Twist-Dependent Electronic Coupling in an Organic Intervalence Radical Cation
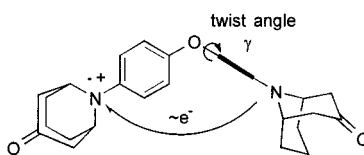
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ABSTRACT

The nearly 90° twist between the reduced dialkylaniline π system and the oxygen atom p lone pair orbital limits electronic interaction between the reduced and oxidized aniline units and makes varying this twist angle a principal factor that facilitates intramolecular electron transfer.

Charge-localized symmetrical intervalence (IV) radical cations $M-B-M^+$ provide simple model systems for electron transfer. They have the same two charge-bearing units (M) symmetrically attached to an organic bridge (B) and are at an oxidation level that puts the M units in different oxidation states. They show an intervalence charge-transfer (IV-CT) optical absorption band corresponding to transferring an electron from one M group to the other. Hush provided a simple theory for estimating the size of the off-diagonal matrix coupling element H_{ab} (often called V) from the position of the absorption maximum ($h\nu_{max}$), width at half-height ($\Delta h\nu_{1/2}$) and maximum molar absorption intensity (ϵ_{max}) of the IV-CT band if the distance the electron is transferred between the two M units is known.[1] This theory uses the Marcus–Hush two state model, in which the diabatic energy surfaces (those that would be present in the absence of electronic coupling) are parabolas centered at 0 and 1 on an electron transfer coordinate, and the adiabatic ground and excited state surfaces resulting from electronic coupling may be analytically described using only two parameters, the vertical excitation energy (Marcus's λ, which is equal to $h\nu_{max}$ for symmetrical intervalence compounds) and H_{ab}.[2] This

simple model appears to adequately describe the surface upon which electron transfer occurs in several cases. This has been demonstrated most recently by measuring the electron-transfer barrier for several localized IV compounds having tetrasubstituted hydrazine and trisubstituted diazenium M units and showing that the λ and H_{ab} parameters obtained from their IV-CT bands predict the rate constant for electron transfer surprisingly accurately.[3] The electron-transfer barrier decreases as H_{ab}/λ inreases, and when H_{ab} exceeds $\lambda/2$, it disappears entirely, the charge becomes delocalized equally over both M units, and $h\nu_{max}$ becomes equal to $2H_{ab}$.[4]

Walter demonstrated that triarylamines having *para* substituents were stable in the radical cation oxidation states,[5] and much work involving cations and polycations having Ar_3N M groups linked *meta* to each other has been done, especially by the groups of Launay,[6] who used Hush theory to extract H_{ab} values, and of Blackstock, who extended the

(1) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005. (c) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135.

(2) For reviews of Marcus theory, see: (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322. (b) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441–99.

(3) (a) Nelsen, S. F.; Ismagilov, R. F.; Trieber, D. A., II. *Science* **1997**, *278*, 846. (b) Nelsen, S. F.; Ismagilov, R. F.; Gentile, K. E.; Powell, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 7108.

(4) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(5) (a) Walter, R. I. *J. Am. Chem. Soc.* **1955**, *77*, 5999. (b) Walter, R. I. *J. Am. Chem. Soc.* **1966**, *88*, 1923, 1930. Good correlation between the ET parameters obtained from the optical spectra for some Class II and Class III systems has been pointed out.[6]

(6) (a) Bonvoisin, J.; Launay, J.-P.; Van der Auweraer, M.; De Schryver, F. C. *J. Phys. Chem.* **1994**, *98*, 5052; **1996**, *100*, 18006. (b) Bonvoisin, J.; Launay, J.-P.; Verbouwe, W.; Van der Auweraer, M.; De Schryver, F. C. *J. Phys. Chem.* **1996**, *100*, 17079.

