

Optically induced electron transfer in an *N,N,N',N'*-tetraanisyl-*o*-phenylenediamine radical cation

Gilbert Nöll* and Manuele Avola

Department of Physical and Theoretical Chemistry, University of Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany

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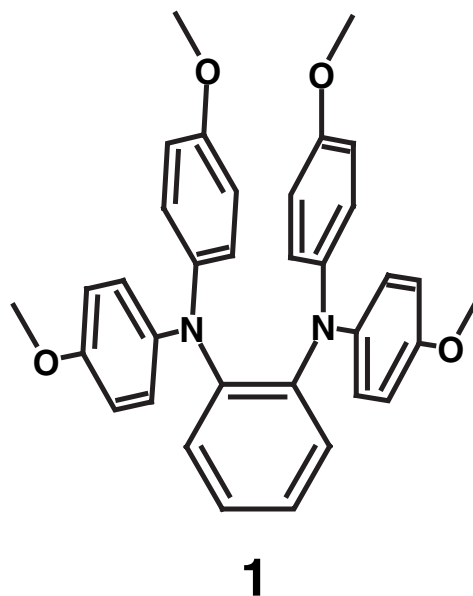
ABSTRACT: Upon electrochemical and spectroelectrochemical investigation the radical cation of tetraanisyl-*o*-phenylenediamine turned out to be an almost delocalized system at the borderline between class II and III with an extremely low reorganization energy. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: electron transfer; mixed-valence compounds; triarylamine; electrochemistry; spectroelectrochemistry

Inorganic as well as organic mixed-valence compounds are of main importance for the understanding of electron transfer processes.¹ In most cases one-dimensional linear systems consisting of two redox centers connected by a bridging unit have been investigated. If the redox centers are at a different redox state, an electron can be transferred thermally or by optical excitation, resulting in an intervalence charge-transfer (IV-CT) band that usually appears in the visible region or in the near-infrared (NIR).¹ A detailed band shape analysis applying the Marcus–Hush theory allows the determination of the electronic coupling between the redox centers.^{1–3} Recently, triarylamine systems turned out to be ideal model compounds for the investigation of one- and more-dimensional electron transfer processes in organic molecules.^{1,4–6} A series of linear bis(triarylamine) systems has been analyzed with respect to several parameters that control the electron transfer rate, such as the redox potentials or the length and electronic nature of the bridge.

Within these studies the radical cations of tetraphenyl-*p*-phenylenediamine and tetraanisyl-*p*-phenylenediamine have been qualified as valence delocalized Robin/Day class III compounds being at the borderline between Robin/Day class II and III (localized/delocalized), whereas the radical cation of tetramethyl-*p*-phenylenediamine is known to be a totally delocalized system.^{1,7–9} In contrast to these molecules where the redox centers are coupled linearly by *para*-phenylene groups, much less is known about *ortho*-coupled systems. Recently, a strong electronic coupling and a very high electron transfer rate constant ($>10^9 \text{ s}^{-1}$) were determined for the radical cation of 1,2-

bis(*N*-phenothiazinyl)-4,5-dimethyl-benzene by electron spin resonance spectroscopy, and an electronic coupling element $V = 1280 \text{ cm}^{-1}$ was calculated.¹⁰ In contrast to phenothiazine radical cations, triarylamine redox centers are known to have significantly lower reorganization energies.¹ To obtain more information about *ortho*-coupled systems, we investigated the electron transfer in the radical cation of tetraanisyl-*o*-phenylenediamine (**1**). Methoxy groups in the *p*-position of the aryl-substituents were chosen in order to prevent electrochemical dimerization upon oxidation.¹¹



The synthesis of compound **1** was carried out by an Ullmann coupling almost identical to the procedure described by Plater and Jackson.¹² In order to avoid the evaporation of any solvent with high boiling point, we carried out the reaction without solvent as a melt at 210 °C.

*Correspondence to: G. Nöll, Department of Physical and Theoretical Chemistry, University of Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany.
E-mail: gilbert.noell@chemie.uni-regensburg.de

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This results in lower yields than described by Plater and Jackson.¹² Melting point: 198–199 °C; ¹H-NMR (400 MHz, acetone-*d*₆): δ = 3.71(s, 12H), 6.65 (m, 8H), 6.74 (m, 8H), 6.96 (m, 2H), 7.03 (m, 2H); ¹³C-NMR (100.6 MHz, acetone-*d*₆): δ = 55.6, 114.7, 125.1, 125.2, 128.9, 142.5, 144.7, 156.1 ppm. C₃₄H₃₂N₂O₄ [532.63]; EI-MS (high resolution, PI): calc.: 532.2362; found: 532.2361, Δ = 0.2 ppm; UV/Vis: λ_{max} in CH₂Cl₂: 296 nm (ϵ = 37000 M⁻¹cm⁻¹), sh. at 340 nm; λ_{max} in MeCN: 293 nm (ϵ = 37500 M⁻¹cm⁻¹), sh. at 336 nm.

