Mo6 functionals (cf. Table S6.12 in the Appendix).

Table 6.3. Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹, bond lengths d_1 , d_2 in Å) with different functional for **DN3** in MeCN^a

functional/ <i>exp.</i>	$E_{xx} = a$	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$
Mo6	0.27	13.59	5.5	1.388	1.465
Mo5	0.28	13.02	3.7	1.393	1.474
BLYP35	0.35	15.09	18.1	1.386	1.462
BMK	0.42	15.13	20.4	1.384	1.459
Mo6-2X	0.54	15.29	30.3	1.387	1.471
Mo5-2X	0.56	15.41	30.4	1.383	1.465
<i>ESR (MeCN)</i> ^[185]			18.4(±0.84)		
<i>ESR (DMF)</i> ^[185]			13.0(±1.25)		

^a TZVP/CPCM results obtained with G09. Results for DCM are provided in Table S6.12. ^b With the center of mass as the origin.

The dinitroaromatic radical anion **DN3** seems to be the first MV system for which ground-state structure optimizations including a solvation model had been carried out. Nelsen, Clark and coworkers used a semi-empirical AM1 Hamiltonian with subsequent single-excitation configuration interaction within an active orbital space of 70 MOs, AM1-CIS(70), together with COSMO solvation for a variety of dielectric constants ϵ .^[42] To connect to the present work, one can have a look at their results for MeCN: charge localization has been obtained, with similar structural distortion as in the BLYP35/TZVP results (somewhat more for the reduced side, less for the neutral side), and an ET barrier of about 30 kJ mol⁻¹ (i.e. too large, best comparable to the Mo5-2X or Mo6-2X results, cf. Table 6.3). The computed IV-CT excitation energy of ca. 8950 cm⁻¹ is also close to the BLYP35 or BMK data (cf. Figure 6.5). Given the semi-empirical basis of the approach, this is an excellent performance. So far it remains unclear, however, whether it could be generalized straightforwardly to other systems (e.g. regarding the active orbital space).

Results with different functionals for the class III system **DN4** are very similar as for **DN1** above and are provided in chapter 12 (Table S6.13 and Figure S6.2). The only difference observed is that the Mo5-2X and Mo6-2X functionals induce first indications of symmetry

breaking in MeCN and DCM (with very small ET barriers but strong effects on the IV-CT excitation energies). All other functionals provide clearly delocalized, symmetrical structures.

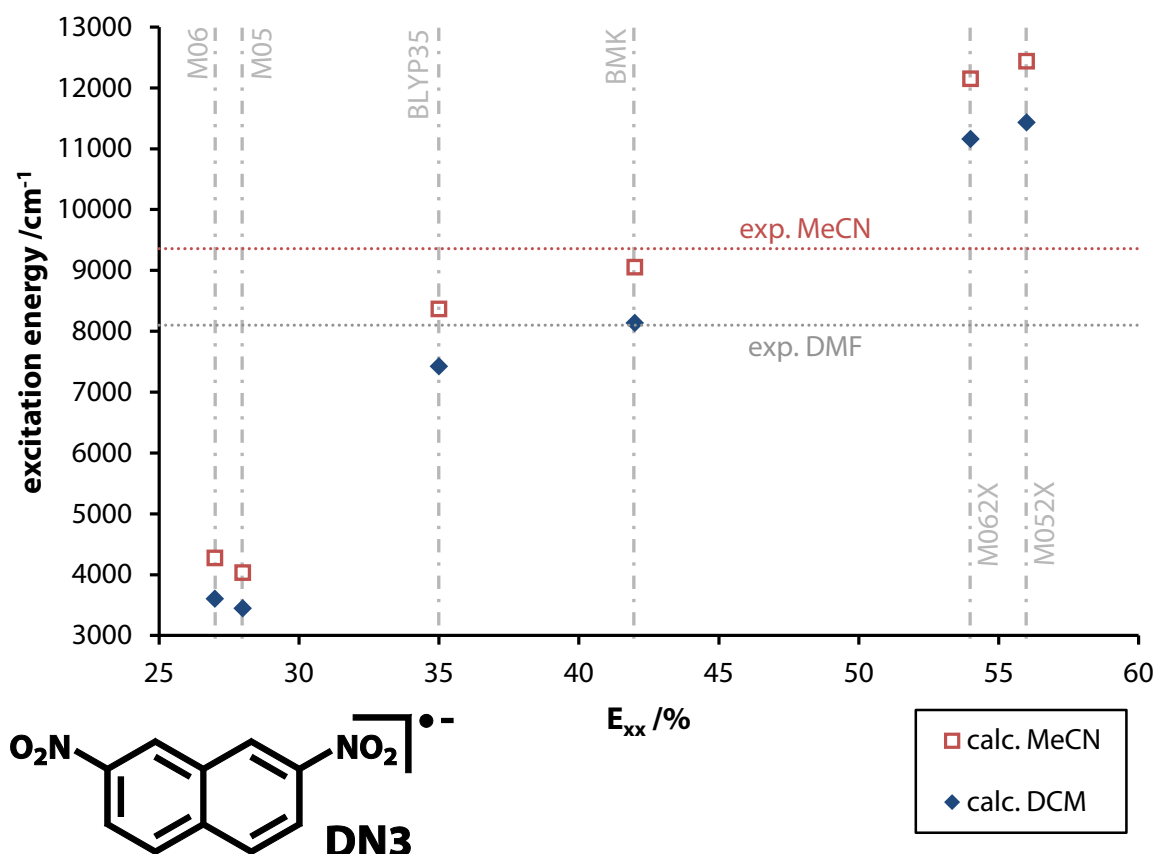


Figure 6.5. Computed excitation energies for the class II system **DN₃** in MeCN and DCM depending on E_{xx} admixture of the density functional, compared to the experimental value in MeCN (9360 cm⁻¹) and in DMF (8100 cm⁻¹) (see refs. [42, 247]).

As discussed above, the tolane-bridged **DN₅** is closest to the class II/III transition in aprotic solvents. It ranges from being delocalized in less polar solvents like HMPA or THF to being localized in DCM or MeCN. Table 6.4 shows that with none of the functionals, the continuum-solvent model-based protocol can reproduce this transition: the M05 or M06 functionals with $a < 0.3$ give a delocalized structure in THF, DCM and MeCN, whereas the other four functionals in the list give localized structures in all three solvents. In this case, the larger ET barriers obtained with the M05-2X and M06-2X functionals appear to be closer to the ESR-derived values in DCM and MeCN than the BLYP35 or BMK results. This

contrasts to all other class II cases in this study, where the Mo5-2X and Mo6-2X barriers are too high. The fact that a continuum solvent model reaches its limits here becomes obvious when comparing THF and DCM: both have very similar dielectric constants (Table 2.1). Yet the system is experimentally on the class III side in the former and on the class II side in the latter. This clearly calls for improved treatments of solvent effects beyond the continuum solvent level (see section 6.4.6).

Table 6.4. Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹) with different functionals for **DN5** in MeCN, DCM and THF^a

functional/exp.	$E_{xx} = a$	μ_o^b	$\Delta H^\ddagger$	μ_o^b	$\Delta H^\ddagger$	μ_o^b	$\Delta H^\ddagger$
		(MeCN)		(DCM)		(THF)	
Mo6	0.27	0.01	0.0	0.13	0.0	0.04	0.1
Mo5	0.28	0.44	0.0	0.25	0.0	0.02	0.0
BLYP35	0.35	19.06	5.5	16.10	2.4	15.21	1.9
BMK	0.42	19.29	6.3	16.69	3.1	15.81	0.1
Mo6-2X	0.54	21.60	14.4	20.03	9.9	19.55	0.1
Mo5-2X	0.56	21.74	15.5	20.24	10.9	19.79	0.0
ESR (MeCN) ^[185]			11.3(±1.7)				
ESR (DMF) ^[185]			13.8(±1.88)				
ESR (DCM) ^[185]					11.5(±0.88)		- ^c

^a TZVP/CPCM results obtained with G09. Further results in DCM are provided in Table S6.14. ^b With the center of mass as the origin. ^c Class III system.

IV-CT excitation energies in MeCN or DCM (Figure 6.6) are dramatically underestimated at Mo5 or Mo6 levels, mainly due to the erroneously delocalized structures. The dependence of these energies on ϵ is significant for the other functionals. Looking at the MeCN results, agreement with experiment is again most favorable for the BLYP35 and BMK functionals, as for other class II systems, whereas Mo5-2X and Mo6-2X overestimate the values by about 3000 cm⁻¹ (Figure 6.6). Computed transition dipole moments are generally overestimated, in particular for the Mo5 and Mo6 functionals, probably again due to the delocalized ground-state structures. IV-CT excitation energies in THF (5860 cm⁻¹) are generally overestimated dramatically (Table S6.14 in the Appendix, which gives also further TDDFT data for several experimentally available excitations). While an overestimate for class III systems is typical, part of the errors arises from erroneous ground-state symmetry

breaking for functionals with $a > 0.3$. Clearly, the solvent description for THF is not realistic, possibly in part due to the ability of THF to coordinate to the counter-cations (see below for D-COSMO-RS calculations in section 6.4.6).

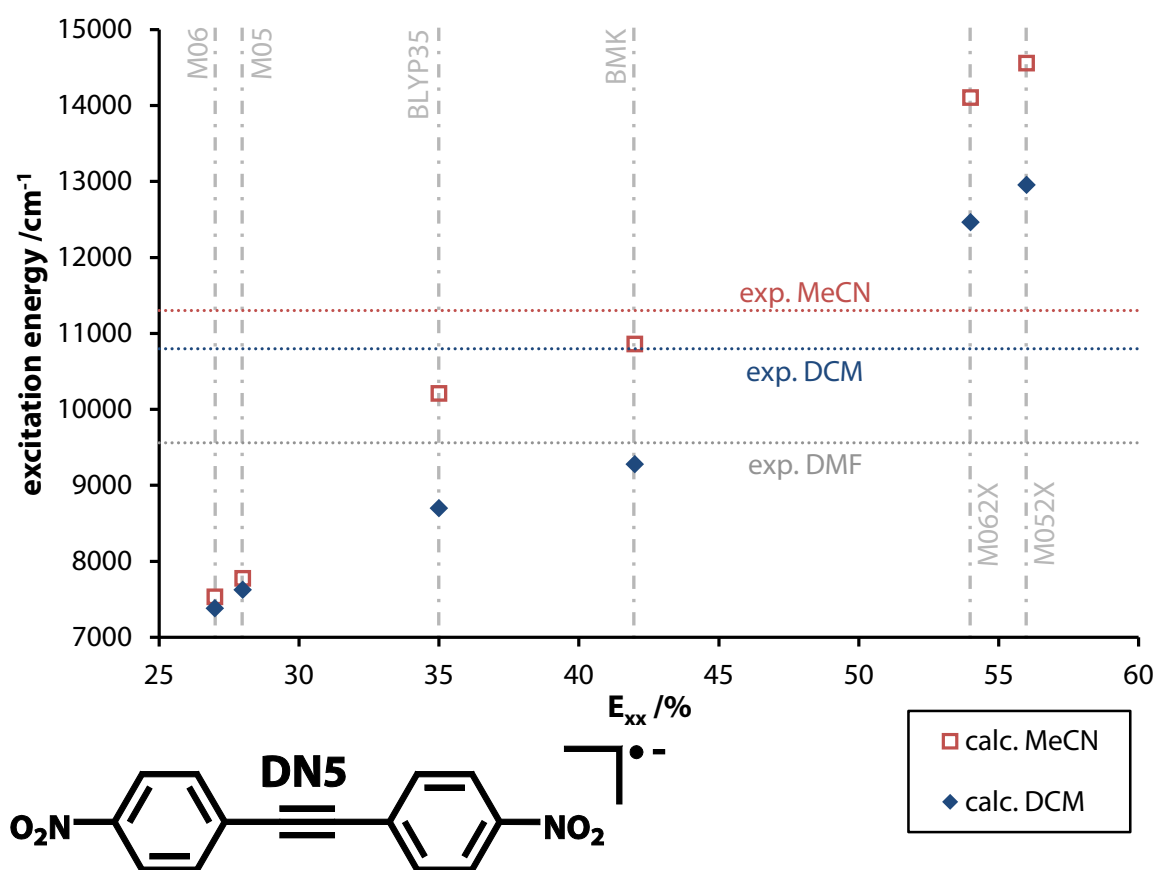


Figure 6.6. Computed excitation energies for **DN5** in MeCN and DMF depending on E_{xx} admixture of the density functional, compared to the experimental values 11300 cm^{-1} (MeCN), 10800 cm^{-1} (DCM), 9560 cm^{-1} (DMF) (see ref. [176]).

Resonance Raman measurements on **DN5** by Telo, Nelsen and coworkers^[183] show a shift of the $\text{C}\equiv\text{C}$ stretching frequency to lower values when going from localized to delocalized ground-state structures by choice of the solvent. In MeCN, two peaks have been observed and were assigned to a localized (2166 cm^{-1}) and a delocalized species (2146 cm^{-1}), while only the latter remains and is shifted to lower values in THF. This shift is reproduced at BLYP35/TZVP/CPCM level (Table 6.5), even though the (unscaled) frequencies are about 100 cm^{-1} too high in absolute terms (a scaling factor of 0.95 brings computed frequencies

close to experiment). The difference between frequencies for localized and delocalized systems diminishes with decreasing polarity of the solvent, as expected.

Table 6.5. Calculated harmonic C≡C stretching frequencies (in cm⁻¹) for **DN5**^a

solvent	localized ^b	delocalized ^c
MeCN	2274.6 (2160.9)	2254.7 (2142.0)
DCM	2262.5 (2149.4)	2253.3 (2140.6)
THF	2260.3 (2147.3)	2253.4 (2140.7)

^a BLYP₃₅/TZVP/CPCM results. Values in parentheses scaled by a factor of 0.95.

^b C₁ minimum structure. ^c Symmetrical transition-state structure.

The dependence of the ground-state properties and IV-CT excitation energies on the functional for **DN6** are in line with the other, relatively clear-cut class II cases **DN2** and **DN3** (see above). The data is provided in Table S6.15 and in Figure S6.3 in the Appendix. It is just noted here, that BLYP₃₅ and BMK again perform best for ET barriers and IV-CT excitation energies, and that the difference of about 5 kJ mol⁻¹ between the ET barriers in MeCN and DMF can of course not be modeled at the continuum solvent level, due to the almost identical dielectric constants of the two solvents. Another potential complication for **DN6** is the twisting between the two phenyl rings of the bridge, as this has been investigated for neutral radical cations in section 4.4.3. The relatively shallow potential energy surface for this twisting motion has to be kept in mind when judging the achievable accuracy, in particular for the IV-CT transition dipole moments (Table S6.15).

The evaluation of functionals can be recapitulated as follows: it has been demonstrated that the exact-exchange admixture of global hybrids influences the performance decisively. The BLYP₃₅ ($a = 0.35$) and BMK ($a = 0.42$) functionals performed best for both class II and class III systems, including ET barriers for the former and IV-CT excitation energies for both. The BMK functional has the advantage of being optimized also for general main-group thermochemistry, but it is not yet available in many efficient codes. The MPW_{1K} global hybrid ($a = 0.428$) may also be an option, it appears to perform similarly as BMK. Lower exact-exchange admixtures tend to overestimate delocalization, higher ones localization, with corresponding consequences for the barriers and IV-CT excitations. In terms of structural symmetry breaking for the class II case **DN2**, performance of the double

hybrid B2PLYP resembled that of global hybrids with high exact-exchange admixture like Mo6-2X. But the computed ET barrier was far too low, apparently due to an over-stabilization of the symmetrical transition state by the MP2 correlation term included in the functional. Among the range hybrids studied, CAM-B3LYP performed well albeit somewhat inferior to the best global hybrids (BLYP35, BMK). The ω B97X and LC-BLYP range hybrids were strongly on the over-localized side, indicating too high exact-exchange admixture. They provided neither good ground-state properties and ET barriers nor realistic IV-CT excitation energies. In general, double hybrids and range hybrids did not offer any advantages over global hybrids for the systems and properties studied. Local hybrid functionals, with position-dependent exact-exchange admixture, appear to be a particularly promising alternative for future studies,^[74, 75, 79] in particular for MV transition-metal complexes. System **DN5**, which is closest to the class II/III transition, exposed clearly the limitations of the continuum solvent models used in the current protocol, providing one of the motivations for turning to the D-COSMO-RS approach in the following section.

6.4.6 Direct COSMO-RS calculations

In the previous sections, several cases have been encountered, where continuum solvent models are beyond their limits. A continuum solvent model is characterized only by its dielectric constant ϵ , and obviously this does not include all necessary information about solvation in the present context. Specific solvation interactions enter the ET processes via outer or solvent reorganization energies, λ_o or λ_s . The most clear-cut case where a continuum solvent model thus fails to describe matters accurately is hydrogen bonding. But it was also described that the lower reorganization energy of THF *vs.* DCM (or of HMPA *vs.* MeCN) may favor a class III situation, in spite of the similar ϵ -values. Similar considerations hold for DMF (or HMPA) *vs.* MeCN. It is, however, possible that the good cation coordination properties^[264] of THF or HMPA play a decisive role, and this remains beyond the scope of the present work. A more realistic microscopic treatment of solvation based on explicit *ab initio* molecular dynamics (MD) simulations, typically with periodic boundary conditions, is in principle possible for the present, moderately sized test systems and will be pursued elsewhere. However, the computational and man-power effort involved in such studies is on an entirely different scale than that of the quantum chemical protocol dis-

cussed so far. Such methods are currently not easily generalized to routine work on a large number of extended systems of chemical interest. A computational scheme covering the middle ground between continuum solvent models and full *ab initio* MD is thus highly desirable. In the context of ET parameters and MV systems, one study on **DN2** using the RISM-MCSCF approach has to be mentioned,^[246] which combines CASSCF calculations on the solute with a molecular-mechanics/Monte-Carlo/statistical thermodynamics treatment of the solvent (MeCN and MeOH were compared). Due to the shortcomings of the ROHF and CASSCF wave functions used (see also above), the computed ET barriers in that work were significantly overestimated, by about a factor 2-3. Yet, the increase in going from aprotic MeCN to the protic MeOH was at least qualitatively reproduced.^[246]

Table 6.6. Comparison of COSMO and D-COSMO-RS results for ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹, bond lengths d_1 , d_2 in Å) and IV-CT excitation energies (E_i in cm⁻¹) of **DN1** in methanol, *n*-octanol, and MeCN^a

solvent	solvent model	μ_o^b	$\Delta H^\ddagger^c$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i
<i>n</i> -octanol	COSMO	0.26	0.0	1.396	1.398	13069
	D-COSMO-RS	8.95	6.6	1.383	1.437	16709
MeOH	COSMO	0.31	0.0	1.395	1.397	13007
	D-COSMO-RS	9.65	8.2	1.384	1.440	17343
MeCN	COSMO	0.47	0.0	1.394	1.398	13008
	D-COSMO-RS	0.08	0.0	1.397	1.398	13097

^a BLYP35/TZVP results with TBM6.3; more detailed results are in Table S6.16. ^b With the center of mass as the origin.

^c The ESR-based experimental free-energy ET barrier ($\Delta G^\ddagger$) is 36 ± 3 kJ mol⁻¹ in *n*-octanol and 26 ± 2 kJ mol⁻¹ in MeOH.^[156]

Together with the BLYP35/TZVP level for treating the electronic structure, some examples out of the test set **DN1-6** will be evaluated by the D-COSMO-RS method (see section 6.3.3).^[123-125, 238, 265] While **DN1** is a delocalized class III system in aprotic solvents, it localizes in alcoholic solvents. Given that alcohols have dielectric constants in a similar range as aprotic solvents (cf. Table 2.1), it is not to be expected that this can be simulated with continuum solvent models. Indeed, at the BLYP35/TZVP/COSMO level, **DN1** remains delocalized in both methanol and *n*-octanol (Table 6.6). When switching to the D-COSMO-RS level, this changes fundamentally: now **DN1** becomes a localized class II system in alcoholic solution, as indicated by the structural distortions, the dipole moment, and the computed ET barrier, which amounts to somewhat less than half of the ESR-based values (Table 6.6). The computed IV-CT excitation energy is also increased dramatically

compared to the COSMO result, as expected for the formation of a double-well potential (see Figure 1.2; no spectra in alcohols are available so far). That is, the corrections that the D-COSMO-RS approach makes to an idealized conductor-like screening do indeed allow a modeling of the transition to class II character in protic solvents. The somewhat too small barrier might suggest a certain underestimate of the specific solvent effects, but the judgment will be reserved until the evaluation of more data below. The control experiment is to compare COSMO and D-COSMO-RS results also in an aprotic solvent like MeCN. Here the differences between the two approaches are much smaller, and the system remains a class III case even upon inclusion of the RS correction terms (Table 6.6). It has to be noted, that ion pairing effects are expected to be much less important in polar, protic solvents than they are in low-polarity solvents (or in the solid state),^[248] and they can be excluded as the origin of the charge localization (cf. section 6.2).

ESR-studies in alcoholic solvents are also available for **DN2** and **DN3**. As both radical anions are already localized in aprotic solvents, the effect of hydrogen bonding must be quantitative rather than qualitative. Indeed, for both radicals the measured ET barriers in alcohols are about twice as large as those in MeCN. Table 6.7 compares the COSMO and D-COSMO-RS results for both systems in MeOH and MeCN. The effect of the RS correction terms for the acetonitrile results is small, as expected. The slightly reduced ET barriers agree better with experiment. In contrast, for MeOH a striking increase of the ET barrier is observed compared to the COSMO data. Indeed, the RS corrections bring the computed values remarkably close to the ESR-based estimates for both radical anions. The extra deepening of the double-well potential due to hydrogen bonding is reflected in more pronounced asymmetry of the minimum structure and a somewhat increased dipole moment in MeOH *vs.* MeCN (D-COSMO-RS results in Table 6.7). The IV-CT excitation energies are also increased substantially in both cases. As no UV/vis data in alcohols are available so far for any of these systems, the magnitude of this increase is a pure prediction for which experimental verification will be interesting to see. The strikingly good agreement of the ET barriers with experiment for **DN2** and **DN3** in alcohols does not support the above presumption based on the results for **DN1**, that the hydrogen-bonding effects may be underestimated by the D-COSMO-RS approach. The results of the only previous applica-

tion of D-COSMO-RS, to g -tensors of nitroxide radicals,^[126] suggest that the effects of hydrogen bonding may have been underestimated somewhat. More work on a diverse set of questions will be needed to evaluate in detail the quantitative accuracy of the model.

Table 6.7. Comparison of COSMO and D-COSMO-RS results for ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹, bond lengths d_1 , d_2 in Å) and IV-CT excitation energies (E_i in cm⁻¹) of **DN2** and **DN3** in MeOH and MeCN^a

molecule	solvent	solvent model	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i
DN2	MeOH	COSMO	12.53	17.6	1.388	1.466	9214
		D-COSMO-RS	14.86	43.1	1.393	1.469	14807
		<i>exp.</i>		43.1 ^c			
	MeCN	COSMO	12.56	17.8	1.388	1.466	9267
		D-COSMO-RS	11.79	12.8	1.387	1.467	7989
		<i>exp.</i>		11.97±0.29 ^d			8320 ^e
DN3	MeOH	COSMO	15.91	23.0	1.387	1.461	9522
		D-COSMO-RS	18.75	48.2	1.390	1.463	15088
		<i>exp.</i>		49.1 ^c			
	MeCN	COSMO	15.95	23.2	1.387	1.461	9591
		D-COSMO-RS	15.06	18.4	1.386	1.462	8219
		<i>exp.</i>		18.4±0.84 ^d			9360 ^e

^a BLYP35/TZVP results with TBM6.3, more detailed results in Table S6.17 and Table S6.18. ^b With the center of mass as the origin. ^c ESR-based experimental free-energy ET barriers ($\Delta G^\ddagger$).^[155] ^d ESR-based $\Delta H^\ddagger$ value.^[185] ^e IV-CT excitation energies from ref. [42].

Less spectacular effects of specific solvation are expected for aprotic solvents. Nevertheless, it has been seen above that, for example, the transition of **DN5** from a class III situation in THF to a class II situation in DCM also cannot be described by a continuum solvent model, given the very similar dielectric constants (Table 2.1). Indeed, the COSMO results are almost equal for THF and DCM (Table 6.8). The RS corrections reduce ET barrier and IV-CT excitation energy somewhat for THF and increase both somewhat for DCM. While these corrections go into the right direction, the qualitative change from a class III system in THF to a class II system in DCM is insufficiently reproduced. For both solvents, extremely shallow double-well potentials are obtained, consistent with the borderline character of **DN5**. The D-COSMO-RS ET barrier in DCM is larger than 5 kJ mol⁻¹, about half the ESR-based estimate, whereas the value in THF is below 2 kJ mol⁻¹. Due to the remaining structural distortion, the IV-CT excitation in THF is overestimated substantially.

One aspect that may be important but cannot be modeled by either COSMO or D-COSMO-RS levels is the better cation coordination ability of THF *vs.* DCM, which may remove some residual ion pairing.

Table 6.8. Comparison of COSMO and D-COSMO-RS results for ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹, bond lengths d_1 , d_2 in Å) and IV-CT excitation energies (E_i in cm⁻¹) of **DN5** in THF and DCM^a

solvent	solvent model	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i
THF	COSMO	16.08	2.9	1.385	1.443	8955
	D-COSMO-RS	13.22	1.6	1.389	1.439	8318
	<i>exp.</i>		- ^c			5860 ^e
DCM	COSMO	17.35	4.0	1.384	1.445	9428
	D-COSMO-RS	18.39	5.3	1.383	1.446	9784
	<i>exp.</i>		11.50±0.88 ^d			10800 ^f

^a BLYP35/TZVP results with TBM6.3, more detailed results in Table S6.20. ^b With the center of mass as the origin.

^c Class III in THF. ^d ESR-based value.^[185] ^e Ref. [176]. ^f Ref. [185].

Going beyond the ground state properties, also substantial quantitative differences of the IV-CT excitation energies in MeCN and DMF for class II systems can be seen, in spite of the very similar dielectric constants of the two solvents. The performance of COSMO *vs.* D-COSMO-RS for **DN2** and **DN3** in MeCN and DMF is evaluated in Table 6.9. As a control, it also provides results for **DN2** and **DN4** in the same solvents. As the latter two radical anions remain class III in both aprotic solvents, a negligible solvent dependence is expected in these cases. This is indeed observed computationally: COSMO provides no, and D-COSMO-RS only small differences between the excitation energies in MeCN and DMF for **DN1** and **DN4**. COSMO also allows no distinction between the two solvents for **DN2** and **DN3**. Experimentally, values in both solvents are available for **DN3**. The band is blue-shifted by about 1260 cm⁻¹ in MeCN. The difference at D-COSMO-RS level is about 500 cm⁻¹. While this underestimates the experimental solvent shift, the approach at least distinguishes qualitatively between the two solvents, while a continuum solvent model does not. In absolute terms, D-COSMO-RS improves the agreement with experimental excitation energies for **DN2** in MeCN and for **DN3** in DMF, whereas the agreement is actually worsened for **DN3** in MeCN. This comparison of absolute excitation energies involves of course also the other possible error sources of the computational approach (e.g. functional,

general quality of the underlying COSMO implementation, non-equilibrium solvation, neglect of counter-ion effects).

Table 6.9. Comparison of COSMO and D-COSMO-RS IV-CT excitation energies (in cm^{-1}) in different solvents for **DN1-4**^a

	solvent model	DCM	MeCN	DMF	<i>exp. (MeCN)</i>	<i>exp. (DMF)</i>
E_1	COSMO	13074	13008	13008		
(DN1)	D-COSMO-RS	13000	13097	13142	11000 ^b	10820 ^c
E_1	COSMO	8049	9267	9268		
(DN2)	D-COSMO-RS	8471	7989	7535	8320 ^c	-
E_1	COSMO	8012	9591	9592		
(DN3)	D-COSMO-RS	8433	8219	7763	9360 ^d	8100 ^d
E_1	COSMO	10134	11188	11189		
(DN4)	D-COSMO-RS	10255	10227	10170	-	8500 ^c

^a BLYP35/TZVP results with TBM6.3, more detailed results in Table S6.16-S6.19. ^b Ref. [247]. ^c Ref. [190]. ^d Ref. [42].

Table 6.10 reports a similar comparison between COSMO and D-COSMO-RS results for the IV-CT excitation energies in MeCN *vs.* DMF of **DN5** and **DN6**. Experimentally, the MeCN results are by 1740 cm^{-1} and 1800 cm^{-1} , respectively, higher than the DMF data. Again, COSMO gives identical values in both solvents. Here D-COSMO-RS provides a significantly too small correction, attaining differences of ca. 240 cm^{-1} and ca. 440 cm^{-1} , respectively. As for **DN3**, this suggests that differences in the solvent reorganization energies upon charge transfer in MeCN *vs.* DMF are underestimated by the current D-COSMO-RS treatment. Solvent effects on ion pairing or possible solvent dynamical effects are of course again not included in the calculations.

The influence of the D-COSMO-RS corrections on the ET barriers of the class II systems in aprotic solvents amounts typically only to a few kJ mol^{-1} (cf. Table S6.17, Table S6.18, Table S6.20 and Table S6.21 in the Appendix). Regarding the differences between MeCN and DMF, no clear-cut improvement is observed relative to the experimental values. Absolute agreement with experimental barriers is also not affected in a systematic way. The differences are obviously too small. Other error sources, both on the experimental (ESR) and computational side, are of similar magnitude.

Table 6.10. Comparison of COSMO and D-COSMO-RS IV-CT excitation energies (in cm⁻¹) in different solvents for **DN5** and **DN6**^a

	<i>solvent model</i>	DCM	MeCN	DMF	<i>exp.</i> (DCM)	<i>exp.</i> (MeCN)	<i>exp.</i> (DMF)
E_1 (DN5)	COSMO	9428	11533	11535	10800 ^b	11300 ^b	9560 ^b
	D-COSMO-RS	9784	10323	10079			
E_1 (DN6)	COSMO	10123	12583	12586	12300 ^c	12800 ^c	11000 ^c
	D-COSMO-RS	10471	10843	10405			

^a BLYP₃₅/TZVP results with TBM6.3. ^b Ref [176]. ^c Ref. [185].

6.5 Conclusions

The current quantum chemical approach, based on suitably chosen hybrid density functionals and either continuum solvent models (section 6.4.5) or the D-COSMO-RS *ansatz* (section 6.4.6), provides the first available methodological framework that allows an essentially quantitative description of the ground-state properties and of the corresponding thermal and optical electron-transfer parameters of many organic mixed-valence compounds, from previously studied triarylamine-based radical cations to the present dinitroaromatic radical anions. ET barriers obtained by ESR are reproduced to a remarkable degree, and the Robin-Day classification in solution can be performed computationally with high predictive quality. IV-CT excitation energies and transition dipole moments are obtained from TDDFT calculations. The extreme importance of the solvent environment for the class II/III character of MV systems has again been demonstrated computationally. Given the success of the computational protocol for properties in solution, previous assumptions on the gas-phase electronic structure of 1,3-dinitrobenzene radical anion **DN2** have to be revised (see section 6.4.3).

The key features of any successful approach in this field are:

- a reasonable balance between inclusion of dynamical and non-dynamical electron correlation and minimal self-interaction errors and
- an appropriate modeling of environmental effects.

On both aspects improvements are still possible: further improved generations of density functionals or accurate post-Hartree-Fock approaches may be envisioned. Even more importantly, still more sophisticated treatments of solvent effects are feasible.

The D-COSMO-RS approach described in this chapter offers a computationally expedient and useful tool. It allows going beyond continuum solvent models at little extra cost and has shown its great potential when dealing with protic solvent environments. Many further applications of D-COSMO-RS in different fields may be imagined, e.g. its employment to solvent mixtures (see chapter 7).

Chapter 7

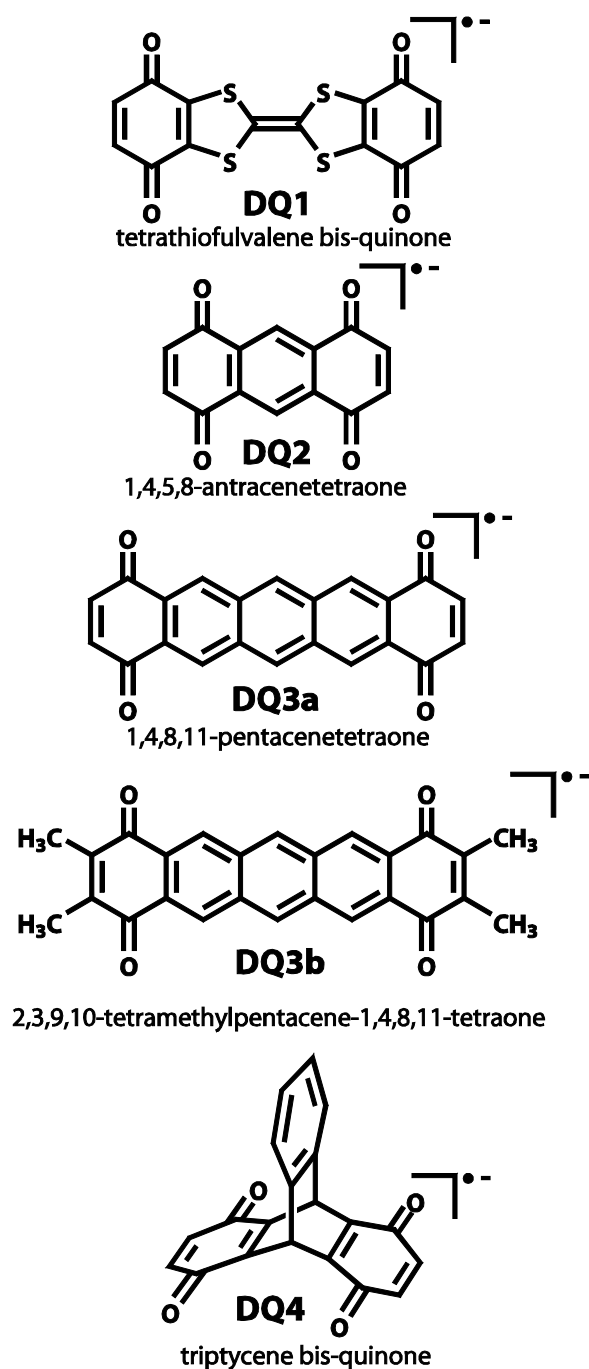
In so far as quantum mechanics is correct, chemical questions are problems in applied mathematics.

-- Henry Eyring

7 Predicting the localized/delocalized Character of Diquinone Radical Anions

7.1 Introduction

As shown in the previous chapters, the quantum chemical approach allows a successful Robin-Day classification by using non-standard global hybrid functionals with 35% exact-exchange admixture (BLYP35) and continuum solvent models.^[44-46] In chapter 6 it has been demonstrated that it is possible to go beyond continuum solvents with moderate computational effort. Inclusion of realistic and specific solvent-solute interactions like hydrogen bonding in alcoholic solvents does not require explicit MD simulations, if the direct conductor-like screening model for real solvents (D-COSMO-RS) is applied.^[46] In general, the solvent environment turned out to be even more important than implied by many of the discussions in previous work. In the gas phase and in nonpolar solvents many of the species studied are delocalized exhibiting symmetry breaking only in polar solvents. Since most previous studies (but note refs. [42, 43, 246]) had neglected the solvent environment in ground-state structure optimizations, they inevitably gave delocalized structures even for cases, where experiments in solution point to a class II behavior.^[182]



Scheme 7.1. Mixed-valence diquinones studied.

In very few cases localization was obtained in gas-phase calculations using special density functionals or forcing the system into a class II electronic structure by adding artificially terms to the Hamiltonian (this has been termed “constrained DFT”, CDFT).^[174, 239] In this context, the radical anion **DQ1** of tetrathiafulvalene diquinone (Q-TTF-Q; Scheme 7.1) has recently received particular attention in two computational studies.^[266, 267] Wu and van Voorhis used **DQ1** to demonstrate gradient optimizations within the CDFT approach. At the gas phase CDFT/B₃LYP/6-31+G(d) level, a localized class II structure was obtained, and an ET barrier was reported. In a subsequent study, Vydrov and Scuseria used unconstrained DFT and advocated the use of the LC- ω PBE range-separated hybrid functional, as this provided a localized double-well potential in gas-phase optimization, in contrast to several other functionals studied.^[67] Both of these computational studies implied that Q-TTF-Q^{•-} is a class II system not only in solution, as found experimentally, but also in the gas phase. In view of the extensive recent experience with a wide variety of cationic,

neutral and anionic organic MV compounds (see chapters 3-6),^[44-46] this interpretation is doubtful. In the present chapter a systematic computational study of Q-TTF-Q^{•-}, **DQ1**, and of three related MV diquinone radical anions **DQ2-4** (Scheme 7.1) is presented using the

abovementioned protocol. Similar to the previous chapter the behavior of the protocol is investigated for gas phase calculations as well as calculations in solution (using continuum solvent models as well as the D-COSMO-RS model for both aprotic and protic solvents). For the first time, solvent mixtures are studied by the D-COSMO-RS approach. In addition, a variety of exchange-correlation functionals is evaluated, including LC- ω PBE. With appropriate exact-exchange admixtures all of these systems exhibit class III character in the gas phase and become class II only in solution depending on both solvent and nature of the bridge. A variety of ground-state properties, ET barriers, and IV-CT excitation energies and transition-dipole moments are provided and general recommendations for the quantum chemical treatment of these and related MV systems are given.

7.2 Available Experimental Information

Interest in radical anion of tetrathiafulvalene-diquinone, **DQ1**, arises mainly from the fact that tetrathiafulvalene (TTF) has been used as a strong π -donor bridge in a variety of organic materials studies.^[30] Observation of a broad IV-CT band and the temperature dependence of the ESR spectra in solvents like DCM, ethyl acetate (EtOAc), *tert*-butanol (*t*-BuOH), and a 10:1 mixture of the latter two solvents indicate a class II situation.^[30] Due to solubility problems, detailed studies of the ET process by ESR were only possible in the (10:1) mixture, giving a broad IV-CT band peaking around 8000 cm⁻¹, an ET barrier of about 30 kJ mol⁻¹, and ¹H-HFCs of 2.47 G at 260 K and 1.23 G at 340 K.^[30] Estimated ET rates in DCM and EtOAc are somewhat higher, whereas the one in pure *t*-BuOH is lower. The previous theoretical work on this system will be compared to the results further below.^[67, 266-269] Both the hyperfine couplings found in ESR ($a_H = 0.9$ G, four signals) and the sharp bands near 6410 cm⁻¹ (1560 nm) with vibrational fine structure in the NIR spectra indicate the 1,4,5,8-anthracenetetraone, **DQ2** (and its substituted analogues), to be a symmetrically delocalized class-III case in aprotic solvents like dimethylformamide (DMF) or dimethylsulfoxide (DMSO).^[270, 271] In contrast, the 1,4,8,11-pentacenetetraone radical anion, **DQ3a**, shows a broad and nearly flat absorption band in NIR from 600 to 2100 nm in DMF, indicating a class II system.^[29] Temperature dependent ESR measurements on the tetramethyl-substituted analogue **DQ3b** (and on its 6,12-dihexyl substituted analogue) in

DMF and DCM indicated localization at 210 K ($a_{\text{H}} = 2.8$ G), whereas at 294 K HFCs to both quinone moieties were observed ($a_{\text{H}} = 1.3$ G), consistent with a fast equilibrium on the ESR time scale. ESR-based Arrhenius plots over relatively narrow temperature ranges suggested adiabatic electron-transfer (ET) barriers, $\Delta H^\ddagger$, on the order of about 15–25 kJ mol⁻¹ in DMF, depending on the substitution pattern and the concentration of counter-ions.^[28] In the less polar 2-methyltetrahydrofuran, **DQ3b** exhibits averaged HFCs down to 160 K, suggesting significantly lower barriers or even a class III behavior.^[272] While the bridge pathway of triptycene-bis-quinone radical anion, **DQ4**, is shorter than that of **DQ3a** and **DQ3b**, interruption of the delocalized π -framework is expected to also reduce electronic coupling between the two quinone moieties. Indeed, ESR in acetonitrile (MeCN) indicated a localization of the spin density around 218 K and an averaged spin density at 298 K.^[273] Arrhenius plots provided an estimated ET barrier of ca. 26 kJ mol⁻¹.

7.3 Computational Details

The previously validated BLYP35 global hybrid functional^[44-46] with $a = 0.35$ (according to eq. (3.1)) turned out to be near optimum for ground-state properties, ET barriers, and IV-CT excitation energies of the previously studied organic MV systems (see chapters 3-6).^[44-46] In section 6.4.5, it has been found that the BMK meta-GGA hybrid functional ($a = 0.42$),^[243] which (in contrast to BLYP35) is simultaneously accurate for general main-group thermochemistry, performs similarly well.^[46] In addition to these two best previous performers for organic MV systems, Truhlar's "double exact-exchange variant" of the Mo5 functional, Mo5-2X ($a = 0.56$)^[241] is again evaluated and along with the range-separated hybrid LC- ω PBE.^[65-68] These two functionals have recently been applied to gas-phase calculations of **DQ1**.^[67] The comparisons of functionals have been done with Gaussian 09 (G09),^[209] with full structure optimization at each level, using the CPCM solvent model with appropriate dielectric constants,^[121, 253] and triple- ζ basis sets (TZVP)^[194] for all atoms. Where necessary, both localized and delocalized starting structures were employed. Symmetry restrictions were applied to locate the symmetric, delocalized transition state for adiabatic electron transfer in case of localized minima. IV-CT excitation energies were computed at time-dependent DFT (TDDFT) level, both for minima and transition states,

with the same functional, basis-set, and solvent (including non-equilibrium solvation). In some cases (for the highest exact-exchange admixtures, see below), negative excitation energies at the symmetrical transition-state structures indicated instabilities of the Kohn-Sham ground-state wave functions with respect to symmetry breaking. In such cases, the “stable=opt” keyword in G09 led to energy lowering (and thus lower ET barriers), symmetry-broken wave functions, and only positive excitation energies in the TDDFT calculations. Spin-density isosurface plots were obtained with the Molekel program.^[195] Subsequent calculations of hyperfine coupling constants (HFCs) at the optimized ground-state structures used IGLO-II basis sets (H (3s1p)/[5s1p], C, N, O (5s4p1d)/[9s5p1d], S (7s6p2d)/[11s7p2s]).^[210]

To go beyond the limitations of continuum solvent models, the COSMO-RS approach^[123] has been applied (see sections 2.3 and 6.4.6). The direct COSMO-RS approach allows a self-consistent treatment of the solute in the potential exerted by the effective chemical potential (σ -potential) of a solvent or solvent mixture, including energy gradients needed for structure optimization, as well as linear response TDDFT calculations. This D-COSMO-RS approach has been adopted to the title systems, including for the first time a solvent mixture (see below). All D-COSMO-RS and COSMO^[120] results are reported at the BLYP35/TZVP level with a local development version of TBM6.3.^[252] For the relevant solvents, BP86/TZVP pre-generated σ -potentials have been obtained from the COSMOtherm program package^[257, 258] and have been used for structure optimizations and TDDFT calculations. The following dielectric constants have been used in COSMO calculations (both those presented and those underlying the generation of the σ -potentials): ethyl acetate (EtOAc, $\epsilon = 5.9867$), dichloromethane (DCM, $\epsilon = 8.93$), *t*-BuOH ($\epsilon = 12.47$), *N,N*-dimethylformamide (DMF, $\epsilon = 36.7$), acetonitrile (MeCN, $\epsilon = 36.64$) and a weighted value for the mixture of EtOAc with *t*-BuOH (10:1, $\epsilon = 6.576$).

7.4 Results and Discussion

7.4.1 General Evaluation of BLYP₃₅/TZVP/CPCM results

Gas phase calculations at the BLYP₃₅/TZVP level give delocalized class III situations for all systems **DQ1-4** of the present work. No experimental gas-phase results are available, and converged high-level post-Hartree-Fock calculations for **DQ1-4** also seem presently out of reach. It has to be noted, however, that for the smaller dinitroaromatic radical anions (see previous chapter), where post-HF gas-phase calculations had been attempted, the very small computed ET barriers most likely would disappear upon convergence to the basis-set limit.^[46] Together with the excellent performance of the BLYP₃₅/TZVP/CPCM approach in reproducing the characteristics of those dinitroaromatic (see section 6.4.4)^[46] and the present diquinone radical anion systems (see below) in solution, the gas phase results seem to be reliable. A delocalized situation at BLYP₃₅/TZVP level pertains also to all systems in a nonpolar solvent like hexane or EtOAc (see also D-COSMO-RS results in section 7.4.3). The underlying assumptions of previous computational studies that **DQ1** is a class II case also in the gas phase (see discussion below), thus seem clearly unwarranted. Only in polar solvents, **DQ1**, **DQ3a**, **DQ3b**, and **DQ4** localize to a class II situation, whereas **DQ2** remains delocalized in all aprotic solvents investigated (but see below for a detailed discussion of protic solvents). These conclusions are supported (Table 7.1) by the computed ground-state dipole moments μ_o , by the adiabatic ET barriers $\Delta H^\ddagger$ and by the C-O bond lengths of both quinone units. Experimentally, the ESR-based ET barriers have been obtained in different solvents for **DQ1**, **DQ3a**, **DQ3b** and **DQ4**. Starting with the DCM-based value for **DQ1** (see below for a more detailed discussion of the solvent dependence for **DQ1**), the roughly estimated ESR-value in this solvent is underestimated only slightly at the BLYP₃₅/TZVP/CPCM level. This holds also for ESR-based ET barrier of **DQ3b** in DMF and the ESR-based barrier of **DQ4** in MeCN both somewhat higher than the computed BLYP₃₅/TZVP/CPCM values (Table 7.1). In general a moderate underestimate of the barriers at this level can be found so far. Previous work, e.g. on dinitroaromatic radical anions, suggested rather good agreement (see chapter 6).^[46]

In any case, the class II/III behavior of all four systems in polar aprotic solvents is well characterized. Most notably, no artificial CDFT constraints are needed to simulate the class II character of **DQ1**, **DQ3a**, **DQ3b**, and **DQ4** in such environments. This provides additional support to the conclusion (see above) that all systems are delocalized class III cases in the gas phase or in non-polar solvents. The computed barrier for **DQ3b** in the moderately polar solvent THF is only about 7 kJ mol⁻¹, indicating a class II/III borderline case. This is consistent with the fact that ESR measurements in 2-methyltetrahydrofuran or in dimethoxyethane (for the 6,12-dihexyl substituted analogue with essentially the same dielectric constant as THF) did not give evidence for any localization down to 160 K.^[272] In the absence of further spectroscopic (e.g. UV/vis or NIR) data, no clearer classification is possible in these less polar solvents.

Due to solubility problems for the present diquinone radical anions, almost no reliable UV/vis or NIR studies of the ET parameters are available. For **DQ1**, NIR spectra have been obtained showing a broad IV-CT band near ca. 8000 cm⁻¹,^[30] but again solubility problems prevented a more quantitative study.^[274] The computed IV-CT excitation energy in DCM is about 2000 cm⁻¹ too low, which is a bit more than at the BLYP35/TZVP/CPCM level for a class II system.^[46] A sharp IV-CT band at 6410 cm⁻¹ has been found for the class III case **DQ2** in DMF.^[270] This is overestimated by ca. 1100 cm⁻¹ in the calculations, again consistent with previous results for class III systems.^[44-46] IR spectra for **DQ2** exhibit a decrease of the carbonyl stretching frequency from 1672 cm⁻¹ for the neutral compound to 1581 cm⁻¹ (with two more bands at 1540 and 1530 cm⁻¹) for the radical anion in DMSO.^[270] This is well reproduced at the BLYP35/TZVP/CPCM level (neutral 1676 cm⁻¹, anion 1571 cm⁻¹) after uniform frequency scaling by 0.95 (as done previously for dinitroaromatic radical anions, see section 6.4.5).^[46] This holds also for **DQ4**, where the experimental IR carbonyl stretching frequencies in DMSO (1650 cm⁻¹ for the quinone side, 1505 cm⁻¹ for the semiquinone side)^[29] are well reproduced by the scaled computed frequencies (1652 cm⁻¹ for the quinone side, 1466 cm⁻¹ for the semiquinone side).

Table 7.1. Computed (BLYP35/TZVP/CPCM)^a ground state dipole moments μ_o (in Debye), ET barriers $\Delta H^\ddagger$ (in kJ mol⁻¹), C-O bond lengths (d_1, d_2 in Å), excitation energies (E_i and $2H_{ab}$ in cm⁻¹)^b and ¹H-HFCs a_H (in G)^c

	environment	μ_o	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}$	$a_H(C_1)$	$a_H(C_{2/i})$
DQ1	gas phase	0.04	0.0	1.230	1.230	1924	1924	1.3 (4)	1.3 (4)
	DCM	17.81	23.2	1.213	1.257	5730	894	-2.5 (2)	1.2 (4)
	DMF	18.27	27.0	1.213	1.257	6318	879	-2.5 (2)	1.2 (4)
	<i>exp.</i>		31			~8000 ^d		2.5 (2) ^e	1.2 (4) ^e
DQ2	gas phase	0.01	-0.1	1.232	1.232	8225	8226	-0.8 (4)	-0.8 (4)
	DCM	0.02	-0.1	1.235	1.235	7495	7494	-0.7 (4)	-0.7 (4)
	DMF	0.31	0.0	1.235	1.237	7547	7532	-0.7 (4)	-0.7 (4)
	<i>exp.</i> ^f		- ^f			6410		0.9 (4)	
	DMSO	0.39	0.0	1.235	1.237	7577	7561	-0.7 (4)	-0.7 (4)
DQ3a	gas phase	0.03	-0.1	1.233	1.233	5135	5137	-1.4 (4)	-1.4 (4)
	DCM	16.12	7.8	1.220	1.255	7645	3767	-3.5 (2)	-1.4 (4)
	DMF	17.12	10.3	1.220	1.256	8033	3780	-3.6 (2)	-1.4 (4)
DQ3b	gas phase	27.94	-0.3	1.235	1.235	4862	4862	0.8 (12)	1.2 (8)
	THF	43.76	7.4	1.222	1.257	6776	3864	2.5 (6)	0.8 (12)
	DCM	44.02	8.0	1.222	1.258	6866	5013	2.5 (6)	0.8 (12)
	DMF	44.93	10.1	1.221	1.259	7198	3824	2.6 (6)	0.7 (12)
	MeCN	44.92	10.1	1.221	1.259	7208	4078	2.6 (6)	0.7 (12)
	<i>exp.</i> ^g		16-20			- ^g		2.9 (6)	1.3 (12)
DQ4	gas phase	4.61	0.0	1.232	1.232	2946	2942	-1.0 (4)	-1.0 (4)
	DCM	10.94	12.3	1.216	1.260	6600	2072	-2.2 (2)	-0.9 (4)
	DMF	11.30	14.6	1.216	1.261	7399	2082	-2.3 (2)	-0.9 (4)
	MeCN	11.30	14.6	1.216	1.261	7394	2257	-2.3 (2)	-0.9 (4)
	<i>exp.</i> ^h		25.9					- ^h	1.1 (4)
	DMSO	11.32	14.7	1.216	1.261	7459	2110	-2.3 (2)	-0.9 (4)

^a G09 BLYP35/TZVP/CPCM results. Dipole moments with the center of mass as the origin. ^b Excitation energies obtained at symmetry broken (E_i) and at $C_{2/i}$ -symmetric structure ($2H_{ab}$). Further excitation energies and corresponding transition dipole moments are given in Table S7.1. ^c HFCs of the quinone units. Other HFCs are provided in Tables S1-S5. Number of signals in parentheses. ^d Broad IV-CT band at 7700 cm⁻¹.^[30] ^e Experimental HFCs for EtOAc/*t*-BuOH (10:1) solvent mixture: 2.5 G (2 protons) at 260 K, 1.2 G (4 protons) at 340 K.^[30] ^f Class III case, IV-CT energy and a_H in DMF from ref. [270]. ^g Broad IV-CT band from 4750-16700 cm⁻¹ in DMF for **DQ3a**.^[29] ET barriers and a_H from temperature-dependent ESR measurements in DMF^[28] and MTHF^[272] for **DQ3b** and in DCM for analogous diquinones.^[28] ^h Data in MeCN from temperature-dependent ESR measurements, pentet with $a_H = 1.1$ G obtained at 298 K, triplet when cooling down to 218 K.^[273]

Table 7.1 shows also computed and experimental ¹H-hyperfine coupling constants (HFCs) on the quinone moieties (see Table S7.1 for other ¹H-HFCs). Calculations for the localized class II minima of **DQ1** give values near 2.5 G on the localized semiquinone moiety and

negligible HFCs on the quinone side, consistent with experimental data at low temperatures.^[30] The symmetrical transition-state structures give half this value on both sides, consistent with full spin delocalization and (averaged) experimental ESR data at higher temperatures.^[30]

Consistent with these hyperfine couplings, Figure 7.1 shows how the computed spin-density distribution in **DQ1** is delocalized in the gas-phase optimization but localized after optimization in DCM. Delocalized **DQ2** gives four signals both computationally and experimentally.^[270] For **DQ3b**, experiments at room temperature in DMF suggests HFCs of 1.34 G to all 12 methyl protons,^[28] due to a fast equilibrium between two localized minima. The delocalized gas-phase calculations or the calculations at the symmetrical transition state structures are consistent with these values (after taking into account rotational averaging of the methyl groups). At lower temperatures, solubility problems hamper the measurements, but the situation is consistent with HFCs of ca. 2.9 G to six methyl protons and of 0.64 G to two anthracene protons on one side. The calculations (Table 7.1) again agree with this situation (after rotational averaging).

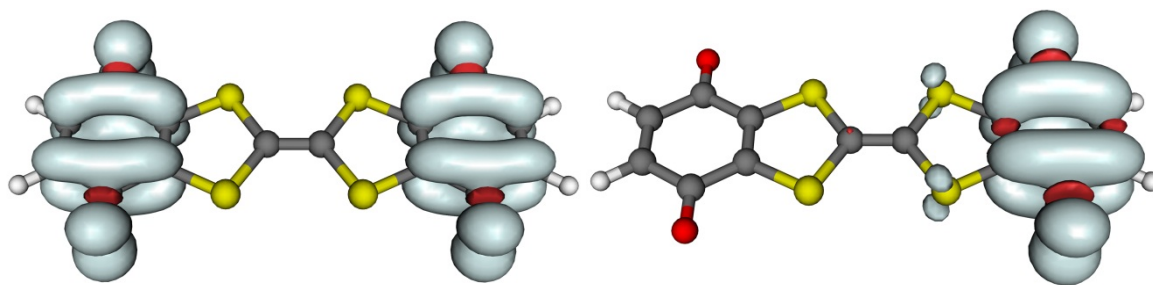


Figure 7.1. Spin-density distributions (isovalue ± 0.001 a.u.) of **DQ1**, calculated with BLYP35/TZVP in the gas phase (left) and in DCM (right).

Calculations are also consistent with experimental results for **DQ4** (Table 7.1): Delocalized structures reproduce the room temperature ESR spectra with HFCs of 1.1 G to four quinone protons,^[273] whereas localized structures produce HFCs to two protons (2.3 G; these could not be observed experimentally, but localization is consistent with the line broadening observed at lower temperatures).

7.4.2 Evaluation of BMK, Mo5-2X and LC- ω PBE density functionals

In the previous study on MV dinitroaromatic radical anions (see chapter 6), the BMK meta-GGA global hybrid with 42% E_{xx} admixture exhibited comparable accuracy as BLYP35. It has the advantage over the latter of good performance for general main-group thermochemistry. Therefore, BMK/TZVP results for **DQ1** in some solvents are compared to those of two other functionals in Table 7.2. It has to be noted that gas-phase BMK results agree with the BLYP35 data in predicting class III behavior for all four systems (see Table 7.2 and Table S7.2-7.5). In agreement with the BLYP35 results, BMK gives localization for **DQ1** in all polar aprotic solvents. Structural symmetry breaking is slightly more pronounced, the computed BMK and BLYP35 dipole moments for a given solvent dielectric constant are very similar. The ET barriers are a few kJ mol^{-1} higher than the BLYP35 results, providing slightly better agreement with experiment. However, due to the higher exact-exchange admixture (42%), unrestricted Kohn-Sham instabilities at some transition-state structures are found, leading to negative excitation energies in subsequent TDDFT calculations. Wave function optimization using the “stable=opt” in Gaussian 09 provides a symmetry-broken spin density and a dipole moment of 17 Debye, despite the symmetrical nuclear framework. The LC- ω PBE range hybrid is also evaluated as Scuseria and Vydrov advocated its use and found a class II localized structure for **DQ1** in the gas phase.^[67] This is confirmed by the LC- ω PBE results reported in Table 7.2: the computed ET barrier of ca. 48 kJ mol^{-1} is almost twice as large as the ESR-based barrier in solution. Indeed, when adding a polar solvent model, completely unrealistic barriers of more than 80 kJ mol^{-1} are obtained (Table 7.2). This indicates far too high exact-exchange admixture and dramatic over-localization. Similar behavior has been found in the study on dinitroaromatic radical anions (see section 6.4.5) when using the LC-BLYP and ω B97-X range hybrids, whereas the CAM-B3LYP range hybrid was much closer to the BLYP35 and BMK results.^[46] It appears that the introduction of full exact exchange at long range in some range hybrids may lead to an overlocalization. Thus, it can be maintained that **DQ1** is most likely a class III system in the gas phase. Scuseria and Vydrov also noted Kohn-Sham wave-function stability problems (see above) at the symmetrical transition state, another indication that too much Hartree-Fock exchange is involved.^[67] In that study, Mo5-2X was also found to give (erroneous) symmetry breaking in the gas phase, but less instability. This is in line with the

results for dinitroaromatic radical anions (see section 6.4.5) where functionals like Mo5-2X or Mo6-2X also over-localized, but not to the same extent as LC-BLYP or ω B97-X.^[46] Indeed, own calculations at Mo5-2X level confirm this notion: symmetry breaking occurs already in the gas phase, and the ET barriers in solution are overestimated appreciably, albeit not as much as for LC- ω PBE. Triplet instabilities at the symmetrical transition-state structures are more pronounced than for BMK (see above), but less than for LC- ω PBE, in contrast to BLYP35, where such instabilities are not found.

Table 7.2. Dependence of computed^a ground state dipole moments μ_o (in Debye), ET barriers $\Delta H^\ddagger$ (in kJ mol⁻¹), C-O bond lengths (d_1 , d_2 in Å), excitation energies (E_i and $2H_{ab}$ in cm⁻¹)^b and ¹H-HFC constants a_H (in G)^c for **DQ1** on exchange-correlation functional.

functional environment		μ_o^d	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}$	$a_H(C_1)$	$a_H(C_2)$
BMK	gas phase	0.52	0.5	1.225	1.226	1674	1657	-1.4 (4)	-1.4 (4)
	DCM	17.98	29.0	1.209	1.251	8189	-491	-2.8 (2)	-1.3 (4)
	DMF	18.44	32.9	1.209	1.251	8791	-521	-2.8 (2)	-1.3 (4)
Mo5-2X	gas phase	14.13	12.0	1.211	1.251	3447	657	-2.5 (2)	-1.3 (4)
	DCM	17.86	43.3	1.211	1.257	8393	-1855	-2.5 (2)	-1.2 (4)
	DMF	18.31	47.2	1.212	1.258	8958	-1868	-2.5 (2)	-1.2 (4)
LC- ω PBE	gas phase	14.67	48.1	1.208	1.248	5267	-2931	-2.3 (2)	-1.1 (4)
	DCM	18.13	81.6	1.209	1.254	3642	-3650	-2.3 (2)	-0.9 (4)
	DMF	18.55	85.6	1.209	1.254	4179	-3663	-2.3 (2)	-0.9 (4)
<i>EtOAc</i> –									
<i>exp.</i> ^[30]	<i>t-BuOH</i>		31			~8000		2.5 (2)	1.2 (4)
	(10:1) ^d								

^a G09 results. Cf. Table 7.1 for BLYP35 data. Data for **DQ2-4**, see Table S7.2-S7.5 ^b Excitation energies are obtained at symmetry-broken minimum (E_i) and at symmetric transition state structure ($2H_{ab}$). ^c ¹H-HFC constants a_H for localized minima and symmetrical transition-state structures. ^d With the center of mass as the origin.

BMK, LC- ω PBE, and Mo5-2X results for **DQ2-4** are provided in Table S7.2-S7.5 in the Appendix. At this position, it is only noted that **DQ2** exhibits (possibly erroneous) incipient symmetry breaking in DMF or DMSO, when using the BMK functional. The barriers remain very small, however. In contrast, Mo5-2X or LC- ω PBE give a class II structure and significant barriers even in DCM. The latter functional provides also vastly overestimated barriers for **DQ3a**, **DQ3b** and **DQ4**. In some cases, unphysically large S² expectation values (> 0.9) at the symmetrical transition-state structures are observed. Together, these findings corroborate the too large exact-exchange admixture and concomitant over-polarization and

over-localization with Mo5-2X, and particularly with LC- ω PBE. It has to be noted, however, that HFCs exhibit only small direct dependence on the functional (Table 7.2) and are influenced mainly by the localized or delocalized structure.

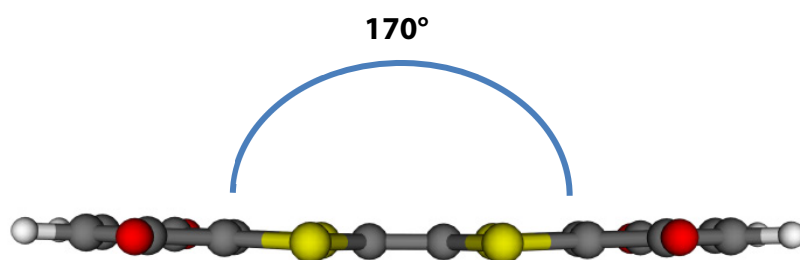


Figure 7.2. Side view of **DQ1** at BLYP35/TZVP/CPCM level in MeCN, showing the non-planarity. The dihedral angle is measured between the sulfur-bound quinone carbon atoms.

As mentioned in the introduction, Wu and Van Voorhis used the CDFT approach to constrain the Fock matrix to a localized state during B3LYP/6-31+G(d) gas-phase structure optimizations. This gave an ET barrier of about 14 kJ mol^{-1} ,^[266] which is lower than the experimental value in polar solvents (cf. above). Although such CDFT gas-phase calculations provide the desired class II behavior, in view of the above-mentioned gas-phase results it has to be considered at best the right answer for the wrong reason, akin to the LC- ω PBE and Mo5-2X gas-phase results above. Furthermore, the CDFT calculations of ref. [266] gave an overall more non-planar structure than, e.g., in the BLYP35/TZVP/CPCM result in MeCN, which is shown in Figure 7.2: the BLYP35/TZVP/MeCN dihedral angle between the two quinone planes is 170° , similar to the unconstrained B3LYP results of ref. [266], in spite of the class II structure. The CDFT dihedral angle was ca. 160° , which is thus probably an artifact of the constraints applied. An additional advantage of the present unconstrained calculations is that the transition state structure is the truly appropriate one for the adiabatic ET, without further approximation. However, the CDFT approach can be useful in creating and studying electronic situations that may be difficult to reach without constraints, or to create diabatic potential curves. CDFT wave functions may furthermore be useful as starting point (initial guess) to converge to solutions that may be difficult to obtain otherwise, e.g. for broken-symmetry wave functions of some antiferromagnetically coupled systems.

7.4.3 Direct COSMO-RS calculations

Due to solubility problems, the more reliable ESR and UV/vis data for **DQ1** had been obtained in a 10:1 mixture of EtOAc and *t*-BuOH^[30] (in particular temperature-dependent ESR spectra, see above). The description of solvation by such a mixture of aprotic and protic solvents is clearly outside the range of applicability of continuum solvent models. Even solvation by a pure alcoholic solvent could not be described. As shown in section 6.4.6 the D-COSMO-RS approach gave a remarkably good simulation of the effects of hydrogen bonding in alcoholic solvents on the structures and ET barriers of MV dinitroaromatic radical anions.^[46] And as COSMO-RS applies also to solvent mixtures, D-COSMO-RS results for **DQ1** (data for **DQ2-4** have also been obtained but will be mentioned only briefly) are reported in Table 7.3. It has to be noted that these are the first D-COSMO-RS results for a solvent mixture. Table 7.3 compares COSMO and D-COSMO-RS data (obtained at BLYP₃₅/TZVP level with TBM6.3, see section 7.3) for **DQ1**, **DQ2**, and **DQ3a**. COSMO calculations in the 10:1 EtOAc/*t*-BuOH mixture used a weighted averaged dielectric constant (but differences compared to the results in the two pure solvents are almost negligible).

Starting with pure aprotic solvents (EtOAc and DCM in the case of **DQ1**), essentially negligible differences between the COSMO and D-COSMO-RS results are found (only the changes in the IV-CT excitation energies are somewhat more notable). In the 10:1 solvent mixture, D-COSMO-RS gives a slightly more distorted structure, a slightly larger dipole moment, and a slightly larger ET barrier than the COSMO data, consistent with a small influence of the protic minority solvent component. The increased D-COSMO-RS barrier in pure *t*-BuOH, due to the effects of hydrogen bonding, is consistent with the slower experimental rate constant (no Arrhenius treatment was possible here due to the limited solubility). Quantitatively, the increase compared to DCM or 10:1 EtOAc/*t*-BuOH appears to be too large (for example, the experimental rate in *t*-BuOH is only by a factor 10 lower than that in DCM).^[274]

Table 7.3. Comparison of COSMO and D-COSMO-RS results (BLYP35/TZVP)^a for ground-state dipole moments μ_o (in Debye), ET barriers $\Delta H^\ddagger$ (in kJ mol⁻¹), C-O bond lengths (d_1 , d_2 in Å), and excitation energies (E_i and $2H_{ab}$ in cm⁻¹)^a of **DQ1**, **DQ2** and **DQ3a**.

	environment	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}$
DQ1	EtOAc	17.55	20.2	1.213	1.256	5381	1379
		(17.37)	(20.9)	(1.213)	(1.257)	(5061)	(1377)
	EtOAc – <i>t</i> -BuOH (10:1)	17.91	23.9	1.213	1.258	5626	1381
		(17.47)	(21.8)	(1.213)	(1.257)	(5200)	(1378)
	<i>exp.</i> ^[30]		30.8			~8000	
	DCM	17.62	24.0	1.214	1.259	5111	1385
		(17.75)	(24.3)	(1.214)	(1.258)	(5585)	(1380)
	<i>t</i> -BuOH	18.82	37.2	1.213	1.264	6517	1389
		(18.01)	(26.4)	(1.214)	(1.258)	(5867)	(1381)
DQ2	<i>t</i> -BuOH	6.78	3.0	1.222	1.257	10314	8115
		(2.00)	(0.0)	(1.232)	(1.242)	(8125)	(8006)
DQ3a	DCM	15.59	7.7	1.223	1.258	8049	4540
		(15.94)	(8.3)	(1.222)	(1.256)	(7924)	(4489)
	<i>exp.</i> ^[28]		16.7 ^c				
	DMF	17.56	12.3	1.221	1.254	8124	4463
		(17.37)	(12.1)	(1.222)	(1.258)	(8511)	(4551)
	<i>exp.</i> ^[28]		17.6 ^c				

^a Values in parentheses obtained by BLYP35/TZVP/COSMO. Further calculated data is available in Table S7.6-S7.10.

^b With the center of mass as the origin. ^c Exp. ET barriers for the 2,3,9,10-tetramethyl-6,12-dihexyl substituted analogue in DCM and DMF respectively.^[28]

Interestingly, the D-COSMO-RS data (not the COSMO data) for **DQ2** in *t*-BuOH suggests incipient symmetry breaking for this radical anion, which is clearly class III in all aprotic solvents (see above). Experimental studies of **DQ2** in alcoholic solvents would thus be very interesting. Note that for some dinitroaromatic radical anions (see section 6.4.6),^[44] where more data in alcohols are available, the increased symmetry breaking caused by hydrogen bonding has been faithfully reproduced by D-COSMO-RS (in contrast to COSMO).

7.5 Conclusions

It has been shown that the computational protocol (see chapters 3-6)^[44-46] is also able to predict the localized/delocalized character of Q-TTF-Q⁻ and of related mixed-valence diquinone radical anions. In contrast to other studies using CDFT, the combination of a

hybrid functional with 35% (BLYP₃₅) or 42% (BMK) exact-exchange admixture in combination with a suitable solvent model can give the right answer, essentially for the right reason. Use of a continuum solvent model (CPCM, COSMO) provides a good description in aprotic solvents (e.g. for experimental ET barriers), and D-COSMO-RS provides an extended description also for protic solvents or for protic/aprotic solvent mixtures. When using a suitable modeling of the environment, global hybrids with intermediate exact-exchange admixtures such as BLYP₃₅ or BMK describe these mixed-valence systems adequately, without the need to apply artificial constraints.

Chapter 8

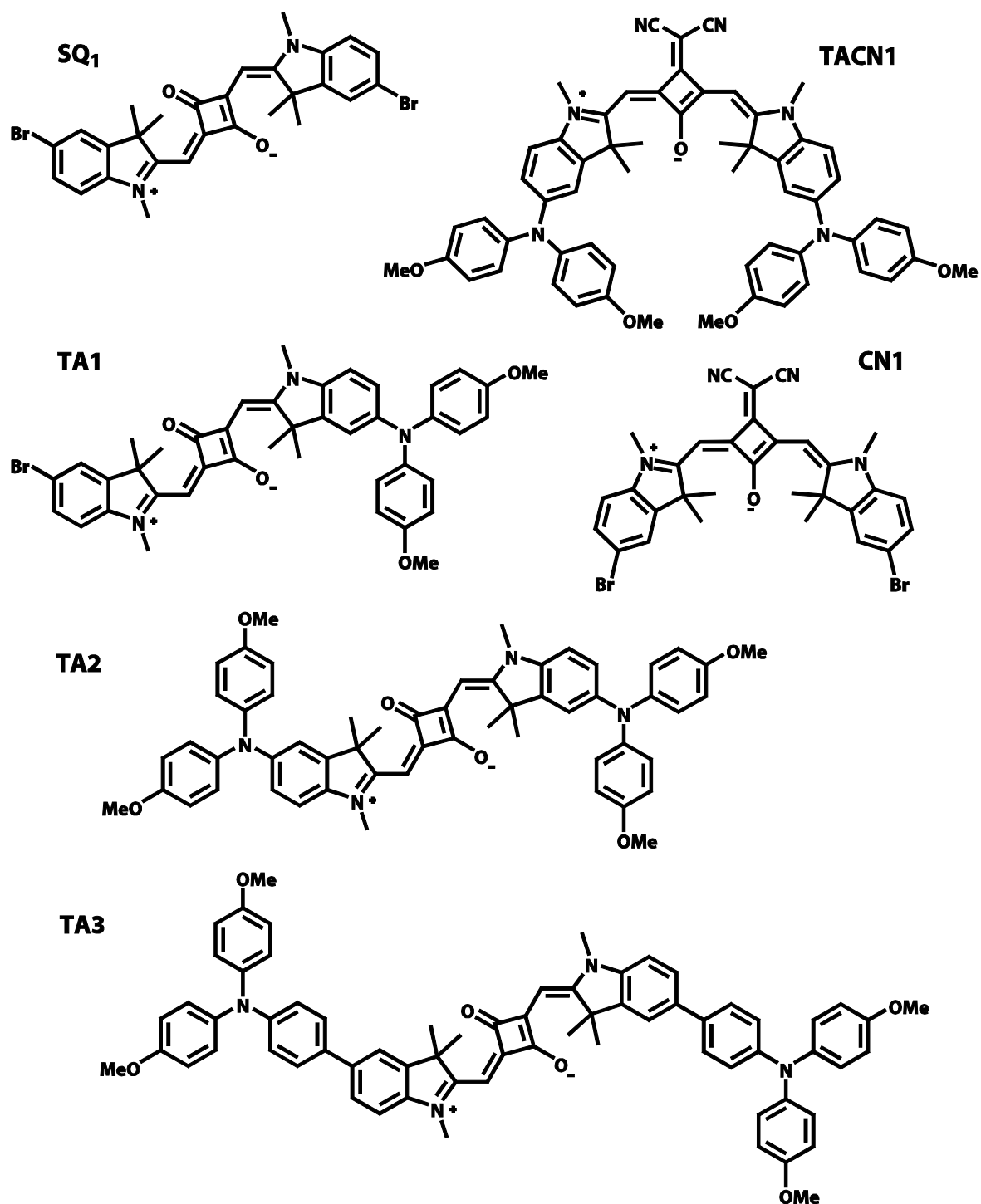
As far as the laws of mathematics refer to reality, they are not certain; and as far as they are certain, they do not refer to reality.

-- Albert Einstein

8 Electron Coupling in Squaraine Dyes

8.1 Introduction

In this chapter, the electron coupling in squaraine dyes will be investigated since these exhibiting strong coupling between the redox centers. Thus, these compounds belong to the Robin-Day class III, despite their large distances between the redox centers particularly in **TA₂**, **TA₃** and **TACN₁**, which consist of the same building blocks (triarylamines) as already used in chapters 3-5. However, the bridge unit (see Figure 1.1) of the previously studied systems is replaced by a central squaraine unit, supplemented by an indolenine moiety on both sides (see Scheme 8.1), which is also the smallest compound investigated (**SQ₁**). This compound is furthermore extended by two triarylamine units, leading to the largest compound, **TA₃**, where the indolenine-squaraine building block really serves as bridge unit. In order to increase the interaction between the amine redox centers, **TA₂** was also investigated, where two diarylamines moieties are directly attached to the squaraine, leading to a somewhat shorter *N-N* distance and avoiding twisting effects present in the biaryl units in **TA₃**.



Scheme 8.1. Six indolenine-squaraine bridged compounds.

In **TACN₁** one oxygen atom of the central squaric ring unit is replaced by a dicyanomethylene group in order to probe the increase of electron acceptor strength on the electronic

properties. For steric reasons, **TACN1** now adopts a *cis*-conformation in contrast to **TA1-TA3** which possess *trans*-conformation. The compounds **SQ1** and **TA1** as well as **CN1**, which are building blocks for **TA2**, **TA3** and **TACN1** respectively, are studied for comparison reasons.

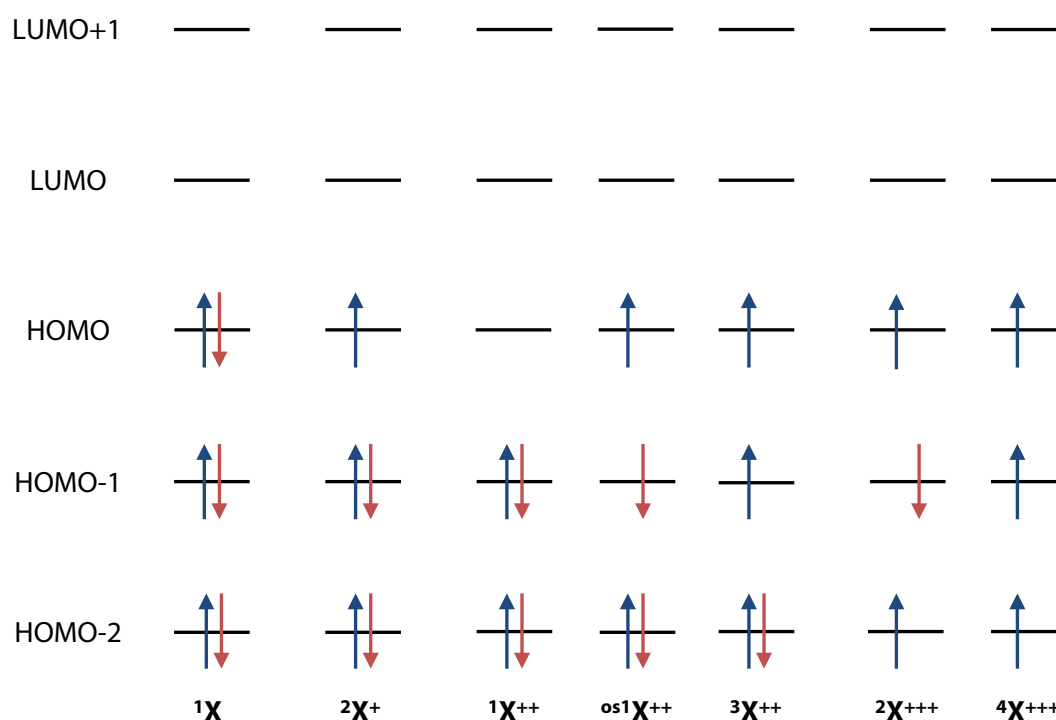


Figure 8.1. Molecular orbitals of the neutral and charged species **TA1-3** and **TACN1**. The HOMO, LUMO, etc. descriptions are technically speaking only valid for the neutral species. ^{*}X = compound, the superscripts define the spin multiplicity, os = open shell (Figure similar to ref. [48]).^[E]

But are these systems really mixed-valent? In an abstract view, these compounds contain at least two redox centers: on the one hand, the triarylamine centers as already described in chapter 3, 4 and 5, and on the other hand the indolenine units. In both cases, the charge upon oxidation will be mainly located at the nitrogen atom, if the redox centers are isolated. However, all compounds exhibit extended π -conjugation, which enforces the coupling between the different redox centers. This is indeed conspicuous since the large distances between them generally favor a weak coupling. Nevertheless, the effect of charge delocalization due to the spacious π -conjugation is much stronger than the effect of charge localization caused by the large distance between the redox centers, so that the compounds studied

here are all typical delocalized systems. Nevertheless, they are anyhow interesting systems for investigations of electron coupling. Detailed experimental research (e.g. spectro-electrochemistry for mono-, di- and trications) has been carried out recently, supported by quantum chemical calculations which are discussed here.^{[48][275][E]} The proper description of the di- and trications is challenging, because different electronic states (see Figure 8.1) are possible. The experimental derivation is unfortunately inaccessible but feasible by quantum chemical methods which also facilitate the determination of the sequence of oxidation.

8.2 Computational Details

Structure optimizations have been performed with the TURBOMOLE (TBM) 5.10 program package.^[192] While the previous computations (see chapters above) on mixed-valence bis-triarylamine cations favored larger exact-exchange admixtures of 35% to obtain good agreement with ground and excited-state properties, application of such functionals to the squaraine systems provided systematically too large excitation energies. Thus the standard B₃LYP hybrid functional^[62] has been used, in combination with SVP basis sets^[193] for all atoms. This may reflect the fact that the squaraine systems exhibit strongly delocalized class III character and should be viewed as single chromophores in all cases. The excitation energies were calculated by TDDFT using the Gaussian 03 program package (Go3).^[196] In both cases, the environment was described by a continuum solvent model (COSMO and CPCM, respectively) with DCM modeled by a dielectric constant of $\epsilon = 8.93$.^[120] As already mentioned above, both implementations differ slightly in technical details like vdW radii, solvent radii or number of tesserae per sphere. But the major difference is that the TDDFT-calculations in Go3 consider non-equilibrium solvation in the excited state, which is not implemented in the TBM version employed (but which can be important to obtain reliable excitation energies, see ref. [44]). For all molecules, several oxidation states have been optimized: neutral (singlet), monocation (doublet), dication (singlet, open-shell singlet, and triplet) and some trications (doublet, quartet). Open-shell broken symmetry states have been optimized by flipping one α -electron to a β -electron in the optimized high spin (triplet/quartet) state. For all molecules, the initial guess for the open-shell broken symmetry wave function of the excited states was created by mixing HOMO and LUMO to

destroy the α - β and spatial symmetries. For all calculations, the large alkyl moieties have been reduced to methyl groups, to minimize the computational effort. Spin-density and molecular-orbital isosurface plots were obtained with the Molekel program.^[195]

8.3 Results and Discussion

8.3.1 Neutral Species

The UV/vis spectra in DCM of all compounds studied show one typical cyanine-like sharp and strong absorption band in the red to NIR region,^[48] which can be assigned to the HOMO→LUMO transition. This is confirmed by the TD-B₃LYP/SVP calculations, see Table 8.1. The agreement with experimental lowest-energy absorption bands is almost perfect for the larger chromophores, while the deviation is larger for the smaller ones (**SQ1** and **CN1**). In all cases, the transition dipole moments are slightly overestimated.

Table 8.1. Calculated^a and experimental (in parentheses)^b ground state dipole moments μ_o (in Debye), excitation energies E_i (in cm⁻¹) and transition dipole moments $\mu_{t,i}$ (in Debye) for the neutral squaraines

	SQ1	CN1	TA1	TA2	TA3	TACN1
μ_o	0.1	5.3	4.5	5.3	0.4	14.2
E_i	17200 (15500)	15800 (14400)	14800 (14800)	14400 (14200)	14900 (14800)	13500 (13200)
$\mu_{t,i}$	15.2 (12.4)	12.5 (11.3)	13.9 (12.6)	16.2 (12.3)	16.0 (13.6)	14.8 (12.3)

^a B₃LYP/SVP. ^b Ref. [48].

The attachment of the diarylamine and triarylamine moieties induces a strong red shift compared to the parent squaraine dye **SQ1**. In case of the diarylamine the shift is 2400 cm⁻¹ (exp. 700 cm⁻¹) for the first amine unit (**TA1** to **SQ1**) and 400 cm⁻¹ (exp. 600 cm⁻¹) (**TA2** to **TA1**) for the second, resulting in a total shift of 2800 cm⁻¹ (exp. 1300 cm⁻¹) for **TA2** vs. **SQ1**. The impact of the triarylamine moieties is not as strong as that of the diarylamines and the absorption maximum only shifts by 2300 cm⁻¹ (exp. 700 cm⁻¹) for **TA3** vs. **SQ1** indicating that the interaction with the squaraine is much weaker. This might be due to the twisted biaryl moiety. Replacing the squaric ring oxygen by a dicyanomethylene moiety also results in a pronounced red shift of the absorption as observed earlier for similar compounds.^[276, 277] This red shift is 1400 cm⁻¹ (exp. 1100 cm⁻¹) for **CN1** vs. **SQ1**. This is due to

the stronger acceptor properties of this group which is also supported by the redox potentials, see below. The by far strongest red shift is, however, observed for the combination of dianisylamino donor groups attached to the squaraine and the concomitant replacement of the carbonyl oxygen by dicyanomethylene, which gives a shift of 3700 cm^{-1} (exp. 2300 cm^{-1} , **TACN1** vs. **SQ1**).

8.3.2 Oxidized Species

Cyclic voltammetry (CV) experiments show one reduction process of the central squaric ring for all squaraines. The dicyanomethylene moiety of **CN1** and **TACN1** in the squaric ring leads to more positive potentials of the reduction and the first oxidation. Any higher oxidation is, however, barely influenced. This shows that the exchange of the squaric oxygen by the dicyanomethylene group results in a stronger acceptor as already demonstrated in the previous section.

For both **TA2** and **TACN1**, five oxidation waves are resolved in CV experiments. The first four oxidations refer to one-electron processes, whereas the last wave covers the transfer of two electrons which leads to a total of six oxidation processes in these compounds. Since two oxidation processes can be assigned to the parent indolenine squaraine system (by comparison to **SQ1** and **CN1**) two oxidations have their origin in the additional amine donor substituents. In comparison with the asymmetric compound **TA1**, it can be seen clearly that the addition of a further donor dramatically reduces the first oxidation potential as result of a delocalized electronic character of the substituted squaraine dyes. For **TA3** the second and the third oxidation process cannot be seen separately whereas in all other compounds they are well separated.

Spin-density distributions confirm the results of the experimental CV spectra, i.e. the first oxidation process in **TA2**, **TA3** and **TACN1** occurs formally at the central indolenine squaraine unit (Figure 8.2). In agreement with experiment, the spin-density distributions show that the second oxidation takes place at one of the dianisylamine/triarylamine groups and the third oxidation again at the central indolenine squaraine unit (see Figure 8.2). But the spin-density distributions of the dications indicate the “two” positive charges at both

dianisylamine/triarylamine groups. Therefore, according to the experimental oxidation potentials (see above and ref. [48]), a kinetically fast migration of the central positive charge to the second dianisylamine/triarylamine group might be assumed, due to electrostatic repulsion of the two positive charges in the dications.

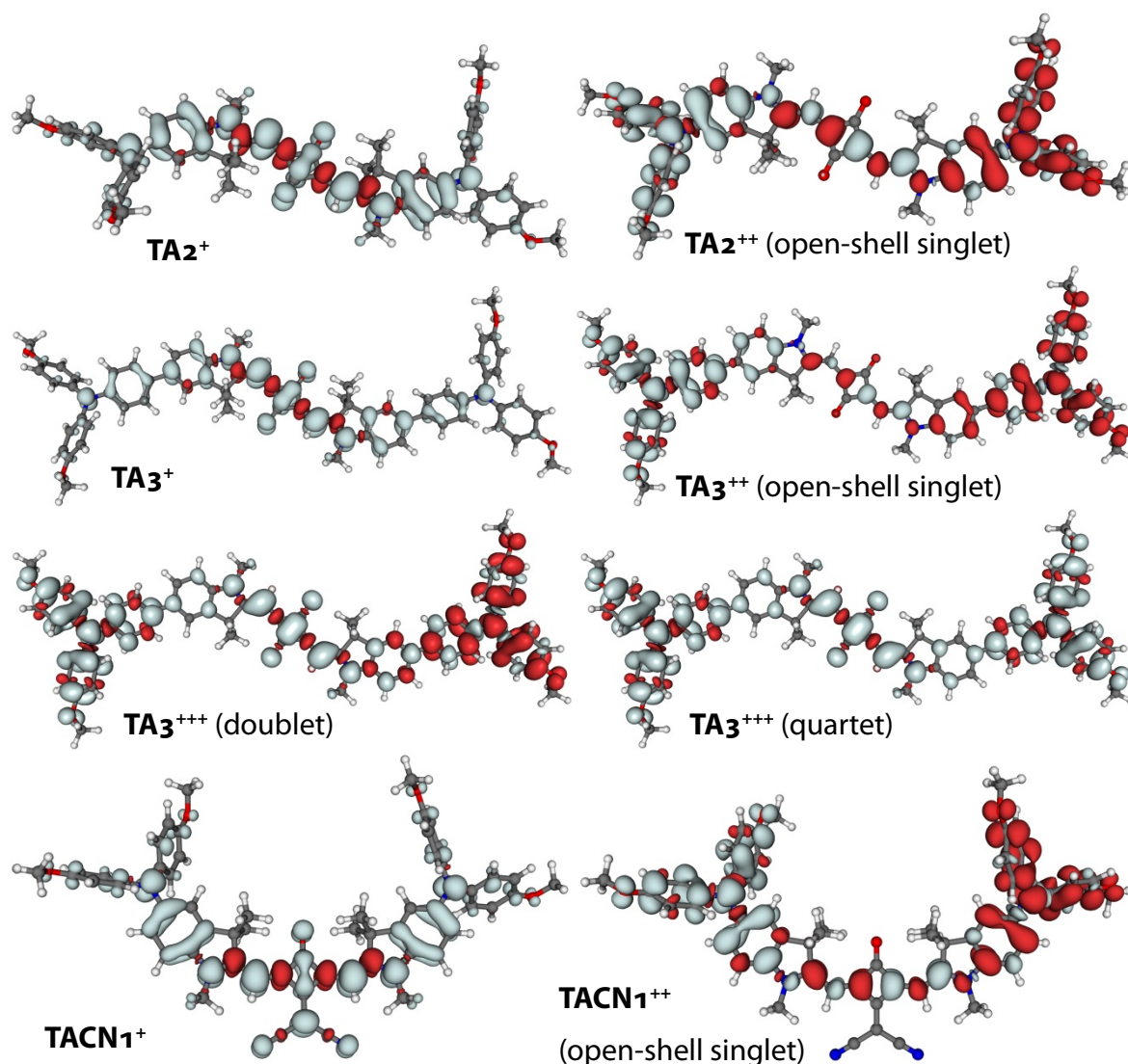


Figure 8.2. Spin-density isosurface plots (isovalues ± 0.001 a.u.) of mono- and dications of **TA₂**, **TA₃** and **TACN1** as well as the trication of **TA₃**.

The migration of charges results in the central indolenine squaraine being “neutral” again so that the central squaraine can be further oxidized, yielding the trications **TA₂⁺⁺⁺** and **TA₃⁺⁺⁺**. The main difference between **TA₂** and **TA₃** is the potential at which this third

oxidation occurs: in TA_3^{++} the squaraine moiety can be oxidized at a distinctly lower potential, presumably just slightly higher than the first oxidation (which refers to the squaraine oxidation of neutral TA_3) because the electrostatic interaction is weak in this large chromophore system. Thus, the third oxidation happens right after the charges have separated in TA_3^{++} , which leads to the apparent two-electron process at the same potential. From this reasoning one can conclude that $E_{1/2}(1) < E_{1/2}(3) < E_{1/2}(2)$ for TA_3 . In contrast, this would be $E_{1/2}(1) < E_{1/2}(2) < E_{1/2}(3)$ for TA_2 with well separated oxidation processes, due stronger electrostatic repulsion of charges resulting of the smaller size extension of the chromophore compared to TA_3 .

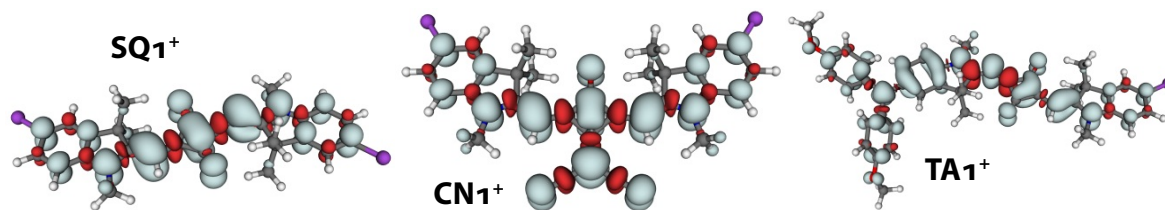


Figure 8.3. Spin-density isosurface plots (isovalue ± 0.001 a.u.) of monocations of SQ_1 , CN_1 and TA_1 .

In case of SQ_1 , CN_1 and TA_1 , spin-density distributions also confirm the first oxidation step to occur at the indolenine squaraine unit (c.f. Figure 8.3), in agreement with experimental oxidation potentials.^[48] The second oxidation in TA_1 occurs at the dianisylamine group. Since similar potentials have been observed for the 4th oxidation of TA_1 and the 5th and 6th of TA_2 , TA_3 , and TACN_1 , it could be assumed that these refer to the second oxidation of the dianisylamine/triarylamine moieties.

Table 8.2. Ground state dipole moments μ_o (in Debye), first excitation energies E_n (in cm^{-1}) with significant transition dipole moments $\mu_{t,n}$ (in Debye) in parentheses for the squaraine monocations

	SQ_1^+	CN_1^+	TA_1^+	TA_2^+	TA_3^+	TACN_1^+
μ_o , calc. ^{a,b}	0.1	2.2	9.7	5.0	0.4	9.3
E_n ($\mu_{t,n}$), calc. ^a	14900 (14.7)	14300 (12.7)	6200 (15.1)	5100 (12.8)	3300 (27.5)	4700 (17.6)
			11300 (9.2)	11700 (19.8)	10800 (7.5)	7100 (8.0)
					14300 (8.9)	11300 (11.0)
E_n ($\mu_{t,n}$), exp. ^c	15200	15300	6500 (10.4)	6200 (10.7)	6600 (13.4)	5700 (9.4)
			11900	12100 (10.9)	11800	8300 (7.5)
					14800	11500 (10.0)

^a B₃LYP/SVP. ^b With the center of mass as the origin. ^c Ref. [48].

Spectroelectrochemical experiments in the vis/NIR region provide further insight into the electronic structure upon oxidation of the compounds, characterizing the mono- and dications (and the trication of **TA3**).^[48] Spectroelectrochemical investigations for different squaraines were performed earlier, but the information about indolenine squaraines is rare.^[278, 279]

Table 8.2 shows computed ground state dipole moments and the comparison of the first excitation energies including the corresponding transition dipole moment. The most intense absorption bands of the squaraine monocations are located between 11500 cm⁻¹ and 12100 cm⁻¹ for the dianisylamine substituted squaraines **TA1**, **TA2** and **TACN1** and between 14800 cm⁻¹ and 15300 cm⁻¹ for **SQ1**, **CN1** and **TA3**.^[48] The sharp and intense band shape (with the exception of **TA3**⁺) indicates that the monocations still have a cyanine like, delocalized, character. The computed relatively small dipole moments, shown in Table 8.2, are another hint towards delocalized monocations. The larger values of **TA1**⁺ and **TACN1**⁺ can be explained either by the asymmetry (**TA1**⁺) or by the C₂-symmetry (**TACN1**⁺). Furthermore, all amine donor-substituted compounds show an additional absorption around 6000 cm⁻¹ in the experiment. A striking difference is a second weaker absorption band (8300 cm⁻¹) of **TACN1**⁺ in this spectral region whose origin is discussed below.

Table 8.3 shows calculated and experimental excitation properties for the dications (**TA1**⁺⁺, **TA2**⁺⁺ and **TACN1**⁺⁺) and the trication **TA3**⁺⁺⁺. Both **TA2**⁺⁺ and **TACN1**⁺⁺ exhibit an intense absorption around 6000 cm⁻¹. Unlike the absorption spectra of the monocation, the spectrum of **TA1**⁺⁺ is different to those of **TA2**⁺⁺ and **TACN1**⁺⁺. The main absorption band of **TA1**⁺⁺ is located at 9900 cm⁻¹. This difference could be due to the charge separation that occurs in **TA2**⁺⁺ and **TACN1**⁺⁺, leading to the two amine centers being oxidized while this cannot take place in **TA1**⁺⁺, where the single amine and the squaraine are oxidized.

In the case of **TA3** just the monocation can be compared with experimental data because the dication formation is rapidly followed by trication formation. Thus, the trication is the only species present at the given electrode potential. For the trication **TA3**⁺⁺⁺, two strong absorption bands are found at 9700 cm⁻¹ and 13300 cm⁻¹.

Table 8.3. Ground state dipole moments μ_o (in Debye), first excitation energies E_n (in cm^{-1}) with significant transition dipole moments $\mu_{t,n}$ (in Debye) in parentheses for the dications (**TA1**⁺⁺, **TA2**⁺⁺, **TACN1**⁺⁺) and the trication (**TA3**⁺⁺⁺)^c

	TA1 ⁺⁺	TA2 ⁺⁺	TA3 ⁺⁺⁺	TACN1 ⁺⁺
μ_o , calc. ^{b,c}	20.0	4.2	0.6	15.0
E_n ($\mu_{t,n}$), calc. ^b	9100 (15.8)	5500 (24.6)	8600 (13.8) 14100 (13.4)	5100 (19.3)
E_n , exp. ^d	9900	6100	9700 13300	5800

^a Only the most stable state is shown, the open-shell singlet for the dications, the doublet for the trication. ^b B₃LYP/SVP.^c With the center of mass as the origin. ^d Ref. [48].

Even though the characteristic absorption spectra of the oxidized species have been obtained in the experiment, the interpretation of the observed bands remained difficult. Yet, the DFT and TDDFT calculations performed here (cf. section 8.2) allow an answer to several questions, such as the localization/delocalization of positive charges, the spin multiplicity of the doubly charged species or the contributions of various orbitals to the excitations. In reference [48], the TD-B₃LYP/SVP computed data are presented as stick spectra together with the experimental spectra, where the strongest measured absorption band was normalized to the oscillator strength of the corresponding computed transition. The spectra of **TA1**, **TA2**, **TACN1** and **TA3** as well as **SQ1** and **CN1** are shown as Figure 10-13 as well as Figure S3 and S4 in this reference. The mapping of the orbitals is equal to Figure 8.1 albeit this assignment of the HOMOs and LUMOs of the neutral molecules in charged species is incorrect.

In the latter two cases (**SQ1** and **CN1**), theory and experiment agree very nicely for the monocations (see Table 8.2), but not at all for the dications. However, for both dications the calculations reveal that the singlet is 80-90 kJ mol^{-1} lower in energy than the triplet. This is due to the highly delocalized charge in these two molecules compared to the other molecules. Therefore, the second oxidation takes place in the same orbital without charge separation and thus favors the singlet state.

For the other monocations, the agreement with experiment is also very good, but excitation energies for the lowest energy transitions are somewhat too low (Table 8.2). These transitions at lowest energy (measured around 6000 cm^{-1}) are due to HOMO-1→HOMO

excitations while the one at next higher energy is mainly due to a HOMO→LUMO excitation at about 11000-12000 cm⁻¹, slightly red-shifted compared to the equivalent transition in the neutral chromophores (see Table 8.1). For **TACN1**⁺ there is a transition in-between which will be discussed below. Again, the transition dipole moments are overestimated as for the neutral species. The striking similarity of this transition to that of the neutral compounds is particularly apparent for **TA1**⁺, **TA2**⁺ and **TACN1**⁺.

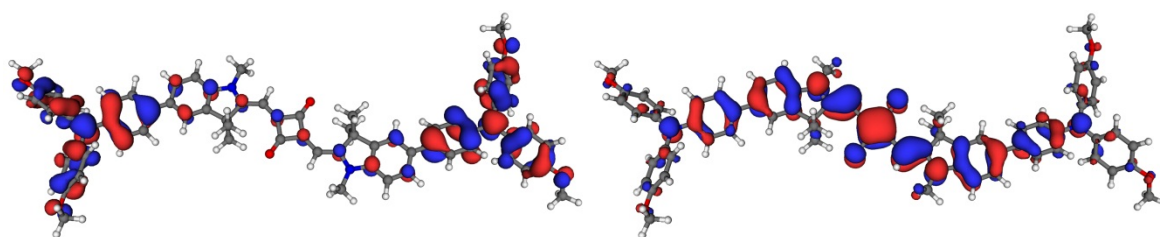


Figure 8.4. Molecular orbitals (β , isovalue ± 0.02 a.u.) of **TA3**⁺ and Left: HOMO-1, Right: HOMO. Orbital assignment according to the neutral species, see Figure 8.1.

Inspection of the orbitals that are involved in these transitions shows that the monocations are delocalized, and the lowest-energy transition at around 6000 cm⁻¹ is due to a degenerate charge transfer from the triarylamine to the squaraine bridge in the case of **TA2**⁺, **TA3**⁺ and **TACN1**⁺ (Figure 8.4 and Figure 8.5). In this respect, “degenerate” refers to diabatic excited states exhibiting the positive charge on either one of the two amine moieties. These two states mix and yield two non-degenerate adiabatic states, which can both be observed separately in **TACN1**⁺: comparing the lowest-energy absorption bands of **TA2**⁺ and **TACN1**⁺, it can be seen that there is only one for **TA2**⁺ (5100 cm⁻¹, exp. 6200 cm⁻¹) but two for **TACN1**⁺ (4700 and 7100 cm⁻¹, exp. 5700 and 8300 cm⁻¹). The latter corresponds to the HOMO-2→HOMO transition. The analogous transition has no transition dipole moment in **TA2**⁺ due to symmetry reasons: squaraine **TA2**⁺ has *C_i* symmetry. The appropriate orbitals are of *a_u* (HOMO-2), *a_g* (HOMO-1) and again *a_u* (HOMO) symmetry. For a transition to be allowed, the direct product of the involved MOs and of the transition dipole moment vector has to include the totally symmetric descriptor, *a_g*. This holds for the HOMO-1→HOMO excitation but not for the HOMO-2→HOMO excitation, which is thus forbidden. The same holds true for **TA3**⁺.

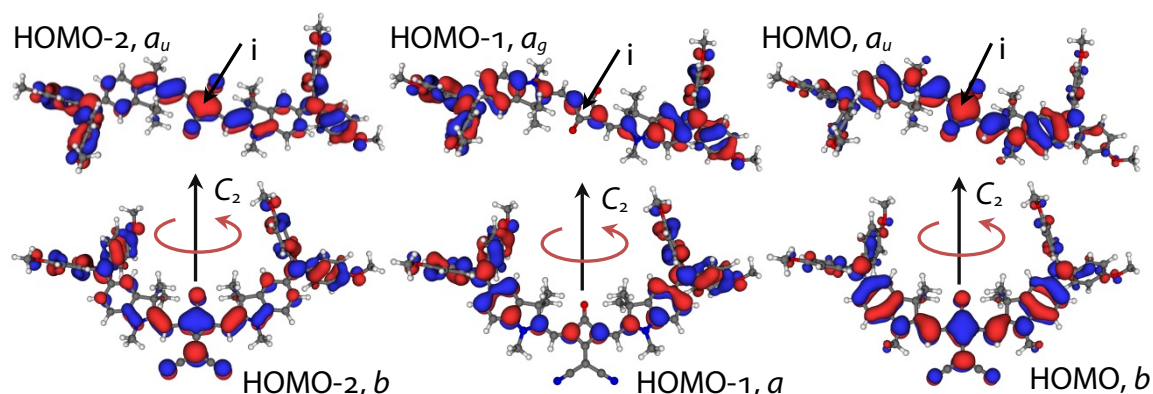


Figure 8.5. Molecular orbitals (β , isovalue ± 0.02 a.u.) of TA2^+ (top) and TACN1^+ (bottom) and its symmetry descriptions. The HOMO labels relate to the neutral molecule, see Figure 8.1.