number of **M** groups and studied dendrimeric systems.[7] Lambert and co-workers have studied the effect of bridge size on H_{ab} of dimeric *para*-linked triarylamines[8] and have shown that even the *p*-phenylenediamine derivative **1**$^+$, which
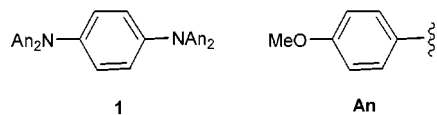
has five bonds separating its nitrogens, is a charge-localized Class II system, although its electron-transfer barrier is so low that the IV-CT band is distinctly distorted from the near-Gaussian shape usually observed for such bands by being cut off on the low energy side.[9] In contrast to **1**$^+$ and analogues with larger bridges, the optical spectrum of **2**$^+$
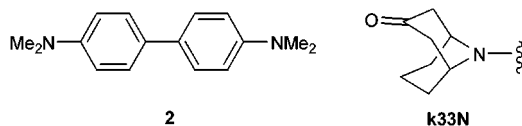
demonstrates that with dialkylaniline-centered **M** groups, delocalization is maintained over the nine bonds between the nitrogens of this biphenyl derivative.[10] In this work we studied **3**$^+$, which has bicyclononyl groups replacing the dimethylamino groups used for **2**$^+$ to confer kinetic stability,[11] showed that it is localized, and examined the importance of twist about its Ar−O bonds on its electron-transfer properties using calculations.
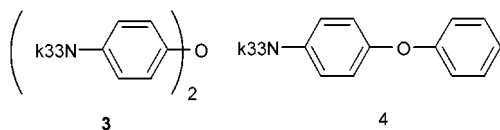
The bis-aniline ether **3** and its monoaniline analogue **4** were prepared by double Michael addition of commercially available aromatic amines to 2,7-cyclooctanedione, as previously described for making the *p*-phenylenediamine derivative.[11] The cyclic voltammogram of **3** shows reversible one electron oxidation waves at +0.70 and +0.95 V vs SCE (in acetonitrile containing 0.1 M tetrabutylammonium perchlorate, measured relative to ferrocene at 0.395 V), and **4** shows a single reversible oxidation wave at +0.77 V. The cations **3**$^+$ and **4**$^+$ were obtained using oxidation by $NO^+PF_6^-$ in CH_2Cl_2, and their optical spectra were recorded (see Figure 1). The brick-red color of **3**$^+$ persists for days if the sample is stored at −22 °C in the absence of air. The visible band
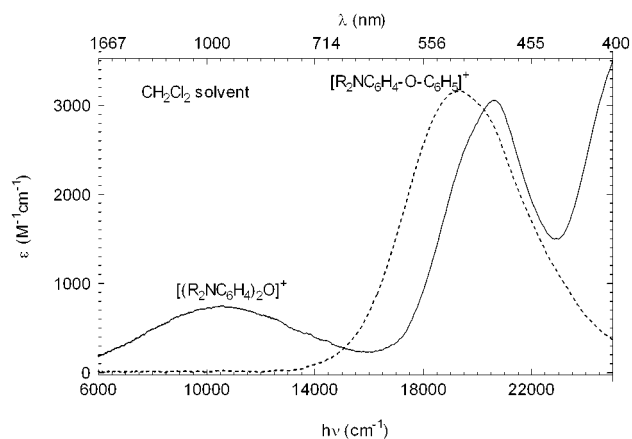
(7) (a) Stickley, K. R.; Blackstock, S. C. *J. Am. Chem. Soc.* **1994**, *116*, 11576. (b) Stickley, K. R.; Selby, T. D.; Blackstock, S. C. *J. Org. Chem.* **1997**, *62*, 448. (c) Selby, T. D.; Blackstock, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 12155.
(8) (a) Lambert, C.; Nöll, G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2107. (b) Lambert, C.; Nöll, G. *J. Am. Chem. Soc.* **1999**, *121*, 8434.
(9) Nelsen, S. F. *Chem. Eur. J.* **2000**, *6*, 581.
(10) Nelsen, S. F.; Tran, H. Q. *J. Am. Chem. Soc.* **1998**, *120*, 298.
(11) Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.

Figure 1. Optical Spectra of **3**$^+$ and **4**$^+$ (broken line) in methylene chloride.