Cyclic voltammetry measurements were performed at room temperature using an undivided electrochemical cell with a three-electrode arrangement and a computer-controlled EG&G Potentiostat/Galvanostat Model 283 A. As a working electrode we used a home-made platinum disk electrode together with an Ag/AgCl pseudo-reference electrode and a platinum counter-electrode. Argon was bubbled through all solutions for some minutes before starting the measurements. As a supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAH) was used. Ferrocene was used as internal standard. For electrochemical experiments 5 mg of the compounds was dissolved in 5–8 ml of the solvent.

Compound **1** undergoes two reversible oxidations at 130 and 535 mV vs. Fc/Fc⁺ in dichloromethane and at 210 and 535 mV vs. Fc/Fc⁺ in acetonitrile, respectively. The cyclic voltammogram of compound **1** in dichloromethane is depicted in Fig. 1.

The large splitting between the first and second oxidation (ΔE = 405 mV in dichloromethane and 325 mV in acetonitrile) already indicates a strong electronic coupling between the redox centers. These values are almost as high as the redox splittings detected for tetraanisyl-*p*-phenylenediamine (485 mV in dichloromethane and 340 mV in dimethyl sulfoxide).¹ The redox splitting of compound **1** is larger than observed for 1,2-bis(*N*-phenothiazinyl)-4,5-dimethylbenzene (ΔE = 340 mV in di-

chloromethane).¹⁰ For the corresponding methyl derivative, tetramethyl-*o*-phenylenediamine, a redox splitting of 240 mV in butyronitrile is reported.¹³ We also investigated tetramethyl-*o*-phenylenediamine in dichloromethane and acetonitrile but we could not obtain reversible cyclic voltammograms under the experimental conditions applied. Spectroelectrochemical measurements of compound **1** were carried out by using an optically transparent thin-layer cell as described elsewhere.¹⁴ The Vis-NIR spectra of the mono-radical cations and dication of compound **1** in dichloromethane and acetonitrile are shown in Figs 2 and 3.

In both solvents a broad low-energy absorption band appears in the mono-radical cations of **1** with a maximum of 4250 cm⁻¹ (ϵ = 2080 M⁻¹cm⁻¹) in dichloromethane and 4500 cm⁻¹ (ϵ = 2130 M⁻¹cm⁻¹) in acetonitrile. This band, which might be caused by an IV-CT absorption, decreases completely when **1**⁺ is oxidized further to the dication. In addition to the IV-CT band, a second and third absorption band appear in **1**⁺ with maxima at 13170 and 16580 cm⁻¹ in dichloromethane and 13340 and 16870 cm⁻¹ in acetonitrile, respectively. These two absorptions have a similar band shape to the two bands that have been detected in the dication of tetraphenyl-*p*-phenylenediamine in dichloromethane.¹ The absorption at about 13200 cm⁻¹ is typical for the so-called $\pi \rightarrow \pi^*$ excitation in triarylamine radical cations.¹ The energy of an IV-CT excitation is the Marcus reorganization energy λ , which comprises an inner (vibronic) part λ_v and a solvent contribution λ_s . Therefore, the maximum of an IV-CT-band should depend strongly on the polarity of the solvent. This is not the case for **1**⁺, leading to the assumption that **1**⁺ is a strongly coupled mixed-valence compound at the borderline between class II and III or a valence-delocalized class III system. In delocalized class III systems the use of terms such as 'IV-CT' is not precise, but in the absence of a more descriptive

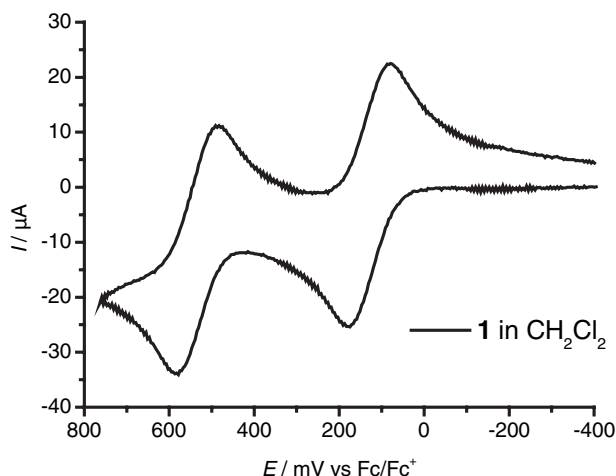


Figure 1. Cyclic voltammogram of compound **1** in dichloromethane at a scan rate of $v = 250 \text{ mV s}^{-1}$ (0.2 M TBAH was used as supporting electrolyte)

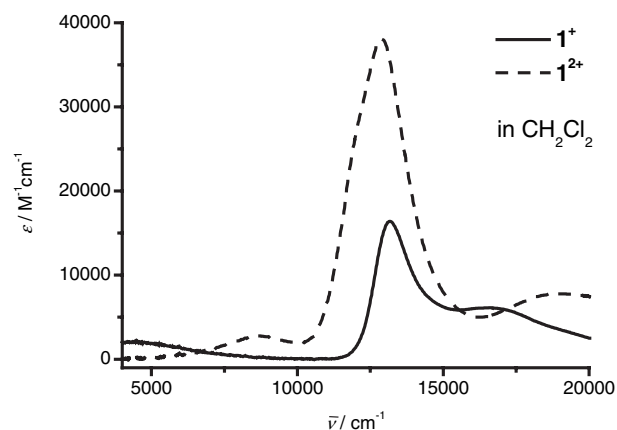


Figure 2. Absorption spectra of **1**⁺ (solid line) and **1**²⁺ (dashed line) in dichloromethane measured by spectroelectrochemistry (0.2 M TBAH was used as supporting electrolyte)

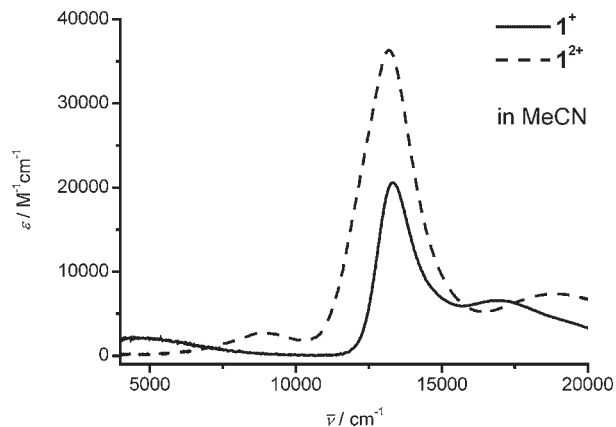


Figure 3. Absorption spectra of 1^+ (solid line) and 1^{2+} (dashed line) in acetonitrile measured by spectroelectrochemistry (0.2 M TBAH was used as supporting electrolyte)

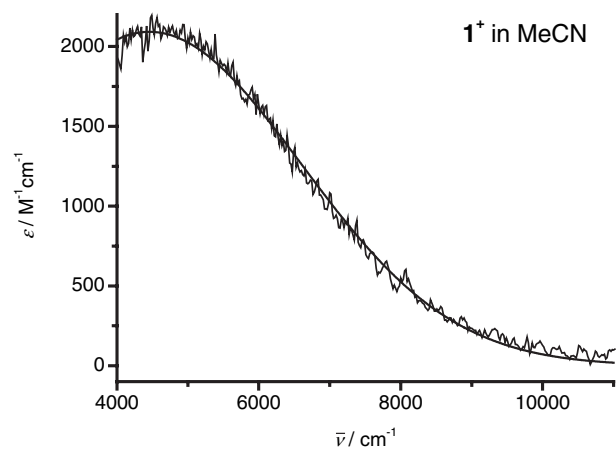


Figure 5. Fit of the IV-CT band of 1^+ in acetonitrile with a single Gaussian function

language, and in keeping with convention, we use this term to describe the NIR transition. The total reorganization energy in 1^+ is significantly lower than in *para*-coupled bis(triarylamine) radical cations.¹ Owing to the extremely low absorption maximum of the IV-CT-band of 1^+ , the low-energy side of this band was out of the spectral range of our instrument, therefore a detailed Marcus–Hush analysis was not possible.⁷ For strongly coupled systems at the borderline between class II and III a detailed band shape analysis revealed a cutoff at the low-energy side of the IV-CT band at $\lambda = 2V$.¹ This results in asymmetric IV-CT bands that show a stronger decrease in absorption at the low-energy side than predicted by a theoretically expected Gaussian-shaped curve.¹ This is also observed for the radical cations of **1** in dichloromethane and acetonitrile, as shown in Figs 4 and 5.

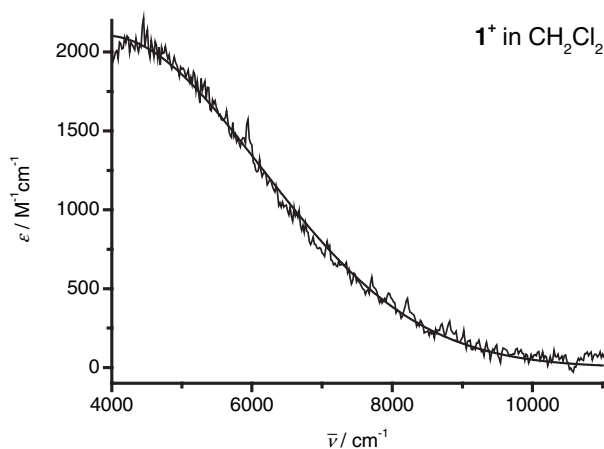


Figure 4. Fit of the IV-CT band of 1^+ in dichloromethane with a single Gaussian function

For fitting the IV-CT band, two Gaussian functions were sufficient in total (one for the IV-CT band and one for the low-energy side of the $\pi \rightarrow \pi^*$ excitation band). The maximum of the fitted Gaussian-shaped curve is somewhat lower in energy than the experimental values (3880 cm^{-1} vs. 4250 cm^{-1} in dichloromethane and 4460 cm^{-1} vs. 4500 cm^{-1} in acetonitrile). When the IV-CT band of 1^+ was detected in pure dichloromethane (without supporting electrolyte TBAH) by titration with SbCl_5 , the band maximum was approximately at 4000 cm^{-1} at the end of the range of our instrument (data not shown). The asymmetric band shape and the negligible solvatochromism of the band maximum observed for 1^+ suggest that, at least in relatively non-polar media, 1^+ is approaching a fully delocalized class III structure. As such, the electronic coupling element V can be estimated from the fitted maximum in dichloromethane by $V = \tilde{\nu}_{\text{max}}/2$ as $V = 1940 \text{ cm}^{-1}$. This value has to be treated with care because the approximation of the Marcus–Hush two-state model that there is no direct interaction between the terminal states (tight binding approximation)¹⁵ is not fulfilled for *ortho*-coupled systems. Furthermore, as stressed by Nelsen *et al.*, the two-state model should not be used to analyze clearly delocalized systems where the optical spectra show vibrational fine structure.¹⁶

An interesting question is whether the electronic coupling in 1^+ is mainly caused by a direct interaction between the two nitrogen lone-pair orbitals (through space) or mediated by the aromatic *o*-phenylene spacer (through a bond). It has been demonstrated that the electronic coupling through phenylene spacers is strong when the redox moieties are attached relative to each other in *ortho* or *para* position, whereas for *meta*-coupled systems only a weak interaction has been observed.^{11,17–19} With respect to these investigations a strong electronic through-bond interaction could be expected for 1^+ . On the other hand, the

dianisylamine redox centers are expected to be almost perpendicular to the *o*-phenylene bridge in $\mathbf{1}^+$. Owing to steric hinderance, planarization is not possible. This might also be the reason for the low reorganization energy λ in $\mathbf{1}^+$. It has been pointed out that the relative conformation of redox centers and bridge is crucial for the through-bond charge transfer probability.^{9,20} The most effective charge transfer geometry is achieved upon planarization, which results in effective through- π -conjugation between neutral and charged redox centers.²⁰ Because this is not possible in $\mathbf{1}^+$ we suggest that direct interaction through space between the two nitrogen lone-pair orbitals plays an important role. Compared to a [phenothiazine/phenothiazine radical cation] CT complex, $[(\text{PH})_2]^+$, the electronic coupling was found to be twice as high in the radical cation of 1,2-bis(*N*-phenothiazinyl)-4,5-dimethyl-benzene, $\text{P}(\textit{o}$ -phenylene) P^+ , owing to an additional bridge connectivity.¹⁰ We conclude that also in $\mathbf{1}^+$ both interactions, through bond as well as through space, contribute significantly to the electronic coupling.

When molecules such as triarylamines are used as hole-conducting materials in electro-optic devices, electron (or hole) transfer occurs as intermolecular charge migration between neutral and charged molecules. One factor that may lead to improved hole mobility is minimization of the reorganization energy λ .^{21–23} Owing to their extremely low reorganization energy, $\mathbf{1}^+$ and related tetraaryl-*o*-phenylenediamines¹² might be highly favorable for applications as hole-conducting materials.^{22,23}

Acknowledgments

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