For TACN1^+ , the central dicyanomethylene group forces the molecule to adopt C_2 -symmetry due to sterical reasons. In this case the analogous orbitals have b (HOMO-2), a (HOMO-1) and again b (HOMO) symmetry as seen in Figure 8.5. Thus, the HOMO-1→HOMO excitation is allowed with its transition moment polarized in x direction, whereas the HOMO-2→HOMO excitation is also allowed but with its transition moment polarized in z direction. While this analysis explains the observation of the electronic transitions reasonably well, inspection of the HOMO orbitals and the spin-density distribution (Figure 8.2) demonstrates at the same time the essentially delocalized character of positive charge in the monocations. The very effective electronic coupling properties of the squaraine gives TA1^+ , TA3^+ and TACN1^+ clearly Robin-Day class III character.

For the dications the question of a triplet vs. singlet ground state arises. While for the triplet state it is obvious to use an unrestricted open-shell wave function, for the singlet states both a restricted closed shell and an unrestricted broken-symmetry open-shell state have been evaluated. For TA1^{++} , large disagreement (about 4000 cm^{-1} in the lowest excitation energy) between calculated and experimental spectra for the triplet state is observed. The latter is thus excluded from further consideration. Computed spectra for the restricted closed shell and the unrestricted broken-symmetry open-shell state agree both well with experiment. However, as the broken-symmetry state is below the closed-shell state by about 10 kJ mol^{-1} at the computational level employed, an antiferromagnetically coupled open-shell singlet is the most likely ground state for this dication. For the broken-symmetry state, the intense lowest-energy transition corresponds to a HOMO-1→HOMO transition much as in the

monocation, with good agreement to experiment (see Table 8.3 and ref. [48]). The analogy of dication and monocation is even more evident for **TA2⁺⁺**. Here again the triplet state can be ruled out for the dication, and the open-shell singlet state is favored based on the lower energy of the antiferromagnetically broken-symmetry state (9 kJ mol⁻¹, see Figure 8.2), and on the excellent agreement of computed and experimental transitions (see Table 8.3 and ref. [48]). The lowest-energy transition is again due to a HOMO-1→HOMO excitation much at the same energy as in the monocation but with distinctly higher intensity. The dication **TACN1⁺⁺** behaves essentially analogously, the broken-symmetry state is favored by about 11 kJ mol⁻¹, and the experimental transitions are reproduced well (Table 8.3 and ref. [48]).

The $\langle S^2 \rangle$ expectation values of the broken-symmetry states of the dianisylamine substituted squaraine dications **TA1⁺⁺** (0.783), **TA2⁺⁺** (0.837), and **TACN1⁺⁺** (0.886) indicate an almost equally weighted mixture of open-shell singlet and triplet character, consistent with the overall description of antiferromagnetic coupling between the amine radical cation units.

For **TA3⁺** the calculation predicts a transition at 3300 cm⁻¹. The single experimental absorption, where this transition could be assigned, is at 6600 cm⁻¹ and therefore the underestimate is much more pronounced than for the other compounds. The absence of a transition at such low energy can be excluded, because the same spectroelectrochemical experiment additionally was carried out in deuterated chloroform from 3125 to 40000 cm⁻¹ since in this solvent the IR region is much less disturbed by solvent bands. The spectra were identical to those measured in DCM which attests the nonexistence of an absorption at lower energy.^[48]

For reasons discussed above, spectra of **TA3** are only available for the trication but not for the dication. For **TA3⁺⁺⁺**, the system may adopt a doublet or a quartet state. While the doublet seems to be the favored state based on its lower energy, a quartet state or mixtures of both cannot definitely be ruled out as the quartet is only 3 kJ mol⁻¹ higher in energy. The $\langle S^2 \rangle$ expectation value (1.75) of the doublet also indicates a broken-symmetry state, whereas the quartet (3.79) is close to a pure state. In both cases, the agreement of calculated transitions with experiment is satisfactory (Table 8.3 and ref. [48]).

8.4 Conclusions

The (electronic) structure of the neutral species, the mono-, di- and (in one case) trications of six squarylium dyes with additional electron donating amine redox centers have been investigated by (TD)-B₃LYP calculations. The results fit quite well with experimental data like cyclic voltammetry and spectroelectrochemistry. The combination of experimental and theoretical methods allows good characterization of these molecules. The unique feature of the DFT calculations is the reliable description of all possible spin states and the correct assignment of molecular orbitals to optical transitions. Comparison of calculated spectra with experimental ones enables the determination of the real spin state.

As expected, all squaraine monocations turned out to be delocalized Robin-Day class III species. Substitution of one squaric ring oxygen by a dicyanomethylene group alters the symmetry of the indolenine squaraine dyes which has direct impact on the excitation energies of the radical monocations. According to the large *N-N* distance of 26 bonds between the triarylamine redox centers, **TA₃⁺** would be characterized normally and intuitively as class II, especially if it is compared to **TAA1-10** (see chapter 3 and 4). Nevertheless, it is completely delocalized (as all other compounds too), obviously due to the strong π -conjugation effect of the squaraine bridge.

The electronic situation is much more complex for the dications: the energetically most stable, computed state of dianisylamine substituted squaraines is a broken symmetry state and can better be described as a mixture of almost equal contributions of open shell singlet and triplet state. Thus, the true ground state is likely an antiferromagnetically coupled open-shell singlet.

Finally, the first oxidation steps are well reproduced by spin-density distributions and facilitate a detailed view on the CV spectra. They also support the class III character of all monocations and enable visualizations where the oxidations take place.

Chapter 9

Some physicists would prefer to come back to the idea of an objective real world whose smallest parts exist objectively in the same sense as stones or trees exist independently of whether we observe them.

This, however, is impossible.

-- Werner Heisenberg

9 Summary and Outlook

This work gave new insights into the quantum chemical description of mixed-valence compounds. Since systematic studies have been lacking so far, the first task in this work was the derivation of a quantum chemical protocol (see chapter 3), which was developed based on a set of four bis-triarylamine radical cations (**TAA1-4**) close to the class II/III borderline. Due to the well-known failures of DFT and HF (see chapter 2) in the description of charge localization/delocalization, the amount of exact-exchange admixture in a hybrid functional was scaled in order to reproduce experimental Robin-Day classifications and properties, especially IV-CT energies. In addition, a strikingly large influence of solvent polarity on the positioning of such organic MV radical cations along the Robin-Day classification coordinate has been found. The combination of ground-state structure optimizations (leading to dipole moments, bond lengths and ET barriers) with the comparison of computed IV-CT excitation energies to experimental transition energies provided an unprecedentedly detailed classification and characterization. In the end, a simple,

practical protocol for reliable calculations on organic MV systems, based on hybrid functionals with about 35% exact-exchange admixture together with suitable dielectric-continuum solvent models (COSMO/CPCM) has been proposed.

This protocol has been validated for a larger number of compounds in chapter 4, including ten cationic bis-triarylamine radical cations (**TAA1-10**) and seven neutral perchlorotriphenylmethyl-triarylamine radicals (**TAA11-17**). The performance of the protocol for the newly included cationic radicals **TAA5-10** is comparable to the reference molecular test set (**TAA1-4**) in chapter 3. Both ground-state properties and IV-CT bands are reproduced quite well. Again, inclusion of a continuum solvent model, especially for the polar solvents DCM and MeCN, provides an accurate description of the localized class II *vs.* delocalized class III character of these MV systems. However, the limits of the suggested protocol are probed by compound **TAA8**, which is so close to the class II/III borderline, that experimentally a change of solvent from MeCN to DCM switches the situation from class II to class III. The ground-state properties (e.g. dipole moments) of the neutral radicals **TAA11-17** are well characterized by the suggested protocol. In contrast, the lowest excitation energies are overestimated by about 2000-3500 cm⁻¹ when using 35% exact-exchange admixture. A reduction to 30% brings computations into better agreement with experimental transition energies.

The study of the six paracyclophane-bridged bis-triarylaminines **PC1-6** follows another question since all belong to the Robin-Day class II (chapter 5). Here, the paracyclophane-bridge is a model system for an intermolecular ET between separated units, i.e. in π -stacked molecular aggregates. Two pathways of the ET are possible: through space (π - π) or through bond (σ). In order to answer this question, the hypothetical dimer **PC2a** (where the linkers have been removed) was studied by a slightly modified protocol including dispersion corrections. In the end, the DFT calculations on **PC2** and the non-bridged dimer **PC2a** favored the through space mechanism. Nevertheless, more detailed evaluation on this topic has to be done in future. In addition, experimental ET barriers, optical transitions, π - π -distances and HFCs were well reproduced by the protocol.

An extensive study has been performed for the dinitroaromatic radical anions **DN1-6** in chapter 6. First of all, the exposed negative charge at the oxygen atoms caused the use of a larger basis set (TZVP *vs.* SVP). The small size of the molecules also facilitated a detailed investigation of common density functionals. Again, the protocol (BLYP35/TZVP/CPCM) led to a reliable description (e.g. ET-barriers, IV-CT energies) of these radical anions in polar solvents. Comparable results have been obtained with the BMK functional, whereas other hybrid functionals (e.g. Mo5, Mo5-2X), even if these were long-range corrected (e.g. LC-BLYP, ω B97X), performed worse. The main reason for this behavior is the “wrong” amount of HF admixture in these hybrid functionals, causing an overlocalization or too delocalized structures. However, the limit of this protocol was reached when MV compounds in protic solvents were studied. The protocol was thus refined by a solvent model (D-COSMO-RS) that also deals with specific solvent effects, especially hydrogen bonding. Among other things, this approach allowed the description of symmetry breaking of **DN1** when going from polar aprotic solvents like MeCN to protic solvents like MeOH.

The improved protocol (BLYP35/TZVP/D-COSMO-RS) was also able to remarkably predict the localized/delocalized character and the corresponding properties (especially ET barriers) of four mixed-valence diquinone radical anions **DQ1-4** in mixtures of protic and aprotic solvents (chapter 7). In case of aprotic, but polar solvents, the “classical” protocol using CPCM or COSMO yielded almost the same results. In contrast to other studies, that are using constrained DFT to force the localization, the given protocol based on hybrid functionals with 35% (BLYP35) or 42% (BMK) exact-exchange admixture combined with a suitable solvent model gave the right answer, essentially for the right reason.

Finally, the electronic structure of the neutral species, the mono-, di- and (in one case) trications of six squarylium dyes with additional electron donating amine redox centers (**SQ1**, **CN1**, **TA1-3**, **TACN1**) have been investigated by (TD)-DFT calculations. In contrast to the previous chapters, the BLYP35 functional was replaced by the B3LYP functional, which gave better results for these strongly coupled systems. In combination with experimental data, the (TD)-B3LYP/COSMO calculations were able to describe all possible spin states and identified a broken-symmetry state to be the ground state for the di- and

trications. The first oxidation steps (by CV) have been well reproduced by spin-density distributions and gave new insight was achieved about the location of the oxidations.

In future, the present quantum chemical protocol will be extended to further classes of organic mixed-valence systems since it has demonstrated its scope, e.g. for the successful description of bulky bis-triarylamine radical cations or small dinitroaromatic anions. Its performance might also be evaluated for the equally important and even larger field of mixed-valence transition-metal complexes, mainly in combination with the D-COSMO-RS solvent model. Despite the good performance of the present protocol, the following points still leave room for further improvements: on the one hand, a reasonable balance between inclusion of dynamical and non-dynamical electron correlation and minimal self-interaction errors is necessary, since BLYP₃₅ somehow benefits from error cancellation and is not a proper functional for thermodynamics. Thus, improved generations of density functionals (e.g. local hybrid functionals) or accurate post-HF approaches may be envisioned in this case. On the other hand and even more importantly, an appropriate modeling of environmental effects is required and feasible, e.g. to compare with D-COSMO-RS calculations. For example, in viscous solvents, explicit solvent dynamics during electron transfer may be important close to the class II/III borderline, and ion-pairing as well as coordination of counter-ions by solvent molecules may also become relevant. Full *ab initio* MD simulations with subsequent thermochemical averaging could account for such effects, but remain costly. Nevertheless, such simulations will definitely be targets for further studies.

10 Bibliography

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12 Appendix

3. Chapter

Table S3.1. Computed dipole moments μ_o (in Debye, with the center of mass as the origin), ET barriers $\Delta H^\ddagger$ (in kJ mol⁻¹) and structural data (in Å) for **TAA-1** at different computational levels

%HF	environment	μ_o	$\Delta H^\ddagger$	bond lengths							
				C _{An} -N	N-C ₁	C ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₄ -C ₅	C ₅ -C ₆	C ₆ -C ₆
BLYP	<i>gas phase</i>	0.02	0.00	1.436	1.407	1.429	1.392	1.433	1.411	1.246	1.351
				1.436	1.407	1.429	1.392	1.433	1.411	1.246	1.351
	<i>hexane</i>	0.05	0.04	1.436	1.407	1.429	1.392	1.433	1.411	1.246	1.352
				1.436	1.407	1.429	1.392	1.433	1.411	1.246	1.352
	<i>DCM</i>	0.02	0.31	1.435	1.406	1.429	1.392	1.433	1.411	1.247	1.353
				1.435	1.406	1.429	1.392	1.433	1.411	1.247	1.353
	<i>MeCN</i>	0.04	0.45	1.435	1.406	1.429	1.392	1.433	1.412	1.247	1.353
				1.435	1.406	1.429	1.392	1.433	1.412	1.247	1.353
	<i>gas phase</i>	0.14	-0.01	1.429	1.391	1.423	1.382	1.424	1.406	1.235	1.351
				1.429	1.390	1.423	1.382	1.424	1.406	1.235	1.351
20	<i>hexane</i>	0.39	-0.03	1.429	1.390	1.423	1.382	1.424	1.406	1.235	1.351
				1.430	1.389	1.423	1.382	1.424	1.406	1.235	1.351
	<i>DCM</i>	0.39	0.19	1.428	1.390	1.423	1.382	1.424	1.407	1.235	1.352
				1.428	1.390	1.423	1.382	1.424	1.407	1.235	1.352
	<i>MeCN</i>	3.56	0.56	1.427	1.391	1.423	1.382	1.424	1.406	1.235	1.352
				1.430	1.389	1.423	1.382	1.424	1.407	1.235	1.352
30	<i>gas phase</i>	0.01	-0.03	1.427	1.381	1.421	1.377	1.420	1.402	1.230	1.349
				1.427	1.381	1.421	1.377	1.420	1.402	1.230	1.349
	<i>hexane</i>	0.02	0.00	1.427	1.380	1.421	1.377	1.420	1.402	1.231	1.349
				1.427	1.380	1.421	1.377	1.420	1.402	1.231	1.349
	<i>DCM</i>	5.03	0.15	1.424	1.382	1.421	1.377	1.421	1.403	1.230	1.351
				1.428	1.381	1.420	1.378	1.420	1.403	1.230	1.351
	<i>MeCN</i>	28.07	3.65	1.409	1.404	1.411	1.382	1.416	1.415	1.225	1.361
				1.430	1.387	1.416	1.383	1.414	1.415	1.226	1.361
35	<i>gas phase</i>	0.03	0.02	1.426	1.377	1.420	1.375	1.418	1.400	1.228	1.348
				1.426	1.377	1.420	1.375	1.418	1.400	1.228	1.348
	<i>hexane</i>	0.02	0.03	1.426	1.377	1.420	1.375	1.419	1.400	1.228	1.349
				1.426	1.377	1.420	1.375	1.419	1.400	1.228	1.349
	<i>DCM</i>	26.82	3.20	1.408	1.399	1.411	1.380	1.414	1.413	1.223	1.360
				1.428	1.385	1.414	1.381	1.411	1.414	1.223	1.360
	<i>MeCN</i>	29.89	7.21	1.406	1.403	1.409	1.381	1.413	1.417	1.222	1.363
				1.428	1.387	1.413	1.382	1.411	1.417	1.222	1.363
40	<i>gas phase</i>	0.03	0.00	1.425	1.372	1.419	1.372	1.417	1.398	1.227	1.347
				1.425	1.372	1.419	1.372	1.417	1.398	1.227	1.347
	<i>hexane</i>	0.06	0.03	1.426	1.371	1.419	1.372	1.417	1.397	1.227	1.347
				1.425	1.372	1.419	1.372	1.417	1.397	1.227	1.347
	<i>DCM</i>	29.33	6.08	1.404	1.401	1.407	1.379	1.411	1.415	1.219	1.363
				1.426	1.385	1.411	1.380	1.408	1.416	1.219	1.363
	<i>MeCN</i>	31.17	10.78	1.402	1.403	1.406	1.380	1.410	1.418	1.218	1.364
				1.426	1.386	1.411	1.381	1.408	1.418	1.219	1.364

Continued.

%HF	environment	μ_o	$\Delta H^\ddagger$	bond lengths							
				C _{At} -N	N-C ₁	C ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₄ -C ₅	C ₅ -C ₆	C ₆ -C ₆
50	<i>gas phase</i>	0.03	-0.01	1.425	1.362	1.418	1.367	1.415	1.392	1.224	1.343
				1.425	1.362	1.418	1.367	1.415	1.392	1.224	1.343
	<i>hexane</i>	19.34	0.16	1.412	1.377	1.413	1.370	1.413	1.401	1.219	1.354
				1.424	1.373	1.411	1.373	1.407	1.406	1.218	1.354
	<i>DCM</i>	31.24	13.27	1.422	1.383	1.407	1.378	1.403	1.418	1.213	1.366
				1.398	1.401	1.402	1.377	1.406	1.417	1.213	1.366
	<i>MeCN</i>	32.27	18.57	1.397	1.402	1.401	1.378	1.405	1.419	1.212	1.367
				1.422	1.382	1.407	1.379	1.403	1.419	1.213	1.367
	<i>gas phase</i>	0.04	-0.01	1.423	1.355	1.417	1.362	1.413	1.387	1.221	1.340
				1.423	1.355	1.417	1.362	1.413	1.387	1.221	1.340
60	<i>hexane</i>	26.42	4.72	1.401	1.384	1.405	1.370	1.406	1.408	1.210	1.361
				1.420	1.375	1.405	1.373	1.400	1.413	1.210	1.361
	<i>DCM</i>	31.89	20.90	1.393	1.398	1.398	1.374	1.401	1.418	1.207	1.367
				1.419	1.379	1.403	1.375	1.398	1.418	1.208	1.367
	<i>MeCN</i>	32.75	25.92	1.393	1.398	1.398	1.375	1.400	1.419	1.207	1.368
				1.419	1.379	1.403	1.376	1.398	1.419	1.208	1.368
70	<i>gas phase</i>	22.09	1.90	1.418	1.368	1.403	1.368	1.397	1.407	1.208	1.355
				1.407	1.363	1.410	1.362	1.408	1.397	1.210	1.355
	<i>hexane</i>	28.24	11.19	1.397	1.381	1.401	1.368	1.402	1.409	1.205	1.363
				1.416	1.373	1.400	1.371	1.395	1.414	1.205	1.363
	<i>DCM</i>	32.17	28.46	1.429	1.388	1.423	1.381	1.425	1.403	1.236	1.350
				1.426	1.392	1.422	1.382	1.424	1.405	1.236	1.350
	<i>MeCN</i>	33.14	33.61	1.388	1.396	1.394	1.372	1.397	1.419	1.202	1.370
				1.415	1.376	1.399	1.373	1.394	1.419	1.203	1.370
80	<i>gas phase</i>	25.38	8.09	1.413	1.368	1.398	1.367	1.392	1.410	1.203	1.359
				1.400	1.364	1.405	1.362	1.403	1.400	1.204	1.359
	<i>hexane</i>	29.13	18.92	1.393	1.378	1.399	1.366	1.399	1.409	1.201	1.365
				1.412	1.371	1.396	1.369	1.391	1.415	1.200	1.365
	<i>DCM</i>	32.23	36.90	1.412	1.372	1.396	1.370	1.390	1.418	1.199	1.369
				1.389	1.387	1.395	1.369	1.396	1.415	1.199	1.369
	<i>MeCN</i>	33.13	41.58	1.386	1.391	1.393	1.370	1.395	1.417	1.199	1.370
				1.412	1.374	1.395	1.370	1.390	1.419	1.199	1.370
90	<i>gas phase</i>	27.30	16.83	1.409	1.367	1.394	1.365	1.388	1.411	1.198	1.361
				1.394	1.366	1.401	1.362	1.400	1.401	1.200	1.361
	<i>hexane</i>	29.91	27.96	1.389	1.375	1.396	1.365	1.397	1.408	1.198	1.365
				1.409	1.370	1.393	1.366	1.387	1.414	1.197	1.365
	<i>DCM</i>	32.22	45.90	1.409	1.371	1.392	1.368	1.387	1.417	1.197	1.369
				1.386	1.380	1.394	1.366	1.395	1.413	1.198	1.369
	<i>MeCN</i>	33.04	51.29	1.384	1.384	1.392	1.367	1.393	1.415	1.196	1.369
				1.409	1.371	1.392	1.368	1.387	1.418	1.196	1.369
100	<i>gas phase</i>	28.37	27.37	1.406	1.367	1.391	1.363	1.385	1.410	1.195	1.361
				1.391	1.364	1.398	1.361	1.398	1.400	1.197	1.361
	<i>hexane</i>	30.21	39.35	1.387	1.371	1.396	1.363	1.395	1.405	1.196	1.364
				1.406	1.367	1.390	1.364	1.385	1.413	1.194	1.364
	<i>DCM</i>	32.32	57.48	1.405	1.369	1.390	1.365	1.385	1.415	1.194	1.367
				1.385	1.375	1.393	1.365	1.394	1.409	1.195	1.367
	<i>MeCN</i>	32.97	62.76	1.382	1.378	1.392	1.365	1.393	1.411	1.194	1.368
				1.406	1.368	1.389	1.366	1.384	1.416	1.193	1.368

Table S3.2. Computed dipole moments μ_o (in Debye, with the center of mass as the origin), ET barriers $\Delta H^\ddagger$ (in kJ mol⁻¹) and structural data (in Å) for **TAA2** at different computational levels.

%HF	environment	μ_o	$\Delta H^\ddagger$	bond lengths						
				C _{An} -N	N-C ₁	C ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₄ -C ₅	C ₅ -C ₅
BLYP	<i>gas phase</i>	0.02	-0.01	1.435	1.408	1.428	1.392	1.432	1.414	1.239
				1.435	1.408	1.428	1.392	1.432	1.414	1.239
	<i>hexane</i>	0.04	0.00	1.435	1.408	1.428	1.392	1.432	1.415	1.239
				1.435	1.408	1.428	1.392	1.432	1.415	1.239
	<i>DCM</i>	0.02	0.10	1.435	1.408	1.428	1.392	1.432	1.415	1.239
				1.435	1.408	1.428	1.393	1.432	1.416	1.239
	<i>MeCN</i>	0.03	0.12	1.435	1.408	1.428	1.393	1.432	1.416	1.239
				1.435	1.408	1.428	1.393	1.432	1.416	1.239
	<i>gas phase</i>	0.14	-0.02	1.429	1.391	1.422	1.382	1.423	1.408	1.230
				1.429	1.390	1.423	1.382	1.423	1.408	1.230
20	<i>hexane</i>	0.10	0.06	1.428	1.391	1.423	1.382	1.423	1.409	1.230
				1.428	1.391	1.423	1.382	1.423	1.408	1.230
	<i>DCM</i>	0.10	0.07	1.428	1.390	1.423	1.382	1.424	1.409	1.230
				1.428	1.390	1.423	1.382	1.424	1.409	1.230
	<i>MeCN</i>	1.39	0.15	1.428	1.390	1.423	1.382	1.424	1.409	1.230
				1.429	1.389	1.423	1.382	1.424	1.409	1.230
	<i>gas phase</i>	0.09	-0.01	1.427	1.382	1.421	1.377	1.420	1.404	1.226
				1.426	1.382	1.420	1.377	1.420	1.404	1.226
	<i>hexane</i>	0.08	0.05	1.427	1.381	1.421	1.377	1.420	1.404	1.226
				1.427	1.381	1.421	1.377	1.420	1.404	1.226
30	<i>DCM</i>	0.07	0.09	1.427	1.389	1.422	1.381	1.423	1.408	1.230
				1.426	1.389	1.422	1.381	1.422	1.407	1.230
	<i>MeCN</i>	0.27	0.18	1.427	1.380	1.422	1.377	1.421	1.403	1.227
				1.427	1.379	1.421	1.377	1.421	1.403	1.227
	<i>gas phase</i>	0.03	-0.01	1.426	1.377	1.420	1.374	1.418	1.402	1.224
				1.425	1.377	1.420	1.375	1.418	1.402	1.224
	<i>hexane</i>	1.25	-0.15	1.428	1.375	1.421	1.374	1.419	1.401	1.225
				1.425	1.377	1.420	1.374	1.419	1.401	1.225
	<i>DCM</i>	10.07	0.11	1.428	1.378	1.419	1.377	1.416	1.406	1.224
				1.421	1.380	1.419	1.374	1.419	1.403	1.224
35	<i>MeCN</i>	20.09	1.54	1.428	1.384	1.415	1.381	1.412	1.415	1.220
				1.412	1.393	1.413	1.378	1.416	1.412	1.220
	<i>gas phase</i>	0.04	-0.03	1.426	1.371	1.420	1.372	1.418	1.398	1.223
				1.426	1.371	1.420	1.372	1.417	1.398	1.223
	<i>hexane</i>	0.18	0.03	1.426	1.371	1.420	1.372	1.418	1.398	1.224
				1.426	1.371	1.420	1.372	1.418	1.398	1.224
	<i>DCM</i>	19.83	0.74	1.427	1.382	1.413	1.379	1.410	1.414	1.218
				1.410	1.390	1.412	1.376	1.414	1.410	1.218
	<i>MeCN</i>	23.30	3.40	1.426	1.385	1.412	1.380	1.408	1.418	1.216
				1.406	1.397	1.409	1.378	1.412	1.415	1.216
40	<i>gas phase</i>	0.01	-0.03	1.424	1.362	1.419	1.366	1.415	1.393	1.221
				1.425	1.362	1.419	1.366	1.415	1.393	1.221
	<i>hexane</i>	0.02	0.02	1.425	1.361	1.419	1.366	1.416	1.393	1.221
				1.425	1.361	1.419	1.366	1.416	1.393	1.221
	<i>DCM</i>	23.14	4.35	1.427	1.388	1.422	1.381	1.423	1.407	1.230
				1.427	1.388	1.422	1.381	1.423	1.407	1.230
	<i>MeCN</i>	25.48	7.54	1.422	1.383	1.407	1.378	1.403	1.420	1.210
				1.399	1.398	1.403	1.376	1.406	1.418	1.210
	<i>gas phase</i>	0.01	-0.03	1.424	1.362	1.419	1.366	1.415	1.393	1.221
				1.425	1.362	1.419	1.366	1.415	1.393	1.221
	<i>hexane</i>	0.02	0.02	1.425	1.361	1.419	1.366	1.416	1.393	1.221
				1.425	1.361	1.419	1.366	1.416	1.393	1.221
50	<i>DCM</i>	23.14	4.35	1.427	1.388	1.422	1.381	1.423	1.407	1.230
				1.427	1.388	1.422	1.381	1.423	1.407	1.230
	<i>MeCN</i>	25.48	7.54	1.422	1.383	1.407	1.378	1.403	1.420	1.210
				1.399	1.398	1.403	1.376	1.406	1.418	1.210
	<i>gas phase</i>	0.01	-0.03	1.424	1.362	1.419	1.366	1.415	1.393	1.221
				1.425	1.362	1.419	1.366	1.415	1.393	1.221
	<i>hexane</i>	0.02	0.02	1.425	1.361	1.419	1.366	1.416	1.393	1.221
				1.425	1.361	1.419	1.366	1.416	1.393	1.221
	<i>DCM</i>	23.14	4.35	1.427	1.388	1.422	1.381	1.423	1.407	1.230
				1.427	1.388	1.422	1.381	1.423	1.407	1.230
	<i>MeCN</i>	25.48	7.54	1.422	1.383	1.407	1.378	1.403	1.420	1.210
				1.399	1.398	1.403	1.376	1.406	1.418	1.210

Continued.

%HF	environment	μ_o	$\Delta H^\ddagger$	bond lengths						
				C _{An} -N	N-C ₁	C ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₄ -C ₅	C ₅ -C ₅
60	<i>gas phase</i>	0.12	0.01	1.423	1.355	1.417	1.362	1.413	1.388	1.219
				1.423	1.355	1.417	1.362	1.413	1.388	1.219
	<i>hexane</i>	0.16	0.08	1.423	1.354	1.417	1.361	1.413	1.388	1.219
				1.423	1.355	1.417	1.362	1.413	1.388	1.219
	<i>DCM</i>	25.17	8.54	1.426	1.389	1.422	1.381	1.423	1.407	1.230
				1.427	1.388	1.422	1.381	1.422	1.407	1.230
	<i>MeCN</i>	26.22	12.01	1.418	1.381	1.402	1.376	1.398	1.421	1.206
				1.394	1.395	1.399	1.373	1.402	1.418	1.206
70	<i>gas phase</i>	0.18	0.05	1.421	1.348	1.415	1.357	1.411	1.383	1.217
				1.421	1.348	1.415	1.357	1.411	1.383	1.217
	<i>hexane</i>	18.33	1.76	1.419	1.366	1.404	1.368	1.398	1.408	1.207
				1.407	1.362	1.410	1.362	1.408	1.399	1.207
	<i>DCM</i>	25.82	13.17	1.427	1.388	1.422	1.381	1.423	1.407	1.230
				1.426	1.389	1.422	1.381	1.423	1.407	1.230
	<i>MeCN</i>	26.35	17.02	1.416	1.376	1.399	1.373	1.394	1.420	1.201
				1.392	1.390	1.397	1.371	1.398	1.417	1.201
80	<i>gas phase</i>	13.92	0.43	1.416	1.358	1.403	1.363	1.398	1.398	1.208
				1.412	1.344	1.414	1.354	1.410	1.387	1.208
	<i>hexane</i>	20.58	5.69	1.416	1.365	1.399	1.367	1.393	1.411	1.202
				1.401	1.362	1.406	1.361	1.403	1.402	1.202
	<i>DCM</i>	25.76	18.44	1.413	1.372	1.396	1.370	1.390	1.419	1.198
				1.389	1.383	1.396	1.368	1.397	1.414	1.198
	<i>MeCN</i>	26.67	22.20	1.412	1.375	1.395	1.370	1.390	1.420	1.198
				1.388	1.386	1.395	1.369	1.396	1.416	1.198
90	<i>gas phase</i>	17.52	4.31	1.412	1.360	1.398	1.362	1.392	1.403	1.202
				1.407	1.342	1.411	1.354	1.406	1.390	1.202
	<i>hexane</i>	23.04	12.30	1.410	1.367	1.394	1.366	1.388	1.413	1.197
				1.392	1.367	1.400	1.362	1.399	1.405	1.197
	<i>DCM</i>	25.74	24.94	1.410	1.369	1.393	1.368	1.387	1.418	1.195
				1.387	1.377	1.395	1.365	1.395	1.412	1.195
	<i>MeCN</i>	26.73	28.56	1.408	1.373	1.392	1.368	1.387	1.419	1.195
				1.387	1.380	1.394	1.366	1.394	1.414	1.195
100	<i>gas phase</i>	21.40	11.84	1.407	1.363	1.392	1.362	1.386	1.408	1.196
				1.393	1.356	1.401	1.358	1.399	1.398	1.196
	<i>hexane</i>	23.98	20.39	1.405	1.367	1.390	1.364	1.386	1.412	1.194
				1.389	1.366	1.397	1.361	1.396	1.404	1.194
	<i>DCM</i>	26.06	33.29	1.406	1.369	1.390	1.366	1.385	1.416	1.193
				1.385	1.373	1.394	1.364	1.394	1.410	1.193
	<i>MeCN</i>	26.84	37.07	1.405	1.371	1.389	1.366	1.385	1.416	1.193

Table S3.3. Computed dipole moments μ_o (in Debye, with the center of mass as the origin), ET barriers $\Delta H^\ddagger$ (in kJ mol⁻¹) and structural data (in Å) for **TAA3** at different computational levels.

%HF	environment	μ_o	$\Delta H^\ddagger$	bond lengths					
				C _{Ar} -N	N-C ₁	C ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₄ -C ₄
BLYP	<i>gas phase</i>	0.02	0.00	1.434	1.410	1.425	1.394	1.429	1.478
				1.434	1.410	1.425	1.394	1.429	1.478
	<i>hexane</i>	0.01	0.00	1.434	1.409	1.426	1.394	1.429	1.478
				1.434	1.409	1.426	1.394	1.429	1.478
	<i>DCM</i>	0.01	0.19	1.434	1.409	1.426	1.394	1.429	1.478
				1.434	1.409	1.426	1.394	1.430	1.478
	<i>MeCN</i>	0.05	0.33	1.434	1.409	1.426	1.394	1.429	1.478
				1.434	1.409	1.426	1.394	1.430	1.478
	<i>gas phase</i>	0.10	-0.02	1.427	1.392	1.420	1.384	1.422	1.466
				1.428	1.391	1.420	1.383	1.422	1.466
20	<i>hexane</i>	0.19	0.04	1.427	1.392	1.420	1.384	1.422	1.466
				1.428	1.391	1.420	1.383	1.422	1.466
	<i>DCM</i>	0.36	0.23	1.427	1.391	1.420	1.383	1.423	1.465
				1.428	1.390	1.421	1.383	1.423	1.465
	<i>MeCN</i>	0.80	0.30	1.428	1.390	1.421	1.383	1.423	1.464
				1.429	1.389	1.421	1.383	1.423	1.464
	<i>gas phase</i>	0.02	-0.02	1.426	1.382	1.418	1.378	1.420	1.459
				1.426	1.382	1.418	1.378	1.420	1.459
	<i>hexane</i>	0.04	0.10	1.426	1.382	1.418	1.378	1.420	1.458
				1.426	1.382	1.418	1.378	1.420	1.458
30	<i>DCM</i>	0.27	0.27	1.426	1.381	1.419	1.378	1.421	1.457
				1.426	1.381	1.419	1.378	1.421	1.457
	<i>MeCN</i>	0.08	0.42	1.427	1.380	1.419	1.377	1.421	1.456
				1.427	1.380	1.419	1.377	1.421	1.456
	<i>gas phase</i>	0.032	-0.0052	1.425	1.377	1.417	1.375	1.419	1.455
				1.425	1.377	1.417	1.375	1.419	1.455
	<i>hexane</i>	0.0304	0.07916	1.426	1.376	1.418	1.375	1.419	1.454
				1.426	1.376	1.418	1.375	1.419	1.454
	<i>DCM</i>	0.05	0.29	1.426	1.375	1.419	1.375	1.420	1.452
				1.426	1.375	1.419	1.374	1.420	1.452
35	<i>MeCN</i>	6.34	0.39	1.427	1.379	1.416	1.377	1.417	1.455
				1.421	1.380	1.417	1.375	1.419	1.455
	<i>gas phase</i>	0.19	-0.31	1.424	1.372	1.416	1.372	1.417	1.451
				1.425	1.373	1.417	1.373	1.417	1.451
	<i>hexane</i>	0.02	0.15	1.425	1.372	1.417	1.372	1.418	1.450
				1.425	1.372	1.417	1.372	1.418	1.450
	<i>DCM</i>	0.17	0.80	1.425	1.372	1.417	1.372	1.419	1.449
				1.425	1.372	1.418	1.372	1.419	1.449
	<i>MeCN</i>	13.28	0.72	1.426	1.381	1.412	1.379	1.410	1.459
				1.414	1.383	1.413	1.375	1.415	1.459
40	<i>gas phase</i>	0.04	0.04	1.424	1.363	1.416	1.367	1.417	1.443
				1.424	1.362	1.416	1.367	1.417	1.443
	<i>hexane</i>	0.09	0.07	1.424	1.362	1.416	1.367	1.417	1.442
				1.424	1.362	1.416	1.367	1.417	1.442
	<i>DCM</i>	0.12	0.74	1.425	1.361	1.417	1.367	1.418	1.440
				1.425	1.361	1.417	1.366	1.418	1.440
	<i>MeCN</i>	18.07	2.27	1.423	1.381	1.406	1.379	1.403	1.465
				1.405	1.388	1.406	1.374	1.408	1.465
	<i>gas phase</i>	0.04	0.04	1.424	1.363	1.416	1.367	1.417	1.443
				1.424	1.362	1.416	1.367	1.417	1.443
50	<i>hexane</i>	0.09	0.07	1.424	1.362	1.416	1.367	1.417	1.442
				1.424	1.362	1.416	1.367	1.417	1.442
	<i>DCM</i>	0.12	0.74	1.425	1.361	1.417	1.367	1.418	1.440
				1.425	1.361	1.417	1.366	1.418	1.440
	<i>MeCN</i>	18.07	2.27	1.423	1.381	1.406	1.379	1.403	1.465
				1.405	1.388	1.406	1.374	1.408	1.465

Continued.

%HF	state	μ_o	$\Delta H^\ddagger$	bond lengths					
				C _{AF} -N	N-C ₁	C ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₄ -C ₄
60	<i>gas phase</i>	0.04	-0.01	1.422	1.355	1.415	1.362	1.415	1.435
				1.422	1.355	1.415	1.362	1.415	1.435
	<i>hexane</i>	0.06	0.08	1.422	1.355	1.415	1.362	1.415	1.434
				1.423	1.354	1.415	1.362	1.415	1.434
	<i>DCM</i>	18.19	2.08	1.420	1.377	1.402	1.376	1.398	1.462
				1.401	1.384	1.403	1.371	1.405	1.462
	<i>MeCN</i>	19.16	4.41	1.419	1.379	1.402	1.377	1.398	1.465
				1.400	1.386	1.402	1.372	1.404	1.465
	<i>gas phase</i>	0.02	0.00	1.420	1.348	1.413	1.358	1.413	1.429
				1.420	1.348	1.413	1.358	1.413	1.429
70	<i>hexane</i>	0.02	0.08	1.420	1.348	1.413	1.358	1.414	1.428
				1.420	1.348	1.413	1.358	1.414	1.428
	<i>DCM</i>	18.33	4.39	1.399	1.377	1.401	1.368	1.402	1.460
				1.416	1.374	1.399	1.373	1.395	1.460
	<i>MeCN</i>	19.69	6.99	1.416	1.377	1.398	1.374	1.394	1.463
				1.396	1.382	1.399	1.369	1.400	1.463
80	<i>gas phase</i>	0.05	-0.02	1.418	1.342	1.411	1.354	1.412	1.423
				1.418	1.342	1.411	1.353	1.412	1.423
	<i>hexane</i>	9.20	0.54	1.416	1.356	1.403	1.361	1.404	1.434
				1.414	1.340	1.413	1.353	1.412	1.434
	<i>DCM</i>	18.88	7.01	1.412	1.373	1.394	1.371	1.392	1.459
				1.396	1.372	1.399	1.365	1.399	1.459
	<i>MeCN</i>	20.02	9.39	1.412	1.375	1.394	1.372	1.390	1.461
				1.393	1.378	1.396	1.367	1.398	1.461
90	<i>gas phase</i>	12.73	0.71	1.412	1.359	1.397	1.362	1.395	1.438
				1.405	1.345	1.407	1.355	1.406	1.438
	<i>hexane</i>	12.18	2.79	1.412	1.358	1.397	1.361	1.398	1.436
				1.411	1.336	1.411	1.352	1.409	1.436
	<i>DCM</i>	19.66	11.61	1.409	1.372	1.391	1.369	1.388	1.457
				1.391	1.371	1.396	1.364	1.397	1.457
	<i>MeCN</i>	19.94	11.78	1.407	1.374	1.390	1.369	1.391	1.458
				1.393	1.366	1.397	1.363	1.399	1.458
100	<i>gas phase</i>	15.45	5.34	1.407	1.361	1.392	1.362	1.390	1.442
				1.397	1.350	1.402	1.356	1.401	1.442
	<i>hexane</i>	16.85	8.87	1.406	1.364	1.391	1.364	1.391	1.446
				1.396	1.351	1.401	1.357	1.401	1.446
	<i>DCM</i>	19.87	17.84	1.405	1.370	1.389	1.367	1.387	1.453
				1.390	1.364	1.396	1.362	1.396	1.453
	<i>MeCN</i>	20.25	18.85	1.404	1.372	1.388	1.367	1.389	1.454
				1.389	1.363	1.395	1.362	1.397	1.454

Table S3.4. Computed dipole moments μ_o (in Debye, with the center of mass as the origin), ET barriers $\Delta H^\ddagger$ (in kJ mol⁻¹) and structural data (in Å) for **TAA4** at different computational levels.

%HF	state	μ_o	$\Delta H^\ddagger$	bond lengths			
				C _{An} -N	N-C ₁	C ₁ -C ₂	C ₂ -C ₂
BLYP	<i>gas phase</i>	0.03	-0.02	1.436	1.407	1.428	1.392
				1.435	1.407	1.428	1.392
	<i>hexane</i>	0.01	0.06	1.434	1.408	1.428	1.392
				1.435	1.407	1.428	1.392
	<i>DCM</i>	0.04	0.35	1.435	1.407	1.428	1.392
				1.435	1.407	1.428	1.392
	<i>MeCN</i>	0.01	0.44	1.435	1.407	1.428	1.392
				1.435	1.407	1.428	1.392
	<i>gas phase</i>	0.02	0.00	1.428	1.389	1.423	1.381
				1.428	1.390	1.422	1.381
20	<i>hexane</i>	0.01	0.04	1.428	1.389	1.423	1.381
				1.428	1.389	1.423	1.381
	<i>DCM</i>	0.02	0.22	1.428	1.388	1.423	1.380
				1.428	1.389	1.423	1.380
	<i>MeCN</i>	0.23	0.38	1.429	1.387	1.423	1.380
				1.428	1.389	1.423	1.380
30	<i>gas phase</i>	0.06	-0.03	1.426	1.380	1.421	1.376
				1.426	1.381	1.421	1.376
	<i>hexane</i>	0.02	0.10	1.426	1.380	1.421	1.375
				1.426	1.380	1.421	1.375
	<i>DCM</i>	0.13	0.18	1.427	1.378	1.421	1.375
				1.426	1.379	1.421	1.375
	<i>MeCN</i>	0.01	0.40	1.426	1.379	1.421	1.375
				1.426	1.379	1.421	1.375
35	<i>gas phase</i>	0.03	-0.02	1.425	1.376	1.420	1.373
				1.425	1.376	1.420	1.373
	<i>hexane</i>	0.03	0.03	1.425	1.376	1.420	1.373
				1.425	1.376	1.420	1.373
	<i>DCM</i>	0.03	0.24	1.425	1.375	1.421	1.372
				1.425	1.375	1.420	1.372
	<i>MeCN</i>	0.01	0.41	1.426	1.374	1.421	1.372
				1.426	1.374	1.420	1.372
40	<i>gas phase</i>	0.16	-0.01	1.425	1.371	1.419	1.370
				1.424	1.372	1.419	1.370
	<i>hexane</i>	0.04	0.02	1.424	1.371	1.419	1.370
				1.424	1.371	1.419	1.370
	<i>DCM</i>	0.33	0.08	1.425	1.370	1.420	1.369
				1.423	1.371	1.419	1.369
	<i>MeCN</i>	0.02	0.46	1.424	1.370	1.420	1.369
				1.424	1.370	1.420	1.369
50	<i>gas phase</i>	0.01	0.03	1.422	1.364	1.417	1.365
				1.422	1.364	1.417	1.365
	<i>hexane</i>	0.01	0.11	1.422	1.363	1.418	1.365
				1.423	1.363	1.418	1.365
	<i>DCM</i>	0.08	0.24	1.422	1.363	1.418	1.364
				1.422	1.363	1.418	1.364
	<i>MeCN</i>	0.06	0.46	1.423	1.361	1.418	1.364
				1.423	1.361	1.418	1.364

Continued.

%HF	state	μ_o	$\Delta H^\ddagger$	bond lengths			
				C _{Am} -N	N-C ₁	C ₁ -C ₂	C ₂ -C ₂
60	<i>gas phase</i>	0.04	0.04	1.420	1.356	1.416	1.360
				1.420	1.356	1.416	1.360
	<i>hexane</i>	0.03	-0.03	1.422	1.354	1.417	1.360
				1.422	1.354	1.417	1.360
	<i>DCM</i>	0.09	0.19	1.421	1.355	1.416	1.360
				1.420	1.355	1.416	1.360
	<i>MeCN</i>	0.01	0.52	1.421	1.354	1.417	1.359
				1.421	1.354	1.417	1.359
	<i>gas phase</i>	0.02	0.01	1.419	1.349	1.415	1.356
				1.419	1.349	1.415	1.356
70	<i>hexane</i>	0.02	0.15	1.419	1.349	1.415	1.355
				1.419	1.349	1.415	1.355
	<i>DCM</i>	0.05	0.17	1.418	1.349	1.415	1.355
				1.418	1.349	1.415	1.355
	<i>MeCN</i>	0.02	0.66	1.419	1.347	1.415	1.354
				1.419	1.347	1.415	1.354
80	<i>gas phase</i>	0.04	0.03	1.416	1.343	1.413	1.352
				1.416	1.343	1.413	1.352
	<i>hexane</i>	0.01	0.11	1.417	1.342	1.413	1.351
				1.417	1.342	1.413	1.351
	<i>DCM</i>	0.05	0.45	1.416	1.342	1.413	1.351
				1.416	1.342	1.413	1.351
	<i>MeCN</i>	0.03	0.75	1.417	1.342	1.414	1.350
				1.417	1.342	1.413	1.350
90	<i>gas phase</i>	0.05	0.01	1.414	1.337	1.411	1.348
				1.414	1.337	1.411	1.348
	<i>hexane</i>	0.03	0.12	1.414	1.337	1.411	1.347
				1.414	1.337	1.411	1.347
	<i>DCM</i>	0.08	0.55	1.414	1.337	1.411	1.347
				1.414	1.337	1.411	1.347
	<i>MeCN</i>	0.06	0.80	1.414	1.336	1.412	1.346
				1.415	1.336	1.412	1.346
100	<i>gas phase</i>	0.09	0.01	1.411	1.333	1.409	1.344
				1.412	1.333	1.410	1.344
	<i>hexane</i>	0.08	0.08	1.411	1.332	1.410	1.344
				1.411	1.333	1.409	1.344
	<i>DCM</i>	0.06	0.72	1.411	1.333	1.409	1.343
				1.411	1.333	1.409	1.343
	<i>MeCN</i>	0.01	1.02	1.412	1.332	1.410	1.343
				1.412	1.332	1.410	1.343
HF	<i>gas phase</i>	8.43	6.95	1.429	1.373	1.418	1.378
				1.414	1.380	1.417	1.378
	<i>hexane</i>	9.47	9.41	1.428	1.378	1.416	1.380
				1.412	1.384	1.415	1.380
	<i>DCM</i>	11.07	14.28	1.424	1.386	1.414	1.383
				1.409	1.390	1.414	1.383
	<i>MeCN</i>	11.44	15.05	1.424	1.388	1.414	1.384
				1.408	1.390	1.414	1.384

Table S3.5. TDDFT results (Go3, CPCM) for **TAA1**. Lowest three excitation energies E (in cm^{-1}) and transition dipole moments μ_t (in Debye)

structures (ground state)	solvent TDDFT	C ₁		C _i		C ₁		C _i		C ₁		C _i	
		E ₁	μ _{t,1}	E ₁	μ _{t,1}	E ₂	μ _{t,2}	E ₂	μ _{t,2}	E ₃	μ _{t,3}	E ₃	μ _{t,3}
% HF TDDFT													
30% HF in DCM													
30	DCM	4445	24.3	4318	25.2	11664	1.7	11576	0.0	15285	4.1	15571	0.0
	MeCN	4867	22.4	4513	24.4	11936	2.8	11692	0.0	15179	4.4	15633	0.0
35	DCM	4652	23.3	3837	27.4	12116	3.1	11706	0.0	15775	4.6	16396	0.0
	MeCN	5563	20.0	4070	26.4	12612	3.9	11829	0.0	15633	4.8	16466	0.0
40	DCM	5664	20.2	3163	30.9	12902	3.8	11825	0.0	16269	4.9	17272	0.0
	MeCN	3567	28.6	3462	29.3	11984	1.3	11956	0.0	17041	3.5	17351	0.0
30% HF in MeCN													
30	DCM	5756	15.9	4430	24.9	12881	4.5	11583	0.0	14547	6.2	15639	0.0
	MeCN	6598	13.9	4622	24.2	13500	4.6	11701	0.0	14540	6.2	15710	0.0
35	DCM	6913	14.0	3968	27.0	13823	4.4	11735	0.0	14873	6.3	16492	0.0
	MeCN	7856	12.5	4197	26.1	14448	4.2	11861	0.0	14863	6.3	16571	0.0
40	DCM	8259	12.7	3327	30.3	14796	3.6	11880	0.0	15220	6.4	17316	0.0
	MeCN	9223	11.6	3616	28.8	15203	6.3	12014	0.0	15404	3.2	17443	0.0
35% HF in DCM													
30	DCM	5668	16.3	4655	24.5	12848	4.6	11676	0.0	14616	6.1	15814	0.0
	MeCN	6511	14.3	4843	23.8	13453	4.7	11789	0.0	14612	6.1	15882	0.0
35	gas phase	4962	21.0	5865	20.9	11568	1.4	12018	0.0	15100	2.4	16210	0.0
	DCM	6800	14.4	4230	26.3	13760	4.5	11874	0.0	14955	6.2	16715	0.0
40	MeCN	7752	12.8	4451	25.4	14376	4.3	11996	0.0	14950	6.2	16791	0.0
	DCM	8134	13.0	3646	29.0	14716	3.9	12072	0.0	15315	6.3	17222	0.0
40	MeCN	9112	11.8	3920	27.8	15279	5.2	12201	0.0	15347	4.9	17343	0.0
35% HF in MeCN													
30	DCM	5760	15.5	4711	24.4	12997	4.8	11699	0.0	14564	6.2	15882	0.0
	MeCN	6627	13.5	4897	23.7	13616	4.8	11814	0.0	14562	6.2	15950	0.0
35	DCM	6969	13.6	4294	26.2	13937	4.6	11910	0.0	14883	6.3	16792	0.0
	MeCN	7930	12.1	4512	25.3	14557	4.4	12032	0.0	14880	6.3	16871	0.0
40	DCM	8360	12.2	3725	28.8	14900	4.0	12121	0.0	15224	6.4	17194	0.0
	MeCN	9339	11.2	3992	27.6	15216	6.4	12251	0.0	15499	3.4	17317	0.0
40% HF in DCM													
30	DCM	5841	15.1	4701	24.3	13102	4.7	11756	0.0	14588	6.3	15900	0.0
	MeCN	6744	13.2	4889	23.7	13754	4.8	11867	0.0	14588	6.3	15963	0.0
35	DCM	7066	13.3	4280	26.2	14064	4.6	11963	0.0	14899	6.4	16805	0.0
	MeCN	8062	11.9	4501	25.3	14709	4.5	12081	0.0	14903	6.3	16878	0.0
40	DCM	8466	12.0	3705	28.8	15037	4.1	12168	0.0	15235	6.4	17284	0.0
	MeCN	9479	11.0	3979	27.6	15227	6.4	12293	0.0	15665	3.4	17400	0.0
40% HF in MeCN													
30	DCM	5897	14.7	4904	23.9	13185	4.8	11791	0.0	14566	6.3	16015	0.0
	MeCN	6813	12.8	5089	23.3	13845	4.9	11908	0.0	14573	6.3	16093	0.0
35	DCM	7161	12.9	4515	25.6	14160	4.7	12044	0.0	14870	6.4	16851	0.0
	MeCN	8164	11.5	4731	24.8	14801	4.9	12169	0.0	14887	6.1	16975	0.0
40	DCM	8590	11.6	3988	27.9	15126	4.7	12301	0.0	15208	6.0	17113	0.0
	MeCN	9607	10.7	4250	26.8	15197	6.5	12435	0.0	15762	3.5	17233	0.0

Table S3.6. TDDFT results (TBM5.10, COSMO) for **TAA1**. Lowest three excitation energies E (in cm^{-1}) and transition dipole moments μ_t (in Debye)

structures (ground state)	solvent TDDFT	C ₁		C _i		C ₁		C _i		C ₁		C _i	
		E ₁	μ _{t,1}	E ₁	μ _{t,1}	E ₂	μ _{t,2}	E ₂	μ _{t,2}	E ₃	μ _{t,3}	E ₃	μ _{t,3}
% HF TDDFT		E ₁	μ _{t,1}	E ₁	μ _{t,1}	E ₂	μ _{t,2}	E ₂	μ _{t,2}	E ₃	μ _{t,3}	E ₃	μ _{t,3}
30% HF in DCM													
30	DCM	5786	20.0	5761	20.3	12044	1.2	15659	4.4	15495	3.5	17408	1.6
	MeCN	5949	18.9	5749	20.3	12302	2.9	15704	4.4	15348	4.0	17421	1.6
35	DCM	5715	20.2	5511	21.3	12358	2.3	16476	4.2	16102	3.8	17869	1.3
	MeCN	6490	17.2	5500	21.4	12992	4.0	16535	4.2	15873	4.4	17887	1.3
40	DCM	6011	19.5	5182	22.6	12878	3.0	17343	4.1	16665	4.0	18332	0.9
	MeCN	7532	15.4	5171	22.6	13849	4.0	17420	4.1	16442	4.5	18357	0.9
30% HF in MeCN													
30	DCM	6179	14.2	5861	20.2	12969	4.5	15707	4.3	15057	5.4	17264	1.5
	MeCN	7061	12.4	5850	20.2	13718	4.5	15752	4.3	14952	5.6	17276	1.5
35	DCM	7148	12.8	5623	21.2	13871	4.3	16551	4.1	15412	5.5	17739	1.2
	MeCN	8240	11.4	5613	21.2	14635	4.0	16608	4.1	15291	5.6	17755	1.3
40	DCM	8377	11.7	5309	22.4	14809	3.6	17448	4.0	15782	5.6	18221	0.9
	MeCN	9554	10.6	5300	22.5	15532	3.1	17525	4.0	15657	5.6	18246	0.9
35% HF in DCM													
30	DCM	6144	14.6	6060	19.9	12965	4.5	15862	4.1	15112	5.3	17097	1.3
	MeCN	6997	12.7	6050	20.0	13688	4.6	15912	4.1	15007	5.5	17111	1.4
35	gas phase	4962	20.9	5868	20.9	11571	1.5	16360	4.0	15094	2.4	17475	1.0
	DCM	7084	13.1	5844	20.9	13844	4.4	16754	4.0	15491	5.4	17601	1.1
40	MeCN	8157	11.6	5836	20.9	14585	4.2	16821	3.9	15361	5.6	17622	1.1
	DCM	8286	12.0	5556	22.0	14757	3.8	17699	3.8	15870	5.5	18123	1.0
40	MeCN	9475	10.8	5548	22.0	15493	3.2	17783	3.8	15744	5.6	18151	1.0
35% HF in MeCN													
30	DCM	6148	13.9	6110	19.9	13089	4.6	15927	4.0	15081	5.4	17064	1.3
	MeCN	7079	11.9	6101	19.9	13860	4.7	15977	4.0	14985	5.6	17078	1.3
35	DCM	7182	12.3	5899	20.8	14008	4.6	16834	3.9	15439	5.6	17575	1.1
	MeCN	8315	10.9	5892	20.8	14774	4.2	16900	3.9	15318	5.7	17597	1.1
40	DCM	8459	11.3	5618	21.9	14932	3.9	17793	3.7	15794	5.6	18106	1.0
	MeCN	9674	10.2	5611	22.0	15642	4.6	17879	3.7	15692	4.6	18136	1.0

Table S3.7. TDDFT results (Go3, CPCM) for **TAA2**. Lowest three excitation energies E (in cm^{-1}) and transition dipole moments μ_t (in Debye)

structures (ground state)	solvent TDDFT	C ₁		C _i		C ₁		C _i		C ₁		C _i	
		E ₁	μ _{t,1}	E ₁	μ _{t,1}	E ₂	μ _{t,2}	E ₂	μ _{t,2}	E ₃	μ _{t,3}	E ₃	μ _{t,3}
% HF TDDFT													
35% HF in DCM													
30	DCM	5693	19.8	5653	20.6	13174	1.4	13046	0.0	15961	4.3	16623	0.0
	MeCN	6048	18.8	5862	20.0	13407	1.8	13158	0.0	15947	4.4	16759	0.0
35	gas phase	6440	18.2	6646	18.1	13264	0.5	13387	0.0	16554	2.6	16862	0.0
	DCM	5745	19.9	5356	21.6	13657	1.7	13340	0.0	16558	4.4	17577	0.0
	MeCN	6310	18.4	5593	21.0	13998	2.1	13461	0.0	16496	4.5	17727	0.0
	DCM	6137	19.1	4972	22.9	14322	1.9	13639	0.0	17109	4.6	18574	4.2
	MeCN	6925	17.4	5247	22.2	14767	2.1	13768	0.0	17026	4.7	18741	0.0
35% HF in MeCN													
30	DCM	5849	17.6	5643	20.6	13508	2.8	13047	0.0	15294	5.4	16637	0.0
	MeCN	6432	16.1	5850	20.1	13945	3.1	13158	0.0	15289	5.5	16771	0.0
35	DCM	6450	16.5	5345	21.6	14278	2.9	13339	0.0	15708	5.5	17590	0.0
	MeCN	7204	15.0	5580	21.0	14790	3.1	13458	0.0	15692	5.6	17738	0.0
40	DCM	7359	15.2	4959	23.0	15186	2.8	13635	0.0	16125	5.7	18586	4.2
	MeCN	8205	13.9	5231	22.2	15731	2.8	13763	0.0	16111	5.7	18751	0.0
40% HF in DCM													
30	DCM	5955	17.4	5807	20.3	13602	2.8	13144	0.0	15350	5.4	16774	0.0
	MeCN	6521	16.0	6014	19.8	14028	3.0	13260	0.0	15337	5.5	16914	0.0
35	gas phase	5979	18.2	6791	17.9	12985	1.2	13488	0.0	15927	2.3	17018	0.0
	DCM	6561	16.3	5530	21.3	14388	2.9	13465	0.0	15765	5.5	17752	0.0
	MeCN	7289	14.9	5764	20.7	14887	3.0	13589	0.0	15740	5.6	17906	0.0
	DCM	7460	15.1	5171	22.5	15305	2.8	13792	0.0	16184	5.7	18773	4.1
	MeCN	8278	13.9	5440	21.8	15835	2.8	13925	0.0	16160	5.6	18945	0.0
40% HF in MeCN													
30	DCM	6014	16.3	5943	20.1	13766	3.2	13165	0.0	15142	5.7	16855	0.0
	MeCN	6646	14.8	6149	19.6	14249	3.4	13282	0.0	15147	5.8	16997	0.0
35	DCM	6800	15.0	5685	21.0	14642	3.2	13514	0.0	15504	5.9	17860	0.0
	MeCN	7569	13.7	5918	20.5	15178	3.3	13640	0.0	15504	5.9	18015	0.0
40	DCM	7848	13.8	5350	22.2	15620	3.1	13873	0.0	15878	6.0	18905	4.0
	MeCN	8679	12.7	5615	21.5	15871	6.0	14008	0.0	16179	2.9	19079	0.0

Table S3.8. TDDFT results (TBM5.10, COSMO) for **TAA2**. Lowest three excitation energies E (in cm^{-1}) and transition dipole moments μ_t (in Debye)

structures (ground state)	solvent TDDFT	C ₁		C _i		C ₁		C _i		C ₁		C _i	
		E ₁	μ _{t,1}	E ₁	μ _{t,1}	E ₂	μ _{t,2}	E ₂	μ _{t,2}	E ₃	μ _{t,3}	E ₃	μ _{t,3}
% HF TDDFT													
35% HF in DCM													
30	DCM	7028	17.2	6947	17.3	13431	0.0	16633	4.0	16661	2.1	18669	1.1
	MeCN	7057	17.2	6976	17.3	13495	0.0	16758	4.0	16792	2.3	18719	1.1
35	gas phase	6731	18.0	6648	18.1	13406	0.0	16863	4.1	16890	3.8	18966	0.9
	DCM	6889	17.8	6798	17.9	13766	0.0	17574	3.9	17617	2.8	19261	1.0
	MeCN	6924	17.8	6832	17.9	13838	0.0	17721	3.9	17766	2.7	19323	1.0
	DCM	6699	18.5	6597	18.7	14110	0.0	18563	3.7	18620	2.9	19870	0.9
	MeCN	6741	18.5	6638	18.6	14190	0.0	18733	3.7	18788	2.7	19944	0.9
35% HF in MeCN													
30	DCM	6762	15.2	6939	17.3	13741	2.9	16632	4.1	15645	4.7	18682	1.1
	MeCN	7214	14.1	6967	17.3	14215	3.2	16757	4.0	15551	4.9	18733	1.1
35	DCM	7229	14.5	6789	17.9	14476	3.1	17575	3.9	16097	4.9	19276	1.0
	MeCN	7922	13.3	6823	17.9	15050	3.1	17721	3.9	15980	5.0	19337	1.0
40	DCM	7988	13.6	6588	18.7	15343	2.9	18563	3.8	16542	5.0	19884	0.9
	MeCN	8866	12.5	6630	18.6	15984	2.8	18730	3.7	16418	5.1	19956	1.0
40% HF in DCM													
30	DCM	6838	15.1	7086	17.2	13807	2.9	16779	4.0	15696	4.7	18668	1.1
	MeCN	7297	14.0	7115	17.1	14292	3.2	16910	3.9	15602	4.9	18724	1.1
35	gas phase	5766	18.8	6581	18.7	13293	1.3	17936	3.9	16879	2.3	19543	0.8
	DCM	7311	14.4	6950	17.8	14558	3.0	17747	3.8	16146	4.9	19278	1.0
	MeCN	8018	13.2	6985	17.7	15156	3.1	17898	3.8	16036	5.0	19344	1.0
	DCM	8095	13.5	6765	18.5	15461	2.9	18762	3.7	16595	5.0	19905	0.9
	MeCN	8941	12.4	6806	18.4	16083	2.8	18932	3.6	16466	5.1	19981	1.0
40% HF in MeCN													
30	DCM	6768	14.3	7206	17.0	13942	3.2	16835	3.9	15554	5.0	18528	0.9
	MeCN	7346	13.0	7237	17.0	14519	3.5	16969	3.8	15467	5.2	18585	0.9
35	DCM	7407	13.4	7085	17.6	14784	3.3	17828	3.7	15952	5.2	19150	0.9
	MeCN	8219	12.1	7123	17.6	15450	3.3	17985	3.7	15846	5.3	19220	0.9
40	DCM	8332	12.4	6919	18.2	15738	3.1	18871	3.6	16351	5.3	19793	0.8
	MeCN	9277	11.4	6963	18.2	16229	5.4	19047	3.5	16432	2.9	19875	0.9

Table S3.9. TDDFT results (Go3, CPCM) for **TAA3**. Lowest three excitation energies E (in cm^{-1}) and transition dipole moments μ_t (in Debye)

structures (ground state)	solvent TDDFT	C_1		C_i		C_1		C_i		C_1		C_i	
		E_1	$\mu_{t,1}$	E_1	$\mu_{t,1}$	E_2	$\mu_{t,2}$	E_2	$\mu_{t,2}$	E_3	$\mu_{t,3}$	E_3	$\mu_{t,3}$
% HF TDDFT													
35% HF in DCM													
30	DCM	6843	16.9	6760	16.9	14832	0.0	14850	0.0	17472	4.4	17405	4.5
	MeCN	7065	16.5	6987	16.5	14958	0.0	14983	0.0	17659	4.3	17609	4.4
35	gas phase	7544	17.5	7469	15.3	15048	0.0	15083	0.0	17385	4.2	17334	0.0
	DCM	6653	17.5	6561	17.5	15264	0.0	15266	0.0	18447	4.2	18367	4.3
	MeCN	6898	17.0	6811	17.1	15400	0.0	15408	0.0	18643	4.1	18577	4.2
	40	DCM	6405	18.2	6299	18.3	15703	0.0	15688	0.0	19427	4.0	19335
	MeCN	6678	17.7	6579	17.8	15847	0.0	15839	0.0	19607	3.7	19530	3.8
50% HF in MeCN													
30	DCM	6790	14.6	7642	15.9	15121	2.3	15158	0.0	15867	5.3	18018	4.0
	MeCN	7264	13.7	7866	15.5	15515	2.5	15318	0.0	15910	5.3	18235	3.9
35	gas phase	6583	15.0	8272	14.5	14158	1.6	15289	0.0	16014	2.1	17872	3.8
	DCM	7294	14.0	7541	16.3	15988	2.5	15719	0.0	16305	5.4	19093	3.8
	MeCN	7881	13.1	7785	15.9	16323	5.2	15889	0.0	16435	2.9	19314	3.7
	40	DCM	8033	13.3	7392	16.9	16733	5.4	16291	0.0	16934	2.5	20153
	MeCN	8699	12.5	7658	16.4	16767	5.5	16471	0.0	17373	2.4	20336	3.2

Table S3.10. TDDFT results (TBM5.10, COSMO) for **TAA3**. Lowest three excitation energies E (in cm^{-1}) and transition dipole moments μ_t (in Debye)

structures (ground state)	solvent TDDFT	C ₁		C _i		C ₁		C _i		C ₁		C _i	
		E ₁	μ _{t,1}	E ₁	μ _{t,1}	E ₂	μ _{t,2}	E ₂	μ _{t,2}	E ₃	μ _{t,3}	E ₃	μ _{t,3}
% HF TDDFT													
35% HF in DCM													
30	DCM	7573	14.8	7903	14.5	15069	0.4	17379	4.1	17063	3.3	20136	0.8
	MeCN	7640	14.7	7971	14.5	15154	0.5	17578	4.0	17189	3.2	20090	0.5
35	DCM	7450	15.3	7807	15.0	15458	0.4	18333	3.9	17896	3.2	20548	0.6
	MeCN	7533	15.2	7883	14.9	15554	0.5	18546	3.8	18020	3.2	20458	0.7
40	DCM	7293	15.8	7667	15.5	15858	0.5	19299	3.7	18733	3.1	20898	0.9
	MeCN	7424	15.6	7754	15.4	15982	0.6	19515	3.5	18800	3.1	20811	1.2
35% HF in MeCN													
30	DCM	7519	14.7	7932	14.5	15080	0.8	17408	4.0	16850	3.5	20133	0.8
	MeCN	7619	14.5	8000	14.4	15200	1.0	17609	4.0	16909	3.6	20089	0.5
35	DCM	7451	15.0	7839	14.9	15509	1.0	18369	3.9	17571	3.6	20549	0.6
	MeCN	7631	14.7	7916	14.9	15682	1.2	18584	3.8	17583	3.6	20460	0.7
40	DCM	7431	15.3	7703	15.4	15985	1.1	19339	3.7	18251	3.6	20901	0.9
	MeCN	7735	14.8	7788	15.3	16220	1.3	19551	3.5	18225	3.7	20816	1.2
50% HF in DCM													
30	DCM	8778	13.8	8678	13.8	15330	0.0	17933	3.6	18017	2.9	20065	1.1
	MeCN	8859	13.7	8757	13.7	15462	0.0	18157	3.5	18242	2.9	20161	1.1
35	DCM	8777	14.1	8664	14.1	15924	0.0	19003	3.5	19104	3.0	20733	1.0
	MeCN	8866	14.0	8752	14.1	16070	0.0	19242	3.4	19344	3.0	20755	0.6
40	DCM	8739	14.5	8613	14.5	16534	0.0	20077	3.2	20193	3.0	21234	0.7
	MeCN	8836	14.4	8709	14.4	16691	0.0	20298	3.0	20410	2.9	21192	1.1
50% HF in MeCN													
30	DCM	7649	12.7	8694	13.8	15235	2.4	17951	3.6	16170	4.7	20068	1.1
	MeCN	8053	12.1	8775	13.7	15718	2.6	18177	3.5	16133	4.8	20164	1.1
35	DCM	8101	12.3	8682	14.1	16110	2.5	19024	3.4	16630	4.8	20739	1.0
	MeCN	8661	11.6	8771	14.1	16558	4.7	19263	3.4	16660	2.9	20765	0.6
40	DCM	8775	11.8	8633	14.5	17032	3.5	20099	3.2	17109	4.2	21249	0.7
	MeCN	9466	11.1	8730	14.4	17014	5.0	20321	3.0	17614	2.4	21208	1.1

Table S3.11. TDDFT results (Go3, CPCM) for **TAA4**. Lowest three excitation energies E (in cm^{-1}) and transition dipole moments μ_t (in Debye)

<i>structures</i> (ground state)	<i>solvent</i> TDDFT	C_1		C_i		C_1		C_i		C_1		C_i	
% HF TDDFT		E_1	$\mu_{t,1}$	E_1	$\mu_{t,1}$	E_2	$\mu_{t,2}$	E_2	$\mu_{t,2}$	E_3	$\mu_{t,3}$	E_3	$\mu_{t,3}$
35% HF in DCM													
0	DCM	9838	8.8	9819	8.7	13642	4.5	13632	4.5	13747	0.0	13731	0.0
20	MeCN	9950	11.0	9906	11.0	16721	5.2	16680	5.3	16876	0.2	16826	0.0
	DCM	10125	10.8	10080	10.8	16895	5.1	16851	5.2	17044	0.1	16992	0.0
30	MeCN	10113	11.4	10054	11.4	18526	5.0	18468	5.1	18661	0.3	18601	0.0
	DCM	10305	11.2	10244	11.1	18719	4.9	18658	4.9	18835	0.1	18777	0.0
35	gas phase	10580	10.4	10526	10.4	18500	4.6	18450	4.7	18641	0.0	18590	0.0
	MeCN	10145	11.6	10078	11.5	19410	0.5	19394	4.9	19461	4.8	19438	0.0
	DCM	10345	11.3	10277	11.3	19540	0.0	19566	0.0	19659	4.7	19590	4.8
40	MeCN	10136	11.8	10060	11.8	20006	0.1	20033	0.0	20397	4.7	20324	4.8
	DCM	10345	11.5	10269	11.5	20134	0.0	20157	0.0	20599	4.5	20524	4.6

Table S3.12. TDDFT results (Go3, IEFPCM) for **TAA4**. Lowest three excitation energies E (in cm^{-1}) and transition dipole moments μ_t (in Debye)

<i>structures</i> (<i>ground state</i>)	<i>solvent</i> <i>TDDFT</i>	C_1		C_1		C_1	
% HF TDDFT		E_1	$\mu_{t,1}$	E_2	$\mu_{t,2}$	E_3	$\mu_{t,3}$
35% HF in DCM							
30	DCM	10157	11.3	18461	4.9	18598	0.2
35	DCM	10192	11.4	19390	4.7	19402	1.0
40	DCM	10187	11.6	20006	0.0	20322	4.6

Table S3.13. TDDFT results (TBM5.10, COSMO) for **TAA4**. Lowest three excitation energies E (in cm^{-1}) and transition dipole moments μ_t (in Debye)

structures (ground state)	solvent TDDFT	C_1		C_i		C_1		C_i		C_1		C_i	
		E_1	$\mu_{t,1}$	E_1	$\mu_{t,1}$	E_2	$\mu_{t,2}$	E_2	$\mu_{t,2}$	E_3	$\mu_{t,3}$	E_3	$\mu_{t,3}$
% HF TDDFT		E_1	$\mu_{t,1}$	E_1	$\mu_{t,1}$	E_2	$\mu_{t,2}$	E_2	$\mu_{t,2}$	E_3	$\mu_{t,3}$	E_3	$\mu_{t,3}$
30% HF in DCM													
30	DCM	10732	10.2	10658	10.2	18403	4.4	18355	4.6	18537	0.9	23735	0.5
	MeCN	10818	10.1	10742	10.1	18594	4.3	18547	4.5	18724	1.1	23864	0.5
35	DCM	10783	10.4	10699	10.4	19299	4.1	19251	4.5	19409	1.4	24679	0.5
	MeCN	10873	10.3	10788	10.3	19498	3.9	19455	4.4	19577	1.7	24820	0.5
40	DCM	10795	10.5	10701	10.6	20063	0.3	20153	4.3	20202	3.8	25628	0.9
	MeCN	10890	10.5	10794	10.5	20183	0.2	20361	4.2	20400	3.5	25764	1.1
30% HF in MeCN													
30	DCM	10738	10.2	10748	10.1	18420	4.5	18394	4.5	18539	0.1	23772	0.5
	MeCN	10824	10.1	10834	10.1	18614	4.5	18588	4.5	18723	0.1	23901	0.5
35	DCM	10788	10.4	10798	10.3	19321	4.4	19291	4.4	19401	0.2	24714	0.5
	MeCN	10879	10.3	10891	10.3	19532	4.3	19506	4.4	19573	0.3	24862	0.5
40	DCM	10801	10.5	10814	10.5	20071	0.0	20209	4.3	20235	4.2	25670	1.0
	MeCN	10896	10.5	10909	10.4	20190	0.0	20422	4.2	20448	4.1	25806	1.1
35% HF in DCM													
30	DCM	10953	10.1	10898	10.1	18578	4.4	18524	4.5	18702	0.0	23928	0.5
	MeCN	11043	10.0	10985	10.0	18778	4.4	18719	4.5	18890	0.0	24060	0.5
35	DCM	11027	10.2	10965	10.2	19501	4.3	19442	4.4	19526	0.1	24886	0.5
	MeCN	11120	10.2	11057	10.2	19660	0.0	19649	4.3	19709	4.3	25027	0.5
40	DCM	11064	10.4	10994	10.4	20146	0.0	20364	4.2	20427	4.2	25841	1.0
	MeCN	11160	10.4	11090	10.4	20265	0.0	20578	4.2	20638	4.1	25977	1.2
35% HF in MeCN													
30	DCM	11052	10.0	11024	10.0	18634	4.4	18575	4.5	18760	0.1	23978	0.5
	MeCN	11144	10.0	11115	9.9	18835	4.3	18774	4.4	18945	0.1	24110	0.5
35	DCM	11139	10.2	11107	10.1	19519	0.1	19507	4.3	19569	4.3	24941	0.5
	MeCN	11235	10.1	11203	10.1	19647	0.0	19717	4.3	19780	4.2	25082	0.5
40	DCM	11186	10.4	11153	10.3	20127	0.0	20442	4.2	20498	4.1	25893	1.0
	MeCN	11288	10.3	11252	10.3	20262	0.0	20659	4.1	20726	4.0	26026	1.2
40% HF in MeCN													
30	DCM	11221	9.9	11125	10.0	18717	4.0	18702	4.4	18892	1.6	24127	0.5
	MeCN	11315	9.9	11215	9.9	18906	3.8	18899	4.4	19051	1.5	24258	0.5
35	DCM	11329	10.1	11216	10.1	19566	0.9	19645	4.3	19660	3.7	25098	0.5
	MeCN	11428	10.0	11313	10.1	19701	0.4	19859	4.2	19857	3.6	25244	0.5
40	DCM	11399	10.2	11269	10.3	20198	0.1	20580	4.1	20568	3.4	26051	1.0
	MeCN	11500	10.2	11369	10.2	20327	0.1	20799	4.1	20760	3.2	26188	1.2
40% HF in DCM													
30	DCM	11224	9.9	11248	9.9	18778	4.4	18751	4.4	18891	0.0	24172	0.5
	MeCN	11319	9.9	11343	9.8	18983	4.3	18951	4.3	19062	0.0	24305	0.5
35	DCM	11329	10.1	11356	10.0	19610	0.0	19704	4.3	19737	4.2	25149	0.6
	MeCN	11428	10.0	11455	10.0	19737	0.0	19918	4.2	19949	4.2	25292	0.5
40	DCM	11397	10.2	11427	10.2	20234	0.0	20659	4.1	20687	4.1	26105	1.1
	MeCN	11500	10.2	11530	10.1	20366	0.0	20881	4.0	20910	4.0	26237	1.3

4. Chapter

Table S4.1. Calculated ground state parameters (total dipole moment μ_o in Debye, ET barrier $\Delta H^\ddagger$, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ in Debye) and ^{14}N -HFCs in MHz for **TAA1**

TAA1	μ_o^a	$\Delta H^\ddagger$	$\langle S^2 \rangle$	$d_1(\text{C}_{\text{Ar}}\text{-N})$ $d_2(\text{C}_{\text{Ar}}\text{-N})$	E_i		$\mu_{t,i}$		$a_{\text{N}1}/a_{\text{N}2}$	
					C ₁	C _i	C ₁	C _i	C ₁	C _i
35% HF in gas phase										
	0.03	0.0	0.78	1.426	5705	5738	21.05	21.00	11.20	11.17
				1.426					11.20	11.17
35% HF in hexane										
	0.02	0.0	0.78	1.426	4189	4234	26.17	26.07	11.35	11.31
				1.426					11.32	11.31
35% HF in DCM										
	26.82	3.2	0.79	1.408	6800	4230	14.39	26.30	23.32	11.39
				1.428					1.67	11.39
35% HF in MeCN										
	29.89	7.2	0.79	1.406	7930	4512	12.13	25.30	24.19	11.40
									1.01	11.40

^a With the center of mass as the origin.**Table S4.2.** Calculated ground state parameters (total dipole moment μ_o in Debye, ET barrier $\Delta H^\ddagger$, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ in Debye) and ^{14}N -HFCs in MHz for **TAA2**

TAA2	μ_o^a	$\Delta H^\ddagger$	$\langle S^2 \rangle$	$d_i(\text{C}_{\text{Ar-N}})$ $d_2(\text{C}_{\text{Ar-N}})$	E_i		$\mu_{t,i}$		$a_{\text{N1}}/a_{\text{N2}}$	
					C ₁	C _i	C ₁	C _i	C ₁	C _i
35% HF in gas phase										
	0.03	0.0	0.77	1.426	6481	6512	18.29	18.25	11.97	11.93
				1.425					11.91	11.93
35% HF in hexane										
	1.25	0.2	0.77	1.428	5276	5199	21.61	21.79	11.38	11.96
				1.425					12.45	11.96
35% HF in DCM										
	10.07	0.1	0.78	1.421	5745	5356	19.86	21.61	16.95	11.88
				1.428					7.21	11.88
35% HF in MeCN										
	20.09	1.5	0.78	1.412	7204	5580	14.98	21.02	22.40	11.85
				1.428					2.90	11.85

^a With the center of mass as the origin.

Table S4.3. Calculated ground state parameters (total dipole moment μ_o in Debye, ET barrier $\Delta H^\ddagger$, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ in Debye) and ^{14}N -HFCs in MHz for **TAA3**

TAA3	μ_o^a	$\Delta H^\ddagger$	$\langle S^2 \rangle$	$d_1(\text{C}_{\text{Ar}}\text{-N})$ $d_2(\text{C}_{\text{Ar}}\text{-N})$	E_i		$\mu_{i,1}$		$a_{\text{N}1}/a_{\text{N}2}$	
					C ₁	C _i	C ₁	C _i	C ₁	C _i
35% HF in gas phase										
	0.05	0.0	0.77	1.426	7544	7206	15.24	15.58	12.89	13.16
				1.426					12.84	13.16
35% HF in hexane										
	0.03	0.1	0.77	1.426	6277	6289	17.88	17.85	13.05	13.03
				1.426					13.01	13.03
35% HF in DCM										
	0.05	0.3	0.77	1.426	6653	6561	17.48	17.55	12.89	12.87
				1.426					12.84	12.87
35% HF in MeCN										
	6.34	0.4	0.77	1.421	6527	6848	17.05	17.03	16.48	12.79
				1.427					9.34	12.79

^a With the center of mass as the origin.

Table S4.4. Calculated ground state parameters (total dipole moment μ_o in Debye, ET barrier $\Delta H^\ddagger$, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ in Debye) and ^{14}N -HFCs in MHz for **TAA4**

TAA4	μ_o^a	$\Delta H^\ddagger$	$\langle S^2 \rangle$	$d_1(\text{C}_{\text{Ar}}\text{-N})$ $d_2(\text{C}_{\text{Ar}}\text{-N})$	E_i		$\mu_{t,i}$		$a_{\text{N}1}/a_{\text{N}2}$	
					C ₁	C _i	C ₁	C _i	C ₁	C _i
35% HF in gas phase										
	0.03	0.0	0.77	1.425	10417	10385	10.54	10.56	16.36	16.30
				1.425					16.29	16.30
35% HF in hexane										
	0.03	0.0	0.77	1.425	9718	9559	11.76	11.84	16.38	16.24
				1.425					16.32	16.24
35% HF in DCM										
	0.03	0.2	0.77	1.425	10145	10078	11.55	11.54	16.33	16.26
				1.425					16.33	16.26
35% HF in MeCN										
	0.01	0.4	0.77	1.426	10473	10437	11.27	11.22	16.36	16.27
				1.426					16.34	16.27

^a With the center of mass as the origin.

Table S4.5. Calculated ground state parameters (total dipole moment μ_o in Debye, ET barrier $\Delta H^\ddagger$, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ and dipole moments μ_i in brackets in Debye) and ^{14}N -HFCs in MHz for **TAA5**

TAA5	μ_o [μ_i] ^a	$\Delta H^\ddagger$	$\langle S^2 \rangle$	$d_i(\text{C}_{\text{Ar-N}})$ $d_2(\text{C}_{\text{Ar-N}})$	E_i		$\mu_{t,i}$		$a_{\text{N1}}/a_{\text{N2}}$	
					C ₁	C _i	C ₁	C _i	C ₁	C _i
35% HF in gas phase										
	0.31	0.0	0.77	1.423	4145	4156	25.56	25.56	10.42	10.42
				1.423					10.51	10.42
35% HF in hexane										
	0.10	0.0	0.77	1.423	2473	2504	34.64	34.54	10.60	10.53
				1.423					10.54	10.53
35% HF in DCM										
	40.15	10.0	0.79	1.406	6969	2421	10.62	35.46	24.40	10.58
	[-34.56]			1.426					0.30	10.58
35% HF in MeCN										
	42.09	15.6	0.79	1.405	8351	2654	9.15	33.49	24.60	10.72
	[-32.13]			1.426					0.20	10.72

^a With the center of mass as the origin.**Table S4.6.** Calculated ground state parameters (total dipole moment μ_o in Debye, ET barrier $\Delta H^\ddagger$, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ and dipole moments μ_i in brackets in Debye) and ^{14}N -HFCs in MHz for **TAA6**

TAA6	μ_o [μ_i] ^a	$\Delta H^\ddagger$	$\langle S^2 \rangle$	$d_i(\text{C}_{\text{Ar-N}})$ $d_2(\text{C}_{\text{Ar-N}})$	E_i		$\mu_{t,i}$		$a_{\text{N1}}/a_{\text{N2}}$	
					C ₁	C _i	C ₁	C _i	C ₁	C _i
35% HF in gas phase										
	0.06	0.0	0.77	1.424	4422	4390	25.27	25.30	9.86	9.90
				1.424					9.84	9.90
35% HF in hexane										
	0.38	0.0	0.77	1.424	2796	2693	33.38	33.61	9.93	10.04
				1.424					9.92	10.04
35% HF in DCM										
	38.93	4.8	0.79	1.407	6828	2537	11.60	34.74	24.04	10.14
	[-33.49] ^a			1.426					0.36	10.14
35% HF in MeCN										
	41.24	10.3	0.79	1.405	8150	2847	9.81	32.78	24.60	10.19
	[-31.42] ^a			1.426					0.24	10.19

^a With the center of mass as the origin.

Table S4.7. Calculated ground state parameters (total dipole moment μ_o in Debye, ET barrier $\Delta H^\ddagger$, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and d_2 in Å), excited state parameters (excitation energies E_{ab} in cm^{-1} and transition moments $\mu_{t,1}$ and dipole moments μ_1 in brackets in Debye) and ^{14}N -HFCs in MHz for **TAA7**

TAA7	$\mu_o [\mu_1]^a$	$\Delta H^\ddagger$	$\langle S^2 \rangle$	$d_1(\text{C}_{\text{Ar}}\text{-N})$ $d_2(\text{C}_{\text{Ar}}\text{-N})$	E_t		$\mu_{t,1}$		$a_{\text{N}1}/a_{\text{N}2}$	
					C_1	C_i	C_1	C_i	C_1	C_i
35% HF in gas phase										
	0.13	0.1	0.77	1.427 1.426	5123	5153	23.83	23.78	8.44 8.59	8.48 8.48
35% HF in hexane										
	0.19	0.1	0.77	1.427 1.427	3841	3942	29.19	28.85	8.34 8.46	8.19 8.19
35% HF in DCM										
	35.21 [-30.51] ^a	3.1	0.79	1.412 1.425	6000	3969	15.66	28.82	22.38 0.81	7.88 7.88
35% HF in MeCN										
	40.02 [-29.60] ^a	8.4	0.79	1.408 1.425	7436	4184	12.04	27.86	24.20 0.30	7.81 7.81

^a With the center of mass as the origin.

Table S4.8. Calculated ground state parameters (total dipole moment μ_o in Debye, ET barrier $\Delta H^\ddagger$, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and d_2 in Å), excited state parameters (excitation energies E_t in cm^{-1} and transition moments $\mu_{t,1}$ and dipole moments μ_1 in brackets in Debye) and ^{14}N -HFCs in MHz for **TAA8**

TAA8	$\mu_o [\mu_1]^a$	$\Delta H^\ddagger$	$\langle S^2 \rangle$	$d_1(\text{C}_{\text{Ar}}\text{-N})$ $d_2(\text{C}_{\text{Ar}}\text{-N})$	E_i		$\mu_{t,1}$		$a_{\text{N}1}/a_{\text{N}2}$	
					C_1	C_i	C_1	C_i	C_1	C_i
35% HF in gas phase										
	0.03	0.0	0.78	1.430 1.429	6260	6294	19.48	19.39	6.56 6.57	6.54 6.54
35% HF in hexane										
	0.03	0.1	0.78	1.430 1.430	5624	5644	22.85	22.78	6.27 6.31	6.27 6.27
35% HF in DCM										
	0.04 [0.19] ^a	0.3	0.78	1.430 1.429	5881	5844	22.27	22.36	5.86 5.87	5.89 5.89
35% HF in MeCN										
	0.05 [0.73] ^a	0.5	0.78	1.430 1.430	6127	6054	21.40	21.57	5.69 5.69	5.73 5.73

^a With the center of mass as the origin.

Table S4.9. Calculated ground state parameters (total dipole moment μ_o in Debye, ET barrier $\Delta H^\ddagger$, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and d_2 in Å), excited state parameters (excitation energies E_1 in cm^{-1} and transition moments $\mu_{t,1}$ and dipole moments μ_1 in brackets in Debye) and ^{14}N -HFCs in MHz for **TAA9**

TAA9	μ_o [μ_i] ^a	$\Delta H^\ddagger$	$\langle S^2 \rangle$	$d_i(\text{C}_{\text{Ar}}\text{-N})$ $d_2(\text{C}_{\text{Ar}}\text{-N})$	E_i		$\mu_{t,i}$		$a_{\text{N}1}/a_{\text{N}2}$	
					C ₁	C _i	C ₁	C _i	C ₁	C _i
35% HF in gas phase										
	0.29	0.0	0.77	1.426	8296	8240	12.80	12.83	14.52	14.34
				1.424					14.04	14.34
35% HF in hexane										
	0.45	0.0	0.77	1.426	7523	7461	14.49	14.56	14.65	14.33
				1.424					13.93	14.33
35% HF in DCM										
	0.80	0.0	0.77	1.426	7891	7874	14.19	14.23	14.60	14.15
	[-1.61]			1.425					13.58	14.15
35% HF in MeCN										
	0.71	0.0	0.77	1.426	8065	8166	13.90	13.82	14.51	14.08
	[-1.44]			1.425					13.65	14.08

^a With the center of mass as the origin.**Table S4.10.** Calculated ground state parameters (total dipole moment μ_o in Debye, ET barrier $\Delta H^\ddagger$, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and d_2 in Å), excited state parameters (excitation energies E_1 in cm^{-1} and transition moments $\mu_{t,1}$ and dipole moments μ_1 in brackets in Debye) and ^{14}N -HFCs in MHz for **TAA10**

TAA10	μ_0 [μ_1] ^a	$\Delta H^\ddagger$	<S ² >	$d_1(\text{C}_{\text{Ar}}\text{-N})$ $d_2(\text{C}_{\text{Ar}}\text{-N})$	E_i		$\mu_{t,1}$		$a_{\text{N}1}/a_{\text{N}2}$	
					C ₁	C _i	C ₁	C _i	C ₁	C _i
35% HF in gas phase										
	0.12	0.2	0.78	1.429	7574	7432	16.33	16.51	11.20	11.25
				1.428					11.04	11.25
35% HF in hexane										
	0.15	0.1	0.78	1.429	6751	6689	18.75	18.83	11.05	11.00
				1.428					10.88	11.00
35% HF in DCM										
	0.06	0.3	0.77	1.429	7211	6959	18.18	18.50	10.45	10.58
	[0.05]			1.429					10.51	10.58
35% HF in MeCN										
	0.08	0.3	0.77	1.429	7661	7390	17.40	17.72	10.19	10.34
	[-0.10]			1.429					10.27	10.34

^a With the center of mass as the origin.**Table S4.11.** Calculated ground state parameters (total dipole moment μ_o in Debye, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and C-C bond lengths d_2 in Å), excited state parameters (excitation energies E_1 in cm^{-1} and transition moments $\mu_{t,1}$ in Debye) and ^{14}N - as well as ^{13}C -HFCs in MHz for **TAA11**

TAA11	μ_o	$\langle S^2 \rangle$	$d_1(\text{C}_{\text{Ar}}\text{-N})/d_2(\text{C}_{\text{Ar}}\text{-C})$	E_1^a	$\mu_{t,1}^a$	$a_{\text{N}}/a_{\text{C}}^b$
35% HF in gas phase						
	6.65	0.79	1.423	14774	3.56	0.20
			1.481	(13567)	(4.50)	97.22
35% HF in hexane						
	6.99	0.79	1.424	14539	4.18	0.22
			1.481	(13189)	(5.07)	97.15
35% HF in DCM						
	7.49	0.79	1.425	14392	4.42	0.24
			1.481	(12956)	(5.24)	96.90
35% HF in MeCN						
	7.64	0.79	1.426	14394	4.39	0.25
			1.481	(12940)	(5.19)	96.89

^a Values in parentheses with BLYP30 ($a = 0.3$) in TDDFT. ^b ^{13}C -HFC-constant of carbon atom in the center of the PCTM.

Table S4.12. Calculated ground state parameters (total dipole moment μ_0 in Debye, spin expectation values $\langle S^2 \rangle$ as well as C-N bond length d_1 and C-C bond lengths d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ in Debye) and ^{14}N - as well as ^{13}C -HFCs in MHz for **TAA12**

TAA12	μ_0	$\langle S^2 \rangle$	$d_1(\text{C}_{\text{Ar}}-\text{N})/d_2(\text{C}_{\text{Ar}}-\text{C})$	E_i^a	$\mu_{t,i}^a$	$a_{\text{N}}/a_{\text{C}}^b$
35% HF in gas phase	7.66	0.80	1.425	15232	4.43	0.33
			1.481	(14087)	(5.26)	96.45
35% HF in hexane	8.05	0.80	1.426	14904	5.18	0.36
			1.481	(13626)	(5.99)	96.36
35% HF in DCM	8.66	0.79	1.427	14782	5.33	0.43
			1.481	(13435)	(6.12)	96.45
35% HF in MeCN	8.86	0.80	1.428	14745	5.34	0.45
			1.481	(13390)	(6.12)	96.24

^a Values in parentheses with BLYP30 ($a = 0.3$) in TDDFT. ^b ^{13}C -HFC-constant of carbon atom in the center of the PCTM.

Table S4.13. Calculated ground state parameters (total dipole moment μ_0 in Debye, spin expectation values $\langle S^2 \rangle$, torsion angle of the biphenyl axis in degree as well as C-N bond length d_1 and C-C bond lengths d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ in Debye) for **TAA13**

TAA13	μ_0	$\langle S^2 \rangle$	torsion angle	$d_1(\text{C}_{\text{Ar}}-\text{N})/d_2(\text{C}_{\text{Ar}}-\text{C})$	E_i^a	$\mu_{t,i}^a$
35% HF in gas phase	3.13	0.79	69.9	1.422	16000	2.01
				1.481	(13899)	(2.09)
35% HF in hexane	3.16	0.79	69.8	1.423	15743	2.19
				1.481	(13628)	(2.29)
35% HF in DCM	3.05	0.79	71.4	1.423	15705	2.06
				1.480	(13562)	(2.15)
35% HF in MeCN	2.83	0.79	70.4	1.423	15596	2.13
				1.481	(13454)	(2.23)

^a Values in parentheses with BLYP30 ($a = 0.3$) in TDDFT.

Table S4.14. Calculated ground state parameters (total dipole moment μ_0 in Debye, spin expectation values $\langle S^2 \rangle$, torsion angle of the biphenyl axis in degree as well as C-N bond length d_1 and C-C bond lengths d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ in Debye) for **TAA14**

TAA14	μ_0	$\langle S^2 \rangle$	torsion angle	$d_1(\text{C}_{\text{Ar}}-\text{N})/d_2(\text{C}_{\text{Ar}}-\text{C})$	E_i^a	$\mu_{t,i}^a$
35% HF in gas phase	3.71	0.79	69.1	1.420	17120	2.08
				1.480	(15087)	(2.12)
35% HF in hexane	3.79	0.79	70.0	1.420	16735	2.15
				1.481	(14674)	2.21
35% HF in DCM ^b	3.94	0.79	69.4	1.421	16534	2.25
				1.480	(14463)	(2.32)
	3.73	0.79	90.0		16709	0.07
	4.28	0.79	50.0		14498	3.91
	4.44	0.79	30.0		15429	4.51
	4.02	0.79	10.0		15121	4.87
	3.87	0.79	72.7	1.421	16624	2.07
diastereomere ^c				1.481		
35% HF in MeCN	4.01	0.79	70.8	1.412	16545	2.10
				1.480	(14457)	(2.16)

^a Values in parentheses with BLYP30 ($a = 0.3$) in TDDFT. ^b The influence of the rotational angle of the biphenyl axis was investigated by single point calculations on the bases on the optimized structure, therefore no C-N/C-C distances are given. ^c The different diastereomere was also studied by the same procedure for DCM.

Table S4.15. Calculated ground state parameters (total dipole moment μ_0 in Debye, spin expectation values $\langle S^2 \rangle$, torsion angle of the biphenyl axis in degree as well as C-N bond length d_1 and C-C bond lengths d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ in Debye) for **TAA15**^a

TAA15	μ_0	$\langle S^2 \rangle$	torsion angle	$d_1(\text{C}_{\text{Ar}}\text{-N})^a/d_2(\text{C}_{\text{Ar}}\text{-C})$	E_i^b	$\mu_{t,i}^b$
35% HF in gas phase	2.96	0.79	70.4	1.415[1.422] 1.481	18158 (16094)	1.91 (1.92)
35% HF in hexane	3.10	0.79	71.9	1.414[1.422] 1.480	17743 (15646)	1.93 (1.95)
35% HF in DCM	3.33	0.79	72.6	1.414[1.423] 1.481	17471 (15351)	1.88 (1.91)
35% HF in MeCN	3.40	0.79	72.0	1.413[1.423] 1.480	17407 (15288)	1.92 (1.95)

^a Values in brackets is the other $\text{C}_{\text{Ar}}\text{-N}$ bond length. ^b Values in parentheses with BLYP30 ($a = 0.3$) in TDDFT.**Table S4.16.** Calculated ground state parameters (total dipole moment μ_0 in Debye, spin expectation values $\langle S^2 \rangle$, torsion angle of the biphenyl axis in degree as well as C-N bond length d_1 and C-C bond lengths d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ in Debye) for **TAA16**

TAA16	μ_0	$\langle S^2 \rangle$	torsion angle	$d_1(\text{C}_{\text{Ar}}\text{-N})/d_2(\text{C}_{\text{Ar}}\text{-C})$	E_i^a	$\mu_{t,i}^a$
35% HF in gas phase	0.48	0.79	72.8	1.417 1.480	19162 (17064)	1.69 (1.67)
35% HF in hexane	0.45	0.79	72.1	1.417 1.480	18674 (16568)	1.89 (1.88)
35% HF in DCM	0.35	0.79	73.6	1.417 1.480	18304 (16167)	1.78 (1.78)
35% HF in MeCN	0.30	0.79	74.5	1.417 1.480	18244 (16092)	1.66 (1.66)

^a Values in parentheses with BLYP30 ($a = 0.3$) in TDDFT.**Table S4.17.** Calculated ground state parameters (total dipole moment μ_0 in Debye, spin expectation values $\langle S^2 \rangle$, torsion angle of the biphenyl axis in degree as well as C-N bond length d_1 and C-C bond lengths d_2 in Å), excited state parameters (excitation energies E_i in cm^{-1} and transition moments $\mu_{t,i}$ in Debye) for **TAA17**^a

TAA17	μ_0^a	$\langle S^2 \rangle$	torsion angle	$d_1(\text{C}_{\text{Ar}}\text{-N})^b/d_2(\text{C}_{\text{Ar}}\text{-C})$	E_i^c	$\mu_{t,i}^c$
35% HF in gas phase	-4.10	0.79	71.6	1.421[1.405] 1.480	20799 (18906)	1.74 (1.74)
35% HF in hexane	-4.43	0.79	69.6	1.422[1.404] 1.480	20274 (18348)	2.07 (2.06)
35% HF in DCM	-5.18	0.79	73.6	1.423[1.400] 1.480	20095 (18031)	1.77 (1.70)
diastereomere ^d	-5.29	0.79	81.2	1.423[1.400] 1.480	20314	1.07
35% HF in MeCN	-5.54	0.79	79.5	1.422[1.398] 1.480	20281 (18118)	1.21 (1.13)

^a Negative sign means that it points in the opposite direction compared to **TAA11-16** (see Figure 4.7) ^b Values in brackets is the other $\text{C}_{\text{Ar}}\text{-N}$ bond length. ^c Values in parentheses with BLYP30 ($a = 0.3$) in TDDFT. ^d The different diastereomere was also studied by the same procedure for DCM.

5. Chapter

Table S5.1. Ground state properties (dipole moments μ_o in Debye, ET barriers $\Delta H^\ddagger$ in kJ mol^{-1} , distance $d_{\pi-\pi}$ and vertical displacement d_{dis} of the benzene rings as well as C-N bond lengths d and d' in Å, and torsion angle of the biphenyl axis α in $^\circ$)^a in different environments for **PC3**, **PC5** and **PC6**

	environment	μ_o^b	$\Delta H^\ddagger$	$d_{\pi-\pi}$	d_{dis}	$d(\text{C}_{\text{Ar}}-\text{N})$	$d'(\text{C}_{\text{Ar}}-\text{N})$	α
PC3	gas phase	0.05	0.0	3.19	0.34	1.410	1.410	44.6±0.1
	hexane	0.05	0.1	3.17	0.40	1.410	1.410	44.6±0.0
	DCM	34.14	17.8	3.20	0.24	1.416	1.400	44.8±1.2
	(DCM) ^c	(35.62)	(18.7)	(3.30)	(0.59)	(1.422)	(1.403)	(47.5±1.5)
	DCM, neutral ^d	0.31	-	3.30	0.63	1.420	1.420	51.1±0.4
	(DCM, neutral) ^{c,d}	(0.39)	-	(3.21)	(0.27)	(1.418)	(1.416)	(46.4±0.5)
	exp., neutral ^e	-	-	3.23	0.52	1.428	1.428	53.2±0.0
PC5	MeCN	34.98	23.3	3.20	0.27	1.416	1.400	44.8±1.1
	gas phase	0.02	-2.8	3.23	1.38	1.410	1.410	49.3±0.0
	hexane	1.32	0.0	3.26	1.36	1.409	1.408	51.3±0.0
	DCM	36.75	20.4	3.24	1.38	1.417	1.400	51.0±0.5
PC6	MeCN	37.52	26.3	3.24	1.38	1.417	1.400	51.3±0.1
	gas phase	0.09	0.0	3.28	1.16	1.416	1.417	-
	hexane	0.22	0.2	3.29	1.15	1.416	1.417	-
	DCM	41.00	15.1	3.80	0.59	1.419	1.404	-
	MeCN	42.28	21.2	3.83	0.60	1.420	1.402	-

^a Mean values of centroid and plane distances/displacements are given. The systematic errors in distance are <0.03 Å and in displacement <0.15 Å. ^b With the center of mass as the origin. ^c Values in parentheses calculated without dispersion corrections. ^d Neutral molecule in DCM. ^e Experimental values for neutral [3,3]paracyclophane from ref. [280].

Table S5.2. Calculated first three excitation energies and electronic coupling (E_n and $2H_{\text{ab}}$ in cm^{-1}) and transition dipole moments $\mu_{t,n}$ in Debye as well as ^{14}N - and ^1H -HFCs a in MHz for **PC1** in different environments

environment	$E_n(\text{C}_1)$	$2H_{\text{ab}}(\text{C}_i)$	$\mu_{t,n}(\text{C}_1)$	$\mu_{t,n}(\text{C}_i)$	$a(\text{N}^{(1)})$	$a(\text{H}^{(1)})$	$a(\text{H}^{(2)})$	$a(\text{H}^{(3)})$
gas phase	1507	1390	14.02	13.56	12.36	-1.04	0.99	-0.82
	9804	9933	6.14	6.21	12.25	-1.02	0.97	-0.79
	11079	11130	4.65	4.19				
hexane	652	604	23.65	23.03	12.60	-1.09	1.02	-0.84
	9908	10008	6.82	6.93	12.25	-1.04	0.99	-0.79
	11211	11276	4.4	3.94				
DCM	5916	516	2.04	26.96	26.33	-2.64	2.09	-2.63
	12714	10087	6.56	6.97	0.24	-0.07	0.09	0.00
	14102	11368	3.45	4.21				
MeCN	7205	739	1.51	22.52	26.67	-2.63	2.06	-2.57
	13328	10153	6.66	6.85	0.08	-0.08	0.09	-0.04
	14853	11408	2.66	4.22				

Table S5.3. Calculated first three excitation energies and electronic coupling (E_n and $2H_{ab}$ in cm^{-1}) and transition dipole moments $\mu_{t,n}$ in Debye as well as ^{14}N - and ^1H -HFCs a in MHz for **PC2** in different environments

environment	$E_n (C_i)$	$2H_{ab} (C_i)$	$\mu_{t,n} (C_i)$	$\mu_{t,n} (C_i)$	$a (N^{(i)})$	$a (H^{(i)}_1)$	$a (H^{(i)}_2)$	$a (H^{(i)}_3)$
gas phase	1794	1781	18.08	18.04	11.16	-0.90	0.74	-0.87
	9041	9029	10.82	10.84	11.16	-0.91	0.75	-0.89
	9901	10865	0.12	1.88				
hexane	811	808	29.82	29.81	11.41	-0.93	0.76	-0.87
	9172	9179	11.05	10.98	11.29	-0.92	0.75	-0.85
	9709	9714	0.26	0.00				
DCM	6560	635	2.13	33.41	0.15	-0.11	0.10	0.23
	11826	9678	9.54	10.53	24.73	-2.91	1.98	-3.64
	14497	10105	1.92	0				
MeCN	7956	868	1.78	28.39	25.21	-2.86	1.92	-3.49
	12439	9879	9.11	10.24	0.06	-0.11	0.10	0.17
	15113	10268	6.38	0				

Table S5.4. Calculated first three excitation energies and electronic coupling (E_n and $2H_{ab}$ in cm^{-1}) and transition dipole moments $\mu_{t,n}$ in Debye as well as ^{14}N - and ^1H -HFCs a in MHz for **PC3** in different environments

environment	$E_n (C_i)$	$2H_{ab} (C_i)$	$\mu_{t,n} (C_i)$	$\mu_{t,n} (C_i)$	$a (N^{(i)})$	$a (H^{(i)}_1)$	$a (H^{(i)}_2)$	$a (H^{(i)}_3)$
gas phase	1073	1135	12.32	12.68	12.13	-0.98	0.94	-2.00
	7903	7887	0.00	0.00	12.08	-0.97	0.93	-1.99
	11154	11135	0.00	0.00				
hexane	463	461	20.54	20.49	12.00	-0.90	0.89	-1.91
	7908	7892	0.00	0.00	12.34	-0.92	0.91	-1.94
	11170	11143	0.00	0.00				
DCM	6274	214	0.77	24.75	0.02	-0.07	0.10	-0.28
	11451	8095	3.94	6.83	26.77	-1.82	1.52	-2.21
	14456	11270	4.82	6.42				
MeCN	7517	352	0.76	18.45	0.00	-0.07	0.09	-0.23
	12194	8176	4.01	6.78	27.03	-1.80	1.46	-2.03
	15068	11339	4.96	6.37				

Table S5.5. Calculated first three excitation energies and electronic coupling (E_n and $2H_{ab}$ in cm^{-1}) and transition dipole moments $\mu_{t,n}$ in Debye as well as ^{14}N - and ^1H -HFC constants a in MHz for **PC4** in different environments

environment	$E_n (C_i)$	$2H_{ab} (C_i)$	$\mu_{t,n} (C_i)$	$\mu_{t,n} (C_i)$	$a (N^{(i)})$	$a (H^{(i)}_1)$	$a (H^{(i)}_2)$	$a (H^{(i)}_3)$
gas phase	2152	2148	20.63	20.61	10.25	-1.44	1.29	-3.59
	7779	7775	0.00	0.00	10.26	-1.44	1.29	-3.59
	10572	10562	0.00	0.00				
hexane	998	995	31.44	31.42	10.46	-1.52	1.36	-3.61
	7406	7407	0.03	0.00	10.46	-1.52	1.36	-3.61
	10563	10559	0.00	0.00				
DCM	6491	789	3.70	34.11	0.22	-0.09	0.22	-0.50
	11039	7611	8.63	0.00	24.21	-2.92	1.99	-4.18
	14059	10796	4.07	0.00				
MeCN	7835	987	3.33	29.69	0.06	-0.04	0.16	-0.32
	11810	7797	8.39	0.00	25.08	-2.74	1.81	-3.72
	14892	10951	3.48	0.00				

Table S5.6. Calculated first three excitation energies and electronic coupling (E_n and $2H_{ab}$ in cm^{-1}) and transition dipole moments $\mu_{t,n}$ in Debye as well as ^{14}N - and ^1H -HFCs a in MHz for **PC5** in different environments

environment	E_n (C_1)	$2H_{ab}$ (C_i)	$\mu_{t,n}$ (C_1)	$\mu_{t,n}$ (C_i)	a ($\text{N}^{(0)}$)	a ($\text{H}^{(0)}_1$)	a ($\text{H}^{(0)}_2$)	a ($\text{H}^{(0)}_3$)
gas phase	1379	1238	14.35	13.66	12.14	-0.52	0.65	-0.97
	10132	10330	0.00	0.00	12.11	-0.52	0.64	-0.97
	13643	13749	0.09	0.00				
hexane	557	553	21.62	21.59	12.81	-0.66	0.72	-0.97
	10384	10405	0.15	0.00	11.89	-0.56	0.63	-0.86
	13799	13823	1.64	0.00				
DCM	6549	447	1.41	23.89	0.08	0.03	0.00	0.02
	13687	10673	5.26	0.00	26.78	-1.32	1.22	-1.67
	15099	14062	6.57	0.00				
MeCN	7863	571	1.21	20.12	0.02	0.03	0.00	0.03
	14395	10796	5.36	0.00	27.05	-1.24	1.13	-1.52
	15197	14141	6.45	0.00				

Table S5.7. Calculated first three excitation energies and electronic coupling (E_n and $2H_{ab}$ in cm^{-1}) and transition dipole moments $\mu_{t,n}$ in Debye as well as ^{14}N - and ^1H -HFCs a in MHz for **PC6** in different environments

environment	E_n (C_1)	$2H_{ab}$ (C_i)	$\mu_{t,n}$ (C_1)	$\mu_{t,n}$ (C_i)	a ($\text{N}^{(0)}$)	a ($\text{H}^{(0)}_1$)	a ($\text{H}^{(0)}_2$)	a ($\text{H}^{(0)}_3$)
gas phase	2614	2620	20.43	20.42	10.33	-1.39	0.73	-2.07
	9138	9155	0.06	0.00	10.31	-1.41	0.74	-2.08
	10407	10403	6.78	6.83				
hexane	1311	1366	30.21	30.12	10.41	-1.35	0.72	-1.99
	8781	8767	0.09	0.00	10.63	-1.43	0.77	-2.08
	10446	10458	7.46	7.40				
DCM	6403	1176	1.35	32.36	0.06	0.00	0.00	0.04
	12028	8922	9.68	0.00	24.96	-2.40	1.54	-3.28
	14611	10705	0.21	7.41				
MeCN	7858	1401	1.08	29.14	0.02	0.00	0.00	0.03
	12619	9048	9.14	0.00	25.31	-2.38	1.51	-3.15
	15166	10798	6.34	7.36				

6. Chapter

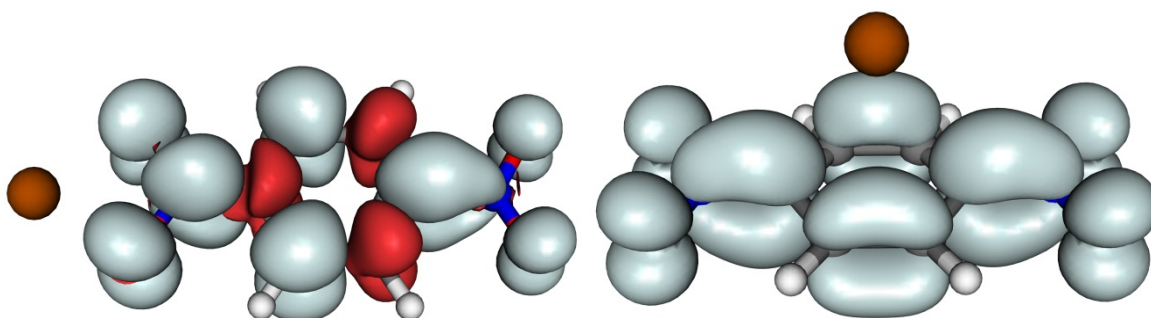


Figure S6.1. Spin-density distributions (isovalue ± 0.001) for **DN1** including a sodium ion near one nitro group (left) or above the benzene ring (right).

Table S6.1. Default radii (in Å) used for cavity construction.

code	radii model	H	C	N	O
Go3	UAo	2.125 ^a	1.925	1.830	1.750
Go9	UFF	1.443	1.926	1.830	1.750
TBM5.10	Bondi	1.404	1.989	1.814	1.778
TBM6.3	optimized	1.300	2.000	1.830	1.720

^a Due to the applied model (UAo), where hydrogen atoms are treated implicitly, this is the radii for CH.

Table S6.2. IV-CT excitation energies E_i and electronic coupling matrix elements $2H_{ab}$ in cm^{-1} for **DN2** obtained at TDDFT levels with different program versions and solvent models^a

μ_o^b	$\Delta H^\ddagger^c$	Go3 ^d		Go9 ^d		TBM5.10 ^d		TBM6.3 ^d	
		E_i	2H _{ab}	E_i	2H _{ab}	E_i	2H _{ab}	E_i	2H _{ab}
35% HF in gas phase									
5.27 (3.23) ^e	0.0 (0.0)	5922	5922	5922	5922	5922	5921	5922	5921
35% HF in DCM									
9.50, [9.81], (8.40)	3.5, [4.5], (4.5)	6381	4247	6054	4564	6502	5318	6324	4811
35% HF in MeCN									
10.44, [10.74], (9.33)	6.4, [7.8], (7.8)	7149	4250	6608	4584	7242	5180	7118	4668
40 % HF in MeCN									
10.77, [11.08], (9.69)	10.0, [11.5], (11.5)	8685	4347	7980	4677	8728	5067	8618	4465

^a BLYP35/SVP/COSMO structures optimized with TBM6.3 or TBM5.10 and subsequent TDDFT calculations. ^b Ground-state dipole moment μ_o (in Debye, with the center of mass as the origin) obtained with TBM6.3 (Bondi radii, optimized radii in brackets), values by TBM5.10 (optimized radii) in parentheses. ^c ET barriers (in kJ mol^{-1}) obtained by TBM6.3 (Bondi radii, optimized radii in brackets), values by TBM5.10 (optimized radii) in parentheses. ^d TDDFT results based on particular ground state structure by TBM6.3 with, respectively, Go3/CPCM, Go9/CPCM, TBM5.10/COSMO, and TBM6.3/COSMO. The experimental IV-CT excitation energy in MeCN is 8320 cm^{-1} . ^e Delocalized ground-state structure in the gas phase.

Table S6.3. Basis set effects on dipole moments (μ_o in Debye), ET barriers ($\Delta H^\ddagger$ in kJ mol^{-1}), O-N bond lengths (d_1 , d_2 in Å), IV-CT excitation energies E_i and electronic coupling matrix elements $2H_{ab}$ (in cm^{-1}) for **DN2** in MeCN^a

basis set	μ_o^b	$\Delta H^\ddagger$	d_1	d_2	E_i	$2H_{ab}$	E_i	$2H_{ab}$	E_i	$2H_{ab}$
			(O-N)	(O-N)	(Go3)		(Go9)		(TBM6.3)	
SVP	10.44	6.4	1.215	1.271	7149	4250	6608	4584	7118	4668
SVP+(O)	12.98	18.6	1.217	1.282	9058	2646	8228	3044	8943	3168
SVP+	12.78	17.8	1.217	1.281	8975	2754	8154	3148	8865	3268
TZVP	12.29	15.9	1.218	1.287	9028	3020	8186	3412	8920	3514

^a BLYP35/COSMO ground-state optimizations with TBM6.3 (using Bondi radii), followed by TDDFT/CPCM or TDDFT/COSMO calculations with different programs. ^b With the center of mass as the origin.

Table S6.4. Comparison of MeCN results for dipole moments (μ_o) in Debye (with the center of mass as the origin), ET barriers ($\Delta H^\ddagger$) in kJ mol^{-1} , first excitation energies (E_i) in cm^{-1} and transition dipole moments ($\mu_{t,i}$) in Debye

	μ_o	μ_o	$\Delta H^\ddagger$	$\Delta H^\ddagger$	E_i	E_i	E_i	$\mu_{t,i}$	$\mu_{t,i}$	$\mu_{t,i}$
	(T6) ^a	(G9) ^b	(T6) ^a	(G9) ^b	(T6T6) ^c	(T6G9) ^d	(G9G9) ^d	(T6T6) ^c	(T6G9) ^d	(G9G9) ^d
DN1	0.5	0.0	0.0	0.0	13008	12925	12864	7.00	7.26	7.28
DN2	12.6	11.8	17.8	12.5	9267	8216	8140	1.38	1.64	1.68
DN3	16.0	15.1	23.2	18.1	9591	8429	8365	1.08	1.24	1.26
DN4	7.3	0.4	0.9	0.0	11188	10669	9750	8.06	8.77	9.68
DN5	21.0	19.1	10.2	5.5	11533	10482	10207	8.08	9.30	9.65
DN6	19.7	18.8	19.5	13.6	12583	11208	11143	2.97	3.41	3.79

^a BLYP35/TZVP/COSMO results using TBM6.3 (T6). ^b BLYP35/TZVP/CPCM results in MeCN using G9 (G9).

^c Subsequent TD-DFT results using TBM6.3 on T6 ground state structure (T6T6). ^d Subsequent TD-DFT results using G9 on either T6 (T6G9) or G9 ground state structure (G9G9).

Table S6.5. Comparison of DCM results for dipole moments (μ_o) in Debye (with the center of mass as the origin), ET barriers ($\Delta H^\ddagger$) in kJ mol^{-1} , first excitation energies (E_i) in cm^{-1} and transition dipole moments ($\mu_{t,i}$) in Debye

	μ_o	μ_o	$\Delta H^\ddagger$	$\Delta H^\ddagger$	E_i	E_i	E_i	$\mu_{t,i}$	$\mu_{t,i}$	$\mu_{t,i}$
	(T6) ^a	(G9) ^b	(T6) ^a	(G9) ^b	(T6T6) ^c	(T6G9) ^d	(G9G9) ^d	(T6T6) ^c	(T6G9) ^d	(G9G9) ^d
DN1	0.1	0.0	0.0	0.0	13074	12762	12735	7.00	7.45	7.46
DN2	11.7	11.3	12.8	9.9	8049	7474	7423	1.66	1.92	1.96
DN3	14.9	14.4	18.0	15.2	8012	7447	7424	1.19	1.37	1.39
DN4	2.4	0.1	0.1	0.0	10134	9709	9593	9.10	9.85	9.97
DN5	17.4	16.1	4.0	2.4	9428	8870	8699	10.22	11.37	11.67
DN6	18.0	17.6	19.6	9.1	10123	9571	9566	4.66	5.16	5.03

^a BLYP35/TZVP/COSMO results using TBM6.3 (T6). ^b BLYP35/TZVP/CPCM results in DCM using G9 (G9).

^c Subsequent TD-DFT results using TBM6.3 on T6 ground state structure (T6T6). ^d Subsequent TD-DFT results using G9 on either T6 (T6G9) or G9 ground state structure (G9G9).

Table S6.6. Comparison of gas phase results for dipole moments (μ_o) in Debye, ET barriers ($\Delta H^\ddagger$) in kJ mol⁻¹, C-N bond lengths d_1 and d_2 in Å, IV-CT excitation energies (E_i) as well as electronic coupling matrix elements ($2H_{ab}$) in cm⁻¹ and transition dipole moments ($\mu_{t,i}$) in Debye^a

	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
DN1	0.0	0.0	1.403	1.403	14384	14382	6.0	6.0
DN2	5.8	0.0	1.418	1.422	5168	5170	4.4	4.4
DN3	7.2	-0.1	1.410	1.438	3185	3260	5.1	5.4
DN4	0.0	0.0	1.410	1.410	11616	11617	7.7	7.7
DN5	0.0	0.0	1.417	1.417	8975	8975	12.2	12.2
DN6	2.1	0.1	1.415	1.415	7710	7776	10.3	10.3

^a BLYP35/TZVP results using TBM6.3. ^b With the center of mass as the origin.**Table S6.7.** Comparison of computed dipole moments (μ_o) in Debye, ET barriers ($\Delta H^\ddagger$) in kJ mol⁻¹, C-N bond lengths d_1 and d_2 in Å, IV-CT excitation energies (E_i) as well as electronic coupling matrix elements ($2H_{ab}$) in cm⁻¹ and transition dipole moments ($\mu_{t,i}$) in Debye^a

	μ_o^b	$\Delta H^\ddagger$	$\Delta H^\ddagger(\text{exp.})$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$E_i(\text{exp.})$	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
DN1	0.04	0.0	- ^c	1.398	1.398	12735	-	12701	7.46	7.48
DN2	11.25	9.9	-	1.386	1.466	7423	-	3397	1.96	5.92
DN3	14.40	15.2	-	1.385	1.462	7424	-	2094	1.39	8.39
DN4	0.08	0.0	- ^c	1.403	1.403	9593	-	9596	9.97	9.97
DN5	16.10	2.4	11.5±0.88 ^d	1.386	1.445	8699	10800 ^d	6454	11.67	16.42
DN6	17.61	9.1	4.2±0.84 ^d	1.388	1.459	9566	12300 ^d	5213	5.03	13.91

^a BLYP35/TZVP/CPCM results in DCM using G09. ^b With the center of mass as the origin. ^c Class III. ^d Exp. values from ref. [185].**Table S6.8.** Comparison of computed dipole moments (μ_o) in Debye, ET barriers ($\Delta H^\ddagger$) in kJ mol⁻¹, C-N bond lengths d_1 and d_2 in Å, IV-CT excitation energies (E_i) as well as electronic coupling matrix elements ($2H_{ab}$) in cm⁻¹ and transition dipole moments ($\mu_{t,i}$) in Debye^a

	μ_o^b	$\Delta H^\ddagger$	$\Delta H^\ddagger(\text{exp.})^c$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$E_i(\text{exp.})^b$	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
DN1	0.47	0.0	- ^d	1.394	1.398	13008	11000	13002	7.00	7.01
DN2	12.56	17.8	12.0	1.388	1.466	9267	8320	3386	1.38	5.47
DN3	15.95	23.2	18.4	1.387	1.461	9591	9360	2384	1.08	7.49
DN4	7.31	0.9	- ^d	1.386	1.425	11188	8500	9901	8.06	9.27
DN5	21.02	10.2	11.3	1.384	1.451	11533	11300	6882	8.08	15.08
DN6	19.74	19.5	8.8	1.391	1.459	12583	12800	5811	2.97	12.58

^a BLYP35/TZVP/COSMO results in MeCN using TBM6.3. ^b With the center of mass as the origin. ^c Exp. values see references in section 6.2. ^d Class III.

Table S6.9. Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹, d_1 , d_2 in Å) as well as excited state properties (E_i , $2H_{ab}$ in cm⁻¹, $\mu_{t,i}$ in Debye) for **DN1** in DCM and MeCN^a

functional	CPCM	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,i}(E_i)^c$	$\mu_{t,i}(2H_{ab})$
M06	DCM	0.04	0.0	1.404	1.405	13586	13573	6.68	6.69
	MeCN	0.05	0.0	1.404	1.404	13694	13688	6.51	6.52
M05	DCM	0.05	0.0	1.412	1.413	13901	13903	6.61	6.60
	MeCN	0.04	0.0	1.412	1.412	14016	14016	6.44	6.44
BLYP ₃₅	DCM	0.04	0.0	1.398	1.398	12735	12701	7.46	7.48
	MeCN	0.05	0.0	1.398	1.398	12864	12846	7.28	7.29
BMK	DCM	0.05	0.0	1.394	1.394	13108	13070	7.45	7.47
	MeCN	0.04	0.0	1.393	1.393	13269	13223	7.26	7.28
M06-2X	DCM	0.05	0.0	1.399	1.399	12482	12465	7.86	7.87
	MeCN	0.02	0.0	1.398	1.399	12659	12634	7.67	7.68
M05-2X	DCM	0.05	0.0	1.395	1.395	12474	12456	7.95	7.96
	MeCN	0.01	0.0	1.394	1.395	12658	12631	7.76	7.77
B2PLYP	DCM	0.03	0.0	1.410	1.410	9751	9738	9.59	9.59
	MeCN	0.05	0.0	1.410	1.410	9963	9966	9.33	9.33
B2PLYPD	DCM	0.03	0.0	1.410	1.410	9761	9744	9.58	9.59
	MeCN	0.04	0.0	1.410	1.410	9975	9975	9.32	9.32
CAM-B3LYP	DCM	0.05	0.0	1.397	1.397	12076	12068	7.98	7.98
	MeCN	0.11	0.0	1.396	1.397	12242	12238	7.79	7.79
LC-BLYP	DCM	6.45	2.4	1.370	1.424	16038	10157	6.98	9.85
	MeCN	7.34	3.8	1.371	1.429	17559	10410	6.30	9.59
ω B97X	DCM	1.94	0.0	1.390	1.407	11752	11336	8.52	8.76
	MeCN	4.43	0.4	1.384	1.421	13494	11535	7.52	8.54

^a TZVP/CPCM results obtained with G09. ^b With the center of mass as the origin. ^c The experimental value is about 4.66 Debye in DMF.^[190]

Table S6.10. Computed ground-state properties (μ_0 in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹, d_1 , d_2 in Å) as well as excited state properties (E_i , $2H_{ab}$ in cm⁻¹, $\mu_{t,i}$ in Debye) for **DN2** in DCM and MeCN^a

functional	CPCM	μ_0^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
Mo6	DCM	8.73	0.4	1.397	1.453	4405	4370	3.78	4.57
	MeCN	9.99	1.6	1.391	1.463	4657	4360	2.97	4.43
Mo5	DCM	7.05	0.0	1.428	1.428	4986	4985	4.54	4.55
	MeCN	8.25	0.1	1.407	1.453	4898	4984	4.02	4.42
BLYP35	DCM	11.25	9.9	1.386	1.466	7423	3397	1.96	5.92
	MeCN	11.79	12.5	1.387	1.467	8140	3420	1.68	5.72
BMK	DCM	11.37	11.5	1.384	1.463	7928	2881	1.85	6.24
	MeCN	11.88	14.2	1.385	1.464	8645	2915	1.62	6.00
Mo6-2X	DCM	11.49	20.5	1.387	1.475	11153	1324	1.62	9.41
	MeCN	11.97	23.5	1.388	1.475	11950	1466	1.48	8.67
Mo5-2X	DCM	11.61	20.0	1.384	1.469	11223	1503	1.65	9.30
	MeCN	12.09	23.1	1.385	1.469	12034	1641	1.51	8.64
B2PLYP	DCM	12.30	-1.5	1.392	1.475	11891	^{-c}	0.67	^{-c}
	MeCN	12.78	0.9	1.393	1.475	12085	^{-c}	0.37	^{-c}
B2PLYPD	DCM	12.31	-1.5	1.392	1.475	11867	^{-c}	0.65	^{-c}
	MeCN	12.78	0.9	1.393	1.476	12056	^{-c}	0.37	^{-c}
CAM-B3LYP	DCM	11.43	16.5	1.386	1.470	9916	2270	1.71	7.76
	MeCN	11.93	19.4	1.387	1.470	10706	2364	1.53	7.39
LC-BLYP	DCM	12.17	36.1	1.378	1.464	17363	^{-c}	1.66	^{-c}
	MeCN	12.62	39.9	1.380	1.464	18193	^{-c}	1.53	^{-c}
wB97X	DCM	11.62	25.3	1.387	1.476	13585	^{-c}	1.67	^{-c}
	MeCN	12.10	28.5	1.388	1.476	14410	^{-c}	1.54	^{-c}

^a TZVP/CPCM results obtained with G09. ^b With the center of mass as the origin. ^c Negative excitation energies have been obtained, indicating stability problems of the ground-state wave function at the symmetrical transition state.

Table S6.11. Excitation energies in cm⁻¹ dependent on TD-DFT functional for **DN2**^a

functional ground state	functional TD-DFT	E_i^b	$\mu_{t,i}^b$
BLYP35	BLYP35	8140	1.68
	B2PLYP	13744	1.14
B2PLYP	B2PLYP	12085	0.37
	BLYP35	7873	1.60

^a TZVP/CPCM results in MeCN with G09. ^b Subsequent TD-DFT properties on the given ground state structure

Table S6.12. Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol^{-1} , d_1 , d_2 in Å) as well as excited state properties (E_i , $2H_{ab}$ in cm^{-1} , $\mu_{t,1}$ in Debye) for **DN3** in DCM and MeCN^a

functional	CPCM	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,1}(E_i)^c$	$\mu_{t,1}(2H_{ab})$
Mo6	DCM	12.74	3.4	1.389	1.463	3603	3051	2.72	6.03
	MeCN	13.59	5.5	1.388	1.465	4272	3151	2.16	5.85
Mo5	DCM	12.01	1.9	1.396	1.470	3444	3425	3.41	6.03
	MeCN	13.02	3.7	1.393	1.474	4032	3524	2.58	5.86
BLYP35	DCM	14.40	15.2	1.385	1.462	7424	2094	1.39	8.39
	MeCN	15.09	18.1	1.386	1.462	8365	2249	1.26	7.98
BMK	DCM	14.46	17.5	1.383	1.459	8132	1403	1.35	9.77
	MeCN	15.13	20.4	1.384	1.459	9052	1610	1.25	9.01
Mo6-2X	DCM	14.60	26.9	1.386	1.471	11159	- ^d	1.38	- ^d
	MeCN	15.29	30.3	1.387	1.471	12150	- ^d	1.32	- ^d
Mo5-2X	DCM	14.74	27.3	1.382	1.465	11431	- ^d	1.37	- ^d
	MeCN	15.41	30.4	1.383	1.465	12437	- ^d	1.30	- ^d

^a TZVP/CPCM results obtained with G09. ^b With the center of mass as the origin. ^c Experimental values are 1.12 Debye in MeCN and 1.35 Debye in DMF (by Hush-approximation) and 1.04 Debye and 1.24 Debye in MeCN and DMF respectively (by Liptay's method).^[42] ^d Negative excitation energies have been obtained, indicating stability problems of the ground-state wave function at the symmetrical transition state.

Table S6.13. Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol^{-1} , d_1 , d_2 in Å) as well as excited state properties (E_i , $2H_{ab}$ in cm^{-1} , $\mu_{t,1}$ in Debye) for **DN4** in DCM and MeCN^a

functional	CPCM	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,1}(E_i)^c$	$\mu_{t,1}(2H_{ab})$
Mo6	DCM	0.03	0.0	1.410	1.410	10587	10582	8.75	8.76
	MeCN	0.05	0.0	1.410	1.410	10695	10697	8.51	8.51
Mo5	DCM	0.04	0.0	1.418	1.418	10792	10792	8.74	8.74
	MeCN	0.04	0.0	1.418	1.418	10908	10907	8.50	8.50
BLYP35	DCM	0.08	0.0	1.403	1.403	9593	9596	9.97	9.97
	MeCN	0.40	0.0	1.401	1.404	9750	9742	9.68	9.69
BMK	DCM	0.08	0.0	1.399	1.399	9753	9750	10.03	10.03
	MeCN	0.05	0.0	1.398	1.398	9916	9908	9.74	9.75
Mo6-2X	DCM	5.80	0.3	1.389	1.428	10514	9200	9.49	10.61
	MeCN	8.29	1.3	1.386	1.438	12016	9367	8.31	10.32
Mo5-2X	DCM	6.59	0.6	1.384	1.427	10923	9023	9.31	10.87
	MeCN	8.79	1.8	1.381	1.436	12525	9203	8.13	10.57

^a TZVP/CPCM results obtained with G09. ^b With the center of mass as the origin. ^c The experimental value in DMF is 7.60 Debye.^[42, 190]

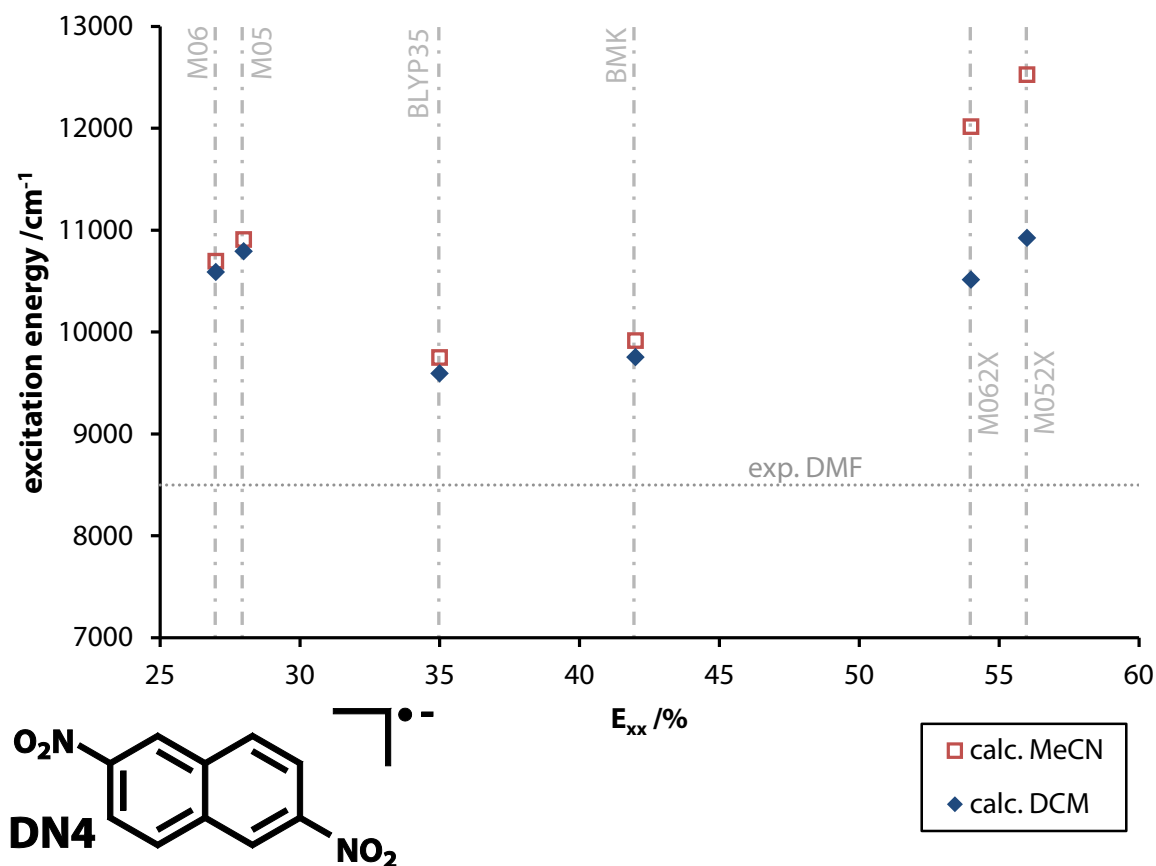


Figure S6.2. Computed excitation energies for the class III system **DN4** in MeCN and DCM depending on density functional, compared to the experimental value in DMF (8500 cm⁻¹) (see ref.[42, 190])

Table S6.14. Computed ground-state properties (μ_0 in Debye with the center of mass as the origin, $\Delta H^\ddagger$ in kJ mol⁻¹, d_1 , d_2 in Å) as well as excited state properties (E_i , $2H_{ab}$ in cm⁻¹, $\mu_{t,i}$ in Debye) for **DN5** in THF, DCM and MeCN^a

functional	CPCM	μ_0	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,i} (E_i)^b$	$\mu_{t,i} (2H_{ab})$
Mo6	THF	0.04	0.1	1.416	1.416	7448	7449	14.14	14.14
	DCM	0.13	0.0	1.416	1.416	7382	7379	14.25	14.26
	MeCN	0.01	0.0	1.415	1.415	7533	7529	13.82	13.82
Mo5	THF	0.02	0.0	1.425	1.425	7690	7686	14.09	14.09
	DCM	0.25	0.0	1.424	1.425	7625	7623	14.21	14.21
	MeCN	0.44	0.0	1.423	1.425	7776	7774	13.77	13.78
BLYP35	THF	15.21	1.9	1.386	1.443	8428	6546	12.08	16.25
	DCM	16.10	2.4	1.386	1.445	8699	6454	11.67	16.42
	MeCN	19.06	5.5	1.384	1.450	10207	6640	9.65	15.89
BMK	THF	15.81	0.1	1.383	1.441	8930	8909	11.89	11.92
	DCM	16.69	3.1	1.383	1.442	9279	6297	11.46	16.90
	MeCN	19.29	6.3	1.381	1.447	10858	6503	9.64	16.34
Mo6-2X	THF	19.55	0.1	1.384	1.462	12066	12065	9.68	9.68
	DCM	20.03	9.8	1.384	1.463	12461	5502	9.43	18.56
	MeCN	21.60	14.4	1.385	1.465	14104	5734	8.29	17.91
Mo5-2X	THF	19.79	0.0	1.38	1.457	12564	12555	9.41	9.41
	DCM	20.24	10.9	1.380	1.458	12955	5238	9.17	19.31
	MeCN	21.74	15.5	1.381	1.460	14557	5491	8.04	18.57

^a TZVP/CPCM results obtained with Go9. ^b The exp. values are 3.61 Debye in MeCN up to 4.46 Debye in DMF.^[176]

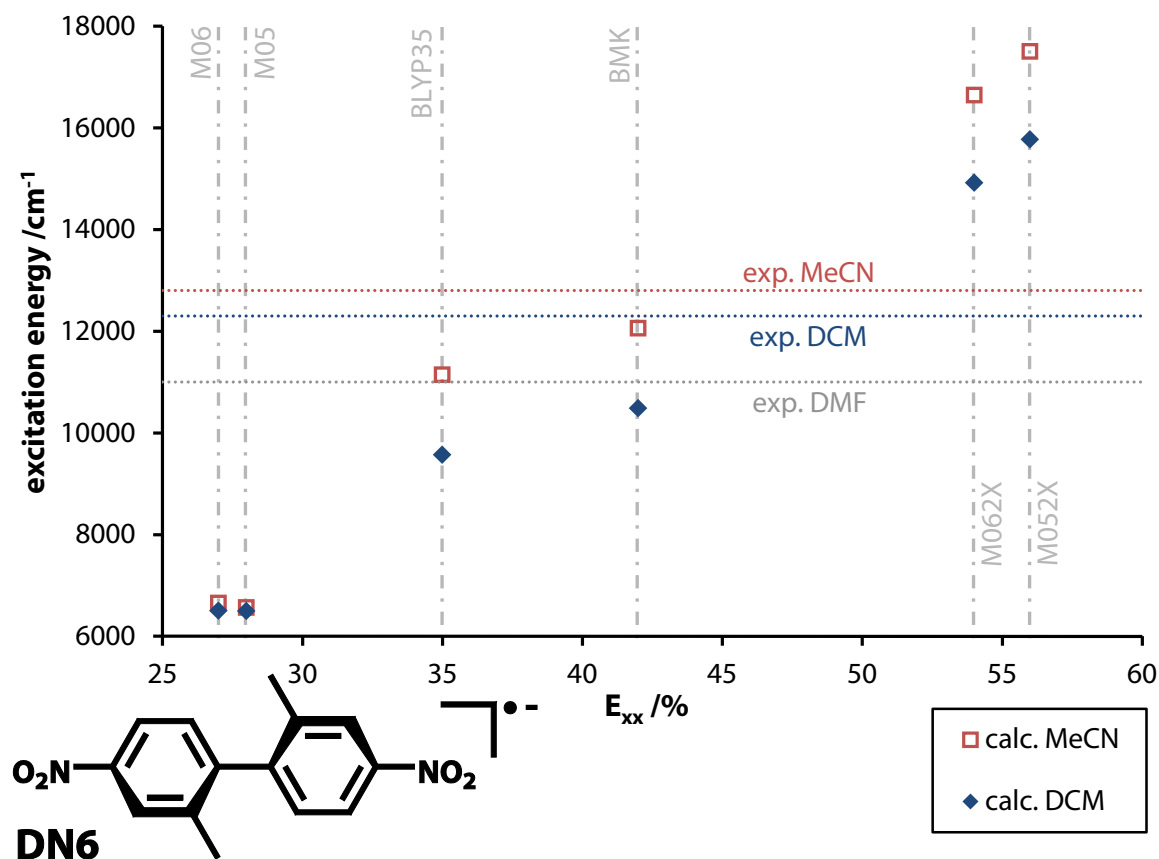


Figure S6.3. Excitation energies for class II system **DN6**, depending on the density functional used, calculated in MeCN and DCM, compared to the experimental value of **DN6** in MeCN of 12800 cm⁻¹, in DCM of 12300 cm⁻¹ and DMF of 11000 cm⁻¹ (see ref. [185]).

Table S6.15. Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹, d_1 , d_2 in Å) as well as excited state properties (E_1 , $2H_{ab}$ in cm⁻¹, $\mu_{t,1}$ in Debye) for **DN6** in DCM and MeCN^a

functional	CPCM	μ_o^b	$\Delta H^\ddagger c$	d_1 (C-N)	d_2 (C-N)	E_1	$2H_{ab}$	$\mu_{t,1}$ (E_1)	$\mu_{t,1}$ ($2H_{ab}$)
M06	DCM	1.18	0.1	1.414	1.415	6502	6561	11.66	11.66
	MeCN	13.25	1.0	1.392	1.449	6651	6733	8.62	11.30
M05	DCM	1.36	0.0	1.422	1.423	6494	6484	11.61	11.61
	MeCN	12.14	0.6	1.399	1.455	6563	6636	9.09	11.25
BLYP35	DCM	17.61	9.1	1.388	1.459	9566	5213	5.03	13.91
	MeCN	18.76	13.6	1.389	1.461	11143	5435	3.79	13.38
BMK	DCM	17.07	9.4	1.385	1.453	10484	5147	5.87	14.50
	MeCN	18.20	13.6	1.386	1.454	12059	5330	4.85	13.96
M06-2X	DCM	18.11	18.9	1.389	1.468	14920	4030	4.71	16.99
	MeCN	18.98	23.9	1.391	1.469	16647	4342	4.05	16.11
M05-2X	DCM	18.43	21.1	1.386	1.464	15774	3498	4.05	18.36
	MeCN	19.23	26.2	1.388	1.464	17501	3873	3.47	17.17

^a TZVP/CPCM results obtained with G09. ^b With the center of mass as the origin. ^c The experimental values are 8.8±1.25, 13.8±1.67 and 4.2±0.82 kJ mol⁻¹ in MeCN, DMF and DCM respectively.^[185]

Table S6.16. Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol^{-1} , d_1 , d_2 in Å) as well as excited state properties (E_i , $2H_{ab}$ in cm^{-1} , $\mu_{t,i}$ in Debye) for **DN1** in different environments^a

solvent	<i>solvent model</i>	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
gas phase	-	0.00	0.0	1.403	1.403	14384	14382	6.04	6.04
DCM	COSMO	0.11	0.0	1.397	1.397	13074	13076	7.00	7.00
	D-COSMO-RS	0.14	0.1	1.396	1.396	13000	12984	7.01	7.01
<i>n</i> -octanol	COSMO	0.26	0.0	1.396	1.398	13069	13067	7.00	7.00
	D-COSMO-RS	8.95	6.6	1.383	1.437	16709	12957	5.12	7.00
MeOH	COSMO	0.31	0.0	1.395	1.397	13007	13005	7.01	7.01
	D-COSMO-RS	9.65	8.2	1.384	1.440	17343	12854	4.83	7.01
MeCN	COSMO	0.47	0.0	1.394	1.398	13008	13002	7.00	7.01
	D-COSMO-RS	0.08	0.0	1.397	1.398	13097	13093	7.00	7.00
DMF	COSMO	0.47	0.0	1.394	1.398	13008	13002	7.00	7.01
	D-COSMO-RS	0.03	0.2	1.399	1.399	13142	13138	7.00	7.00

^a BLYP35/TZVP results with TBM6.3. ^b With the center of mass as the origin.**Table S6.17.** Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol^{-1} , d_1 , d_2 in Å) as well as excited state properties (E_i , $2H_{ab}$ in cm^{-1} , $\mu_{t,i}$ in Debye) for **DN2** in different environments^a

solvent	<i>solvent model</i>	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
gas phase	-	5.83	0.0	1.418	1.422	5168	5170	4.35	4.35
DCM	COSMO	11.70	12.8	1.387	1.466	8049	3609	1.66	5.43
	D-COSMO-RS	12.00	15.1	1.387	1.466	8471	3405	1.53	5.47
MeOH	COSMO	12.53	17.6	1.388	1.466	9214	3396	1.39	5.47
	D-COSMO-RS	14.86	43.1	1.393	1.469	14807	3050	1.02	5.54
MeCN	COSMO	12.56	17.8	1.388	1.466	9267	3386	1.38	5.47
	D-COSMO-RS	11.79	12.8	1.387	1.467	7989	3574	1.65	5.41
DMF	COSMO	12.56	17.8	1.388	1.466	9268	3386	1.38	5.47
	D-COSMO-RS	11.51	11.1	1.387	1.467	7535	3679	1.78	5.38

^a BLYP35/TZVP results with TBM6.3. ^b With the center of mass as the origin.**Table S6.18.** Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol^{-1} , d_1 , d_2 in Å) as well as excited state properties (E_i , $2H_{ab}$ in cm^{-1} , $\mu_{t,i}$ in Debye) for **DN3** in different environments^a

solvent	<i>solvent model</i>	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
gas phase	-	7.20	-0.1	1.410	1.438	3185	3260	5.14	5.41
DCM	COSMO	14.86	18.0	1.385	1.461	8012	2407	1.19	7.36
	D-COSMO-RS	15.17	19.8	1.385	1.460	8433	2321	1.14	7.46
MeOH	COSMO	15.91	23.0	1.387	1.461	9522	2386	1.08	7.48
	D-COSMO-RS	18.75	48.2	1.390	1.463	15088	2206	0.83	7.72
MeCN	COSMO	15.95	23.2	1.387	1.461	9591	2384	1.08	7.49
	D-COSMO-RS	15.06	18.4	1.386	1.462	8219	2473	1.21	7.35
DMF	COSMO	15.96	23.2	1.387	1.461	9592	2384	1.08	7.49
	D-COSMO-RS	14.76	16.8	1.386	1.463	7763	2524	1.25	7.29

^a BLYP35/TZVP results with TBM6.3. ^b With the center of mass as the origin.

Table S6.19. Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹, d_1 , d_2 in Å) as well as excited state properties (E_i , $2H_{ab}$ in cm⁻¹, $\mu_{t,i}$ in Debye) for **DN4** in different environments^a

solvent	solvent model	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
gas phase	-	0.02	0.0	1.410	1.410	11616	11617	7.70	7.70
DCM	COSMO	2.44	0.1	1.395	1.409	10134	10016	9.10	9.23
	D-COSMO-RS	3.95	0.6	1.391	1.413	10255	9900	8.90	9.27
MeCN	COSMO	7.31	0.9	1.386	1.425	11188	9901	8.06	9.27
	D-COSMO-RS	3.04	0.4	1.394	1.412	10227	10030	9.02	9.23
DMF	COSMO	7.31	0.9	1.386	1.425	11189	9901	8.06	9.27
	D-COSMO-RS	1.95	0.2	1.398	1.409	10170	10092	9.12	9.20

^a BLYP₃₅/TZVP results with TBM6.3. ^b With the center of mass as the origin.**Table S6.20.** Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹, d_1 , d_2 in Å) as well as excited state properties (E_i , $2H_{ab}$ in cm⁻¹, $\mu_{t,i}$ in Debye) for **DN5** in different environments^a

solvent	solvent model	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
gas phase	-	0.01	0.0	1.417	1.417	8975	8975	12.15	12.15
THF	COSMO	16.08	2.9	1.385	1.443	8955	7084	10.89	14.92
	D-COSMO-RS	13.22	1.6	1.389	1.439	8318	7232	12.13	14.79
DCM	COSMO	17.35	4.0	1.384	1.445	9428	7044	10.22	14.95
	D-COSMO-RS	18.39	5.3	1.383	1.446	9784	6907	9.66	15.05
MeCN	COSMO	21.02	10.2	1.384	1.451	11533	6882	8.08	15.08
	D-COSMO-RS	18.97	6.5	1.384	1.449	10323	7048	9.29	14.94
DMF	COSMO	21.02	10.2	1.384	1.451	11535	6882	8.08	15.08
	D-COSMO-RS	18.36	5.6	1.385	1.450	10079	7116	9.60	14.88

^a BLYP₃₅/TZVP results with TBM6.3. ^b With the center of mass as the origin.**Table S6.21.** Computed ground-state properties (μ_o in Debye, $\Delta H^\ddagger$ in kJ mol⁻¹, d_1 , d_2 in Å) as well as excited state properties (E_i , $2H_{ab}$ in cm⁻¹, $\mu_{t,i}$ in Debye) for **DN6** in different environments^a

solvent	solvent model	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-N})$	$d_2(\text{C-N})$	E_i	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
gas phase	-	2.08	0.1	1.415	1.415	7710	7776	10.29	10.28
DCM	COSMO	18.04	19.6	1.388	1.457	10123	4722	4.66	12.36
	D-COSMO-RS	18.52	13.1	1.389	1.458	10471	5805	4.13	12.58
MeCN	COSMO	19.74	19.5	1.391	1.459	12583	5811	2.97	12.58
	D-COSMO-RS	18.46	13.6	1.389	1.458	10843	5913	4.33	12.52
DMF	COSMO	19.75	19.5	1.391	1.459	12586	5811	2.95	12.58
	D-COSMO-RS	18.07	12.1	1.388	1.459	10405	6019	4.67	12.47

^a BLYP₃₅/TZVP results with TBM6.3. ^b With the center of mass as the origin.

7. Chapter

Table S7.1. Calculated spectroscopic data (excitation energies E_n in cm^{-1} and transition dipole moments μ_{tn} in Debye and ^1H -HFCs a_{H} in G), dependent on functional and environment^a

	environment	$E_1 (\mu_{t,1})$	$E_2 (\mu_{t,2})$	$E_3 (\mu_{t,3})$	a_{H}^b
DQ1	gas phase	1924 (7.67)	3273 (0.00)	11519 (1.12)	-1.3 (4)
		[1924 (7.67)]	[3267 (0.00)]	[11515 (1.12)]	[-1.3 (4)]
	DCM	5730 (0.12)	8690 (1.31)	8820 (1.04)	-2.5 (2)
		[894 (12.73)]	[3450 (0.00)]	[11518 (1.40)]	[-1.2 (4)]
	DMF	6318 (0.11)	9379 (1.33)	10106 (0.93)	-2.5 (2)
		[879 (12.85)]	[3490 (0.00)]	[11538 (1.39)]	[-1.2 (4)]
DQ2	gas phase	8225 (6.47)	16192 (0.00)	24205 (0.00)	-0.8 (4), 1.8 (2)
		[8226 (6.47)]	[16192 (0.00)]	[21310 (0.00)]	[-0.8 (4), 1.8 (2)]
	DCM	7495 (7.74)	16216 (0.00)	21847 (0.03)	-0.7 (4), 1.8 (2)
		[7494 (7.74)]	[16220 (0.00)]	[21844 (0.03)]	[-0.7 (4), 1.8 (2)]
	DMF	7547 (7.72)	16222 (0.03)	21908 (0.03)	-0.7 (4), 1.8 (2)
		[7532 (7.72)]	[16226 (0.00)]	[21906 (0.03)]	[-0.7 (4), 1.8 (2)]
DQ3a	gas phase	7577 (7.68)	16225 (0.04)	21911 (0.03)	-0.7 (4), 1.8 (2)
		[7561 (7.69)]	[16230 (0.00)]	[21909 (0.03)]	[-0.7 (4), 1.8 (2)]
	DCM	5135 (11.22)	5399 (0.00)	12817 (0.10)	-1.4 (4), 1.3 (2), 1.0 (4)
		[5137 (11.22)]	[5404 (0.00)]	[12830 (0.10)]	[-1.4 (4), 1.3 (2), 1.0 (4)]
	DMF	7645 (1.32)	8258 (6.63)	13499 (0.40)	-3.5 (2), -0.2 (2), 0.4 (4)
		[3767 (15.28)]	[6490 (0.00)]	[13183 (0.06)]	[-1.4 (4), 1.5 (2), 1.0 (4)]
DQ3b	gas phase	8033 (1.38)	9246 (6.00)	13702 (0.52)	-3.6 (2), -0.3 (2), 0.3 (4)
		[3780 (15.29)]	[6642 (0.00)]	[13228 (0.04)]	[-1.4 (4), 1.5 (2), 1.0 (4)]
	THF	4862 (0.00)	5136 (12.11)	12848 (0.08)	1.2 (8), 1.3 (2), 1.0 (4)
		[4862 (0.00)]	[5136 (12.11)]	[12847 (0.08)]	[1.2 (8), 1.3 (2), 1.0 (4)]
	DCM	6776 (1.25)	7982 (7.49)	13378 (0.29)	4.1 (2), 3.3 (2), 0.4 (2), -0.2 (2), 0.4 (2)
		[3864 (15.90)]	[5559 (0.00)]	[13168 (0.04)]	[1.1 (8), 1.4 (2), 1.0 (4)]
DQ4	gas phase	6866 (1.25)	8206 (7.34)	13378 (0.32)	4.1 (2), 3.4 (2), 0.4 (2), -0.2 (2) 0.4 (2)
		[5013 (0.00)]	[5110 (12.10)]	[12751 (0.10)]	[1.2 (8), 1.3 (2), 1.0 (4)]
	DMF	7198 (1.32)	9262 (6.65)	13503 (0.41)	4.3 (2), 3.4 (2), 0.3 (2), -0.3 (2) 0.4 (2)
		[3824 (16.06)]	[5679 (0.00)]	[13217 (0.04)]	[1.1 (8), 1.3 (2), 1.0 (4)]
	MeCN	7208 (1.26)	9295 (6.50)	13503 (0.39)	4.3 (2), 3.4 (2), 0.3 (2), -0.3 (2) 0.4 (2)
		[4078 (15.28)]	[5689 (0.00)]	[13217 (0.04)]	[1.1 (8), 1.3 (2), 1.0 (4)]
DQ4	gas phase	2946 (5.24)	15107 (0.25)	19357 (0.03)	-1.0 (4), 0.1 (4)
		[2942 (5.24)]	[15097 (0.25)]	[19352 (0.03)]	[-1.0 (4), 0.1 (4)]
	DCM	6600 (1.53)	13891 (0.03)	19527 (0.15)	-2.2 (2), 0.1 (2)
		[2072 (7.17)]	[14321 (0.17)]	[18239 (0.00)]	[-0.9 (4), 0.1 (4)]
	DMF	7399 (1.38)	14043 (0.03)	19615 (0.04)	-2.3 (2), 0.1 (2)
		[2082 (7.18)]	[14213 (0.15)]	[18137 (0.00)]	[-0.9 (4), 0.1 (4)]
DQ4	MeCN	7394 (1.36)	14041 (0.03)	19616 (0.04)	-2.3 (2), 0.1 (2)
		[2257 (6.79)]	[14215 (0.15)]	[18149 (0.00)]	[-0.9 (4), 0.1 (4)]
	DMSO	7459 (1.37)	14043 (0.04)	19602 (0.04)	-2.3 (2), 0.1 (2)
		[2110 (7.12)]	[14206 (0.15)]	[18132 (0.00)]	[-0.9 (4), 0.1 (4)]

^a Obtained by BLYP35/TZVP/CPCM, values in brackets at transition state structure ($C_{i/2}$ -symmetry). ^b Number of signals in parentheses.

Table S7.2. Dependence of computed^a ground state dipole moments μ_o (in Debye), ET barriers $\Delta H^\ddagger$ (in kJ mol⁻¹), C-O bond lengths (d_1 , d_2 in Å), excitation energies (E_i and $2H_{ab}$ in cm⁻¹)^b and corresponding transition dipole moments $\mu_{t,1}$ (in Debye) for **DQ2** on exchange-correlation functional

functional	environment	μ_o^c	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}$	$\mu_{t,1}(E_i)$	$\mu_{t,1}(2H_{ab})$
BMK	gas phase	0.01	0.1	1.228	1.228	7978	7983	6.72	6.72
	DCM	0.57	0.0	1.230	1.232	7193	7174	8.06	8.07
	DMF	3.45	0.1	1.224	1.239	7795	7211	7.49	8.06
	DMSO	3.57	0.2	1.224	1.240	7863	7241	7.42	8.02
Mo5-2X	gas phase	0.00	0.0	1.231	1.231	7617	7624	7.15	7.14
	DCM	5.64	1.3	1.221	1.249	9444	6656	6.58	8.67
	DMF	6.30	2.0	1.221	1.251	10152	6694	6.22	8.65
	DMSO	6.34	2.1	1.221	1.251	10217	6729	6.18	8.60
LC- ω PBE	gas phase	0.50	0.0	1.228	1.231	7292	7261	7.92	7.94
	DCM	7.61	6.0	1.216	1.251	13617	5965	5.55	9.87
	DMF	8.04	7.2	1.216	1.252	14352	6009	5.35	9.84
	DMSO	8.06	7.3	1.216	1.252	14413	6055	5.32	9.78

^a G09 results. Cf. Table 7.1 and Table S7.1 for BLYP35 and experimental data. ^b Excitation energies are obtained at symmetry-broken minimum (E_i) and at symmetric transition state structure ($2H_{ab}$) in C_2 -symmetry. ^c With the center of mass as the origin.

Table S7.3. Dependence of computed^a ground state dipole moments μ_o (in Debye), ET barriers $\Delta H^\ddagger$ (in kJ mol⁻¹), C-O bond lengths (d_1 , d_2 in Å), excitation energies (E_i and $2H_{ab}$ in cm⁻¹)^b and corresponding transition dipole moments $\mu_{t,1}$ (in Debye) for **DQ3a** on exchange-correlation functional

functional	environment	μ_o^c	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}$	$\mu_{t,1}(E_i)$	$\mu_{t,1}(2H_{ab})$
BMK	gas phase	0.02	-0.1	1.228	1.229	4653	4652	12.08	12.08
	DCM	17.10	12.1	1.216	1.250	8354	2930	1.41	17.67
	DMF	17.97	14.8	1.215	1.251	8876	2939	1.48	17.68
Mo5-2X	gas phase	10.05	1.8	1.220	1.246	5692	3587	9.32	14.66
	DCM	17.66	20.9	1.218	1.256	9729	- ^d	1.61	- ^d
	DMF	18.40	23.8	1.218	1.257	10138	- ^d	1.64	- ^d
LC- ω PBE	gas phase	14.08	20.5	1.214	1.247	5288	- ^d	1.52	- ^d
	DCM	19.10	45.3	1.214	1.253	6142	- ^d	1.73	- ^d
	DMF	19.72	48.6	1.215	1.254	6211	- ^d	1.71	- ^d

^a G09 results. Cf. Table 7.1 and Table S7.1 for BLYP35 and experimental data. ^b Excitation energies are obtained at symmetry-broken minimum (E_i) and at symmetric transition state structure ($2H_{ab}$) in C_i -symmetry. ^c With the center of mass as the origin. ^d Negative excitation energies due to triplet-instability of the ground state at the saddle point; cf. section 7.4.

Table S7.4. Dependence of computed^a ground state dipole moments μ_o (in Debye), ET barriers $\Delta H^\ddagger$ (in kJ mol⁻¹), C-O bond lengths (d_1 , d_2 in Å), excitation energies (E_i and $2H_{ab}$ in cm⁻¹)^b and corresponding transition dipole moments $\mu_{t,i}$ (in Debye) for **DQ3b** on exchange-correlation functional

functional	environment	μ_o^c	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
BMK	gas phase	28.08	0.0	1.230	1.231	4154	4158	0.00	0.00
	DCM	44.88	10.3	1.217	1.252	7233	3021	1.30	18.41
	DMF	45.73	12.7	1.217	1.253	7690	3028	1.37	18.42
	MeCN	45.72	12.7	1.217	1.253	7701	3354	1.32	17.20
Mo5-2X	gas phase	38.54	3.1	1.221	1.249	5443	3571	0.86	15.76
	DCM	45.67	19.0	1.219	1.259	8935	- ^d	1.52	- ^d
	DMF	46.34	21.7	1.219	1.260	9311	- ^d	1.56	- ^d
	MeCN	46.33	21.7	1.219	1.260	9325	581	1.50	43.54
LC- ω PBE	gas phase	42.43	15.0	1.215	1.250	4551	- ^d	1.57	- ^d
	DCM	47.06	38.3	1.215	1.256	5441	- ^d	1.89	- ^d
	DMF	47.59	42.8	1.215	1.257	5631	- ^d	1.85	- ^d
	MeCN	47.58	42.8	1.215	1.257	5652	- ^d	1.77	- ^d

^a G09 results. Cf. Table 7.1 and Table S7.1 for BLYP35 and experimental data. ^b Excitation energies are obtained at symmetry-broken minimum (E_i) and at symmetric transition state structure ($2H_{ab}$) in C_i -symmetry. ^c With the center of mass as the origin. ^d Negative excitation energies due to triplet-instability of the ground state at the saddle point; cf. section 7.4.

Table S7.5. Dependence of computed^a ground state dipole moments μ_o (in Debye), ET barriers $\Delta H^\ddagger$ (in kJ mol⁻¹), C-O bond lengths (d_1 , d_2 in Å), excitation energies (E_i and $2H_{ab}$ in cm⁻¹)^b and corresponding transition dipole moments $\mu_{t,i}$ (in Debye) for **DQ4** on exchange-correlation functional

functional	environment	μ_o^c	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}$	$\mu_{t,i}(E_i)$	$\mu_{t,i}(2H_{ab})$
BMK	gas phase	4.62	0.0	1.228	1.228	2689	2688	5.54	5.54
	DCM	11.07	15.5	1.212	1.254	7765	1673	1.31	8.16
	DMF	11.42	17.7	1.212	1.255	8570	1690	1.21	8.16
	MeCN	11.41	17.7	1.212	1.255	8565	1911	1.19	7.56
	DMSO	11.44	17.9	1.212	1.255	8624	1726	1.20	8.06
Mo5-2X	gas phase	8.41	6.6	1.213	1.253	4700	1762	2.02	7.04
	DCM	11.09	25.5	1.214	1.260	11447	- ^d	1.03	- ^d
	DMF	11.42	27.8	1.215	1.261	12256	- ^d	0.99	- ^d
	MeCN	11.42	27.8	1.215	1.261	12248	- ^d	0.97	- ^d
	DMSO	11.45	27.9	1.214	1.261	12304	- ^d	0.98	- ^d
LC- ω PBE	gas phase	8.73	28.2	1.211	1.252	12737	- ^d	0.97	- ^d
	DCM	11.17	48.0	1.212	1.258	15721	- ^d	0.06	- ^d
	DMF	11.49	50.3	1.212	1.258	15831	- ^d	0.06	- ^d
	MeCN	11.49	50.2	1.212	1.258	15829	- ^d	0.06	- ^d
	DMSO	11.51	50.4	1.212	1.258	15837	- ^d	0.06	- ^d

^a Gaussian 09 results. Cf. Table 7.1 and Table S7.1 for BLYP35 and experimental data. ^b Excitation energies are obtained at symmetry-broken minimum (E_i) and at symmetric transition state structure ($2H_{ab}$) in C_2 -symmetry. ^c With the center of mass as the origin. ^d Negative excitation energies due to triplet-instability of the ground state at the saddle point; cf. section 7.4.

Table S7.6. Calculated properties (dipole moments μ_o in Debye, ET barriers $\Delta H^\ddagger$ in kJ mol⁻¹, C-O distances d_1 and d_2 of the both quinones in Å, excitation energies E_i and $2H_{ab}$ (in cm⁻¹) and corresponding transition dipole moments $\mu_{t,i}$ in Debye) for **DQ1**, dependent on solvent model^a

environment	solvent model	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}^c$	$\mu_{t,i} (C_1)$	$\mu_{t,i} (C_i)$
gas phase	-	0.05	0.0	1.230	1.230	1923	1922	7.67	7.67
hexane	COSMO	0.54	0.0	1.231	1.232	1365	1363	9.85	9.85
MeCN	COSMO	18.45	30.3	1.214	1.259	6407	1384	0.10	9.81
DMF	COSMO	18.45	30.3	1.214	1.259	6407	1384	0.10	9.81
	D-COSMO-RS	18.79	28.5	1.214	1.256	6997	1393	0.10	9.84

^a Obtained by TBM6.3, BLYP35/TZVP. ^b With the center of mass as the origin. ^c Excitation energy at the transition state structure (C_i-symmetry).

Table S7.7. Calculated properties (dipole moments μ_o in Debye, ET barriers $\Delta H^\ddagger$ in kJ mol⁻¹, C-O distances d_1 and d_2 of the both quinones in Å, excitation energies E_i and $2H_{ab}$ (in cm⁻¹) and corresponding transition dipole moments $\mu_{t,i}$ in Debye) for **DQ2**, dependent on solvent model^a

environment	solvent model	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}^c$	$\mu_{t,i} (C_1)$	$\mu_{t,i} (C_2)$
EtOAc	COSMO	0.70	0.1	1.234	1.238	7946	7928	7.17	7.19
	D-COSMO-RS	0.61	0.1	1.234	1.237	7897	7881	7.19	7.20
EtOAc – <i>t</i> -BuOH (10:1)	COSMO	0.90	0.1	1.234	1.239	7967	7940	7.15	7.18
DCM	COSMO	0.92	0.1	1.234	1.239	8009	7976	7.13	7.16
	D-COSMO-RS	1.45	0.0	1.234	1.241	8074	8012	7.08	7.15
DMF	COSMO	3.11	0.2	1.230	1.245	8364	8057	6.80	7.12

^a Obtained by TBM6.3, BLYP35/TZVP. ^b With the center of mass as the origin. ^c Excitation energy at the transition state structure (C₂-symmetry).

Table S7.8. Calculated properties (dipole moments μ_o in Debye, ET barriers $\Delta H^\ddagger$ in kJ mol⁻¹, C-O distances d_1 and d_2 of the both quinones in Å, excitation energies E_i and $2H_{ab}$ (in cm⁻¹) and corresponding transition dipole moments $\mu_{t,i}$ in Debye) for **DQ3a**, dependent on solvent model^a

environment	solvent model	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}^c$	$\mu_{t,i} (C_1)$	$\mu_{t,i} (C_i)$
EtOAc	COSMO	0.04	0.0	1.239	1.239	4460	4454	13.33	13.33
	D-COSMO-RS	0.21	0.1	1.238	1.238	4424	4416	13.37	13.38
EtOAc – <i>t</i> -BuOH (10:1)	COSMO	0.05	0.0	1.239	1.239	4470	4464	13.32	13.32
	D-COSMO-RS	16.46	10.0	1.221	1.258	8084	4463	1.24	13.33
<i>t</i> -BuOH	COSMO	16.48	9.6	1.222	1.257	8142	4512	1.23	13.26
	D-COSMO-RS	18.38	17.7	1.221	1.267	9199	4708	1.31	13.01

^a Obtained by TBM6.3, BLYP35/TZVP. ^b With the center of mass as the origin. ^c Excitation energy at the transition state structure (C_i-symmetry).

Table S7.9. Calculated properties (dipole moments μ_o in Debye, ET barriers $\Delta H^\ddagger$ in kJ mol⁻¹, C-O distances d_1 and d_2 of the both quinones in Å, excitation energies E_i and $2H_{ab}$ (in cm⁻¹) and corresponding transition dipole moments $\mu_{t,i}$ in Debye) for **DQ3b**, dependent on solvent model^a

environment	solvent model	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}^c$	$\mu_{t,i} (C_1)$	$\mu_{t,i} (C_i)$
gas phase	-	0.14	0.0	1.235	1.235	4865	5133	0.01	12.12
DCM	COSMO	15.78	6.9	1.223	1.259	6979	4494	1.12	14.11
	D-COSMO-RS	15.53	6.6	1.224	1.260	7145	4522	1.11	14.05
<i>t</i> -BuOH	COSMO	16.32	8.1	1.223	1.260	7185	4511	1.15	14.08
DMF	COSMO	17.21	10.3	1.223	1.261	7539	4542	1.21	14.03

^a Obtained by TBM6.3, BLYP35/TZVP. ^b With the center of mass as the origin. ^c Excitation energy at the transition state structure (C_i-symmetry).

Table S7.10. Calculated properties (dipole moments μ_o in Debye, ET barriers $\Delta H^\ddagger$ in kJ mol^{-1} , C-O distances d_1 and d_2 of the both quinones in Å, excitation energies E_i and $2H_{ab}$ (in cm^{-1}) and corresponding transition dipole moments $\mu_{t,1}$ in Debye) for **DQ4**, dependent on solvent model^a

environment	solvent model	μ_o^b	$\Delta H^\ddagger$	$d_1(\text{C-O})$	$d_2(\text{C-O})$	E_i	$2H_{ab}^c$	$\mu_{t,1}(C_1)$	$\mu_{t,1}(C_2)$
EtOAc	COSMO	10.66	11.9	1.216	1.260	6175	2410	1.54	6.29
	D-COSMO-RS	10.62	10.6	1.217	1.258	5798	2432	1.66	6.30
EtOAc – <i>t</i> -BuOH (10:1)	COSMO	10.74	12.5	1.216	1.260	6361	2412	1.49	6.28
	D-COSMO-RS	11.06	16.1	1.216	1.262	7630	2427	1.24	6.29
DCM	COSMO	10.94	14.1	1.217	1.261	6886	2450	1.39	6.27
	D-COSMO-RS	10.93	13.9	1.217	1.262	6867	2442	1.38	6.26
<i>t</i> -BuOH	COSMO	11.14	15.4	1.217	1.261	7324	2463	1.31	6.27
	D-COSMO-RS	11.76	26.5	1.216	1.268	10468	2439	0.91	6.24
MeCN	COSMO	11.47	17.8	1.217	1.262	8122	2474	1.19	6.26
	D-COSMO-RS	11.34	15.5	1.217	1.260	7438	2494	1.31	6.28
DMF	COSMO	11.47	17.8	1.217	1.262	8123	2474	1.19	6.26
	D-COSMO-RS	11.48	15.4	1.217	1.259	7323	2503	1.34	6.28

^a Obtained by TURBOMOLE 6.3, BLYP35/TZVP. ^b With the center of mass as the origin. ^c Excitation energy at the transition state structure (C_i -symmetry).