at $h\nu_{max} = 18\,700$ cm^{-1} in **4**$^+$ moves to higher energy, 20 300 cm^{-1} in **3**$^+$, and a near-IR (nIR) band appears, having $h\nu_{max} = 10\,600$ cm^{-1} ($\epsilon_{max} = 720$ M^{-1} cm^{-1}, width at half-height $\Delta h\nu_{1/2} = 7000$ cm^{-1}). The bandwidth is substantially larger than the 4930 cm^{-1} lower limit for a Class II IV-CT band at $h\nu_{max} = 10\,600$ cm^{-1}.[1,2] We assign the visible band as a π,π^* excitation in the aryloxyaniline cation portion of the molecule, and the nIR band as the Hush-type IV-CT transition for a Class II (localized) intervalence compound. The above parameters make the transition dipole on the adiabatic surface $\mu_{12} = 2.17$ D, and the product $d_{ab}H_{ab} = 4780$ Å cm^{-1}, where d_{ab} is the electron transfer distance on the diabatic surface, using nomenclature and equations that were recently discussed in detail.[12] Although the distance between the nitrogens from the X-ray structure of neutral **3** is 9.97 Å, the d_{ab} required to calculate H_{ab} will be significantly smaller than that, because charge will be delocalized into the benzene rings of **3**$^+$. Using the dipole moments calculated by AM1,[13] we obtain an average distance on the adiabatic surface, d_{12} of 5.83 Å, which using experimental μ_{12} as previously described,[12] gives an estimated d_{ab} value of 5.90 Å. Thus the optical estimate of H_{ab} for **3**$^+$ using Hush's equations is 810 cm^{-1} (2.3 kcal/mol). This is about twice the value for the biphenyl-bridged bishydrazine previously studied,[3b] which surprised us because the calculated geometry for **3**$^+$ is very unfavorable for electronic interaction between the aniline units. H_{ab} is known to depend approximately upon the cosine of twist angles between p-orbitals at the bonds connecting the charge-bearing units.[1,2] As shown in Scheme 1, there are four single bonds involved, two N,Ar bonds (twist angle θ) and two O,Aryl bonds (twist angle γ). The X-ray structure of neutral **3** (see Supporting Information) gave θ values of 16° and 22° and γ angles of 1° and 62°. Such twist angles

(12) Nelsen, S. F.; Newton, M. D. *J. Phys. Chem A.* **2000**, *104*, 10023.
(13) (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) Our AM1 calculations were carried out using various versions of Timothy Clark's program VAMP. Rauhut, G.; Chandrasekhar, J.; Alex, A.; Steinke, T.; Clark, T. *VAMP 5.0*, Oxford Molecular: Oxford, 1994.
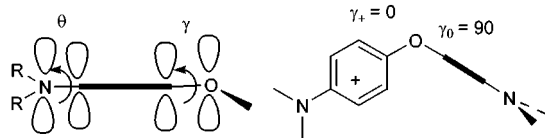
are rather easy to change from their optimum values; they might be different in solution and would certainly be different for 3^+, which is the oxidation state of interest. We have carried out AM1 calculations on 3^+ in both its charge-localized ground state (we will abbreviate it c^+, for cation) and with C_2 symmetry imposed (t^+, for transition state, to allow calculation of H_{ab} using Koopmans' theorem (we call this value V_K, as we did previously[10]). This Koopmans' approximation used with AM1 calculations has been demonstrated to work well for charge-delocalized amino-substituted aromatic intervalence compounds such as 2^+ and 5^+ (that is, $2V_K$ values are close to the observed transition
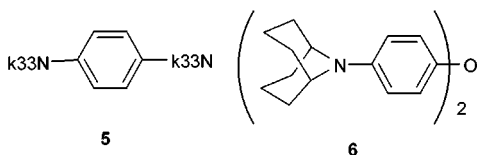
energies)[10] and also to work rather well for aromatic-bridged bis(hydrazine) IV compounds for which H_{ab} has been determined optically, when the value calculated at the θ value of the transition state is adjusted to that for the relaxed cation using $\cos\theta$ relationships.[14,15] We suggest that the Ar,N θ values should be small enough for 3^+ that both $\cos\theta$ values will be close to 1. For simplicity, our calculations were carried out on the compound without the keto groups, 6^+. Work on the p-phenylene diamine derivatives has shown that the geometries about the nitrogens are very similar with and without the keto groups.[10,16] The θ values for c^+ calculated by AM1 are $\theta_+ = 13°$ and $\theta_0 = 25°$ and for t^+ $\theta = 19°$, but AM1 calculations are known to predict too much twisting for structures containing 9-azabicyclo-[3.3.1]nonyl and related bicyclic ring systems, and the X-ray structure of 5^+

has $\theta = 1°$.[16] Despite the tendency of AM1 to predict twists that are too large, the Ar,O twist angle γ is calculated to be close to 0° at the oxidized end ($\gamma_+ = 0.2°$ for the unconstrained system, and 0.1° when the θ values are fixed at 0°). In contrast, γ_0 is calculated to be 82° ($\cos\gamma_0 = 0.14$) for the unconstrained system and 87° ($\cos\gamma_0 = 0.05$) when the θ values are fixed at 0°. If such large values were the only ones that mattered, twist would nearly shut down electron transfer in 3^+ and make the IV-CT band too weak to observe, in contrast to experiment. However, twisting about the O−Ar bond that changes γ_0 is calculated to be very facile. As we pointed out previously, for accurate estimation of the expectation values for calculated quantities that change significantly over a rather flat energy surface, simple Boltzmann averaging over the appropriate energy surface suffices.[17] Such averaging using the calculated energy curve for changing γ_0 (see Figure 2) produces an H_{ab}
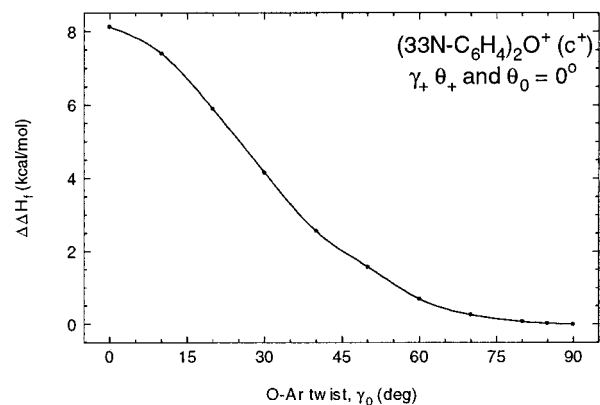

Figure 2. UHF/AM1-calculated enthalpy versus γ_0 twist angle plot (γ_+ and both θ angles held at 0°).

prediction about 20% as large as the 8 kcal/mol predicted for 3^+ at $\gamma = 0°$. This occurs because (for example) it only costs 0.26 kcal/mol to twist to $\gamma_0 = 70°$, where the "attenuation factor" in H_{ab} caused by the twisting is $\cos70° = 0.34$. The Boltzmann averaged AM1 calculation gives remarkably close to the experimental value of H_{ab}, although the real energy surface is considerably more complex than the simple one twist angle averaging done here. These calculations show that the twist angle γ_0 will be an especially important factor controlling the ET rate constant in 3^+, because its most stable form has an especially unfavorable γ_0 twist angle for electronic interaction between the charge-bearing anilino units. Thus in contrast to the p-phenylenebis-(hydrazines) previously studied, which have electron transfer rate constants that are principally limited by their large internal reorganization energies, the low-frequency Ar−O twist for 3^+ should be important for its electron transfer. We

(14) (a) DFT and ab initio calculations: Blomgren, F.; Larsson, S.; Nelsen, S. F. *J. Comput. Chem.* **2001**, *22*, in press. (b) AM1 calculations: Nelsen, S. F.; Blomgren, F. *J. Org. Chem.*, in revision.

(15) In the Marcus−Hush model, H_{ab} is constant at all points on the ET coordinate. Calculations show that for aromatic bridged hydrazines, H_{ab} depends significantly upon the position on the ET coordinate because θ is smaller at the transition state than at the relaxed ground-state structure.[14] This makes the experimental fact that simplest Marcus−Hush theory suffices for calculating the ET rate constant[3] seem anomalous. We suggest that this dilemma will be resolved by the observation of Talaga and Zink that the same adiabatic surface as for Marcus−Hush theory may be obtained for the same ET parameters λ and H_{ab} when a different two state model that makes H_{ab} depend on position on the ET coordinate is employed: Talaga, D. S.; Zink, J. I. *J. Phys. Chem.* **1996**, *100*, 8712. (Note: their nomenclature differs greatly from that used in this paper. They do not discuss λ at all and employ ϵ for H_{ab}. Nevertheless, their Model 1 is equivalent to Marcus−Hush theory and Model 3 is the one that presumably applies to 3^+).

(16) Nelsen, S. F.; Ramm, M. T.; Ismagilov, R. F.; Nagy, M. A.; Trieber, D. A., II; Powell, D. R.; Chen, X.; Gengler, J. J.; Qu, Q.; Brandt, J. L.; Pladziewicz, J. R. *J. Am. Chem. Soc.* **1997**, *119*, 5900.

(17) (a) Nelsen, S. F.; Frigo, T. B.; Kim, Y.; Blackstock S. C. *J. Am. Chem. Soc.* **1989**, *111*, 5387. (b) If the values calculated are not accurate, of course, the answer will not be, but summing up values calculated at various points on the energy surface weighted by $e^{-\Delta E/RT}$ is a good approximation.

hope to report on such studies on 3^+ and related compounds with other bridging atoms the future.

Supporting Information Available: Preparations of **3** and **4** and the X-ray crystallographic structure of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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