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Comparison of the Singlet, Triplet Energy Gap of a Symmetrical Diradical Dication with ET Parameters Derived from Its Optical Spectrum

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A relationship between the magnetic super-exchange coupling (J),[1] a two-electron interaction, and the electron transfer (ET) super-exchange coupling (V), a one-electron interaction, was first postulated by Kramers in 1934, and largely developed by Anderson in considering the magnetic properties of solid insulators.[2] Considering antiferromagnetic exchange interactions in π-stacked crystals, Soos pointed out an approximate relationship using the transition energy of the charge transfer (CT) band ($h\nu_{CT}$): $J \sim V^2/h\nu_{CT}$.[3] For an intramolecular ET system, the stabilization of the adiabatic minima relative to parabolic diabatic ($V = 0$) surfaces that interact by an electronic coupling matrix element V is $-V^2/(\lambda + \Delta G°)$, where λ is the vertical reorganization energy and $\Delta G°$ is the free energy change for the reaction, and $h\nu_{CT} = \lambda + \Delta G°$.[4] Figure 1 shows the relationship between the diabatic and adiabatic surfaces for a $\Delta G = 0$ ET reaction. Okamura and co-workers gave eq 1, which describes a diradical pair where the singlet state is stabilized by ET and the triplet state is not.[5] They replaced the naturally occurring ubiquinone in the quinone,iron center of bacterium R.26 with menaquinone

$$|E(\text{singlet}) - E(\text{triplet})| = V^2/(\lambda + \Delta G°) \qquad (1)$$

(Q). After reduction to Q^-Fe^{2+}, low temperature photolysis produced the intermediate acceptor center (I, bacteriophytin) in its reduced state, which had a relatively long lifetime at low temperature, and the $I^-Q^-Fe^{2+}$ units showed an ESR spectrum from which the singlet, triplet energy gap, $|2J|$, was determined. The rate constant for ET within this complex to produce $IQ^{2-}Fe^{2+}$ was also measured, and eq 1 was used to extract the energy parameters associated with the ET reaction.[5] Extensive additional modeling of photocenters has been carried out,[6] including the development of artificial model systems which resemble the ESR spectral and ET properties of the natural ones.[7]

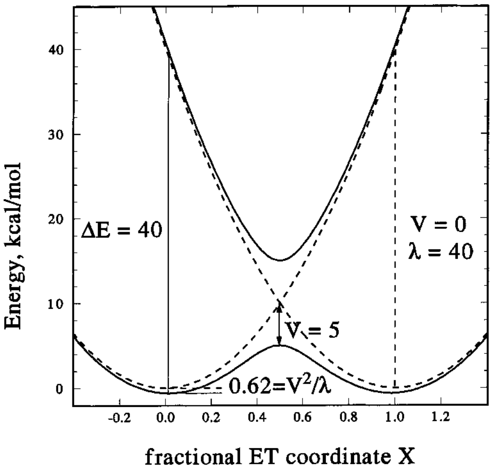
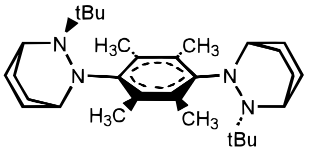


Figure 1. Marcus−Hush plot showing the relationship between the parabolic diabatic ($V = 0$) surfaces (broken lines) and adiabatic surfaces for $V = 5$ kcal/mol (solid lines) for a $\Delta G = 0$ ET having $\lambda = 40$ kcal/mol.

The work described here provides the first quantitative experimental test of the relationship between J, V, and $(\lambda + \Delta G°)$, based upon the properties of the +1 and +2 oxidation states of the symmetrical bis-hydrazine **1**. Both $\mathbf{1}^+$ and $\mathbf{1}^{2+}$ have been isolated as tetraphenylborate salts and their crystal structures determined.[8] $\mathbf{1}^+$ is a symmetrical, charge-localized intervalence compound so it has $\Delta G° = 0$ for intramolecular ET. This makes $\lambda(\mathbf{1}^+) = h\nu_{CT}(\mathbf{1}^+) = 40.3$ kcal/mol in acetonitrile and 36.1 kcal/mol in methylene chloride. Hydrazines have exceptionally large internal reorganization energies (the λ_v component of λ).[9] Even $\mathbf{2}^+$, the demethylated analogue of $\mathbf{1}^+$, which has a significantly larger V value because it is less twisted at its N-aryl bonds, is charge localized.[10] Charge localization requires that V be less than $\lambda/2$ for both molecules.[4] $V(\mathbf{1}^+)$ was estimated by using Hush's method (eq 2).[11] Analysis of the CT band gives $h\nu_{CT}$, the



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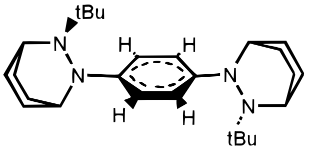

2

$$V = 0.0206(h\nu_{CT}\Delta\nu_{1/2}\epsilon_{max})/d \qquad (2)$$

bandwidth at half-height ($\Delta\nu_{1/2}$), and extinction coefficient at the CT band maximum (ϵ_{max}). The ET distance (d), which is also required to evaluate $V(\mathbf{1}^+)$, is not known even though the atom

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(1) We use the spectroscopists' convention, in which the energy difference between the triplet and singlet states of a biradical is $2J$, corresponding to the convention of designating the minimum separation between the ground state and excited-state surfaces for an ET reaction as $2V$.[5,9] Others use different nomenclature,[5] including calling the triplet, singlet energy gap J.

(2) For a review, see: Anderson, P. W. In *Magnetism*; Rado, G. T., Suhl, H., Eds.; Academic Press: New York, 1965; Vol. 1, Chapter 2, p 25.

(3) (a) Soos, G. T. *Annu. Rev. Phys. Chem.* **1974**, *25*, 121. (b) For a recent, generalized treatment applied to copper oxide superconductors, see: Wang, Y. J.; Newton, M. D.; Davenport, J. W. *Phys. Rev. B* **1992**, *46*, 11935.

(4) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441−99. See eq 33.

(5) (a) Okamura, M. Y.; Fredkin, D. R.; Isaacson, R. A.; Fehler, G. *Tunneling in Biological Systems*; Chance, B., DeVauld, D. C., Frauenfelder, H., Marcus R. A., Schrieffer, J. B., Sutin, N., Eds.; Academic Press: New York, 1979; pp 729−43. (b) Okamura, M. Y.; Isaacson, R. A.; Fehler, G. *Biochim. Biophys. Acta* **1979**, *546*, 394.

(6) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435−61.

(7) (a) Wasielewski, M. R.; Gaines, G. L., III.; O'Niel, M. P.; Svec, W. A.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1990**, *112*, 4559. (b) Wasielewski, M. R.; Gaines, G. L., III.; Wiederrecht, G. P.; Svec, W. A.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1993**, *115*, 10442.

(8) (a) Nelsen, S. F.; Ismagilov, R. F.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 10213. (b) About 1% smaller values for $V(\mathbf{1}^+)$ calculated by using (2) are quoted in ref 8a because a slightly larger d was employed in their calculation. Use of about 15% smaller values for V in acetonitrile, based upon a modification of (2) that puts the square root of the refractive index into the denomonator, is also discussed in ref 8a, but for simplicity, only Marcus−Hush theory is employed here.

(9) (a) Nelsen, S. F. *Molecular Structures and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 3, Chapter 1, p 1. (b) Nelsen, S. F.; Adamus, J.; Wolff, J. J. *J. Am. Chem. Soc.* **1994**, *116*, 1589. (c) Nelsen, S. F.; Ramm, M. T.; Wolff, J. J.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 6863.

(10) Nelsen, S. F.; Ismagilov, R. F.; Powell, D. R. *J. Am. Chem. Soc.* **1996**, *118*, 6313.

(11) (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*, 135−57.

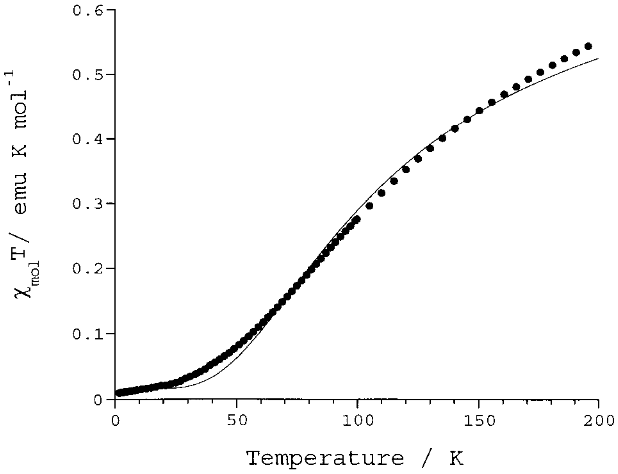

Figure 2. Plot of χT vs T for polycrystalline $\mathbf{1}^{2+}(Ph_4B^-)_2$ superimposed with a calculated curve[10] for $-J = 103k_B$T.

positions are available from the X-ray structure. We used $\mathbf{1}^{2+}$ to estimate d for $\mathbf{1}^+$.[8] $\mathbf{1}^{2+}$ has a singlet bis-radical ground state but a small enough J that the triplet can be observed, and its dipolar splitting (D) measured. Because the concept of an average ET distance appears close to the concept of an average distance between the electrons in a triplet diradical (d_{esr}), we have used the triplet form of $\mathbf{1}^{2+}$ as a model to estimate the d value for $\mathbf{1}^+$. Using the point-dipole approximation, d_{esr} is proportional to the negative cube root of D.[12] $\mathbf{1}^{2+}$ in a 1:1:1 acetonitrile, butyronitrile, methylene chloride glass exhibits a triplet spectrum having $D/hc = 0.0147(4)$ cm^{-1}, E/hc ca. 0, and line width ca. 30 G. This D/hc value corresponds to $d_{esr} = 5.62(5)$ Å, 0.9(9)% smaller than the X-ray crystallographic distance between the N_{Ar} nitrogens in $\mathbf{1}^{2+}(Ph_4B^-)_2$ of 5.673 Å. When the N,Ar twist angle is smaller because fewer methyls are placed on the aryl ring, more spin density appears in the aryl ring, and d_{esr} becomes significantly smaller than the distance between the N_{Ar} nitrogens, as expected.[8] The values obtained from the optical spectrum of $\mathbf{1}^+$ using (2) with $d = 5.62$ Å are $V(\mathbf{1}^+) = 3.32$ and 3.34 kcal/mol in acetonitrile and methylene chloride, respectively.[8b]

SQUID measurements on polycrystalline $\mathbf{1}^{2+}(Ph_4B^-)_2$ produce the $\chi_{mol}T$ versus T plot of Figure 2, which has the shape characteristic for a ground-state singlet diradical having an antiferromagnetic interaction. Analysis of these data between 1.8 and 200 K with use of the dimer model[13] gives $-J = 103(7)k_B$T $= 0.205(14)$ kcal/mol. Analysis of the ESR spectral intensities between 4 and 113 K in the above glass gives $-J = 89k_BT = 0.18$ kcal/mol, showing that J is not very sensitive to whether the sample is polycrystalline or in a glass. In contrast to Okamura's case, which is a two-state system, $\mathbf{1}^{2+}$ is a three-state system because the ground state, which may be abbreviated $\mathbf{Hy}^+$-$\mathbf{B}$-$\mathbf{Hy}^+$ (**Hy** stands for charge-bearing hydrazine unit and **B** for the aromatic bridge), has two equal energy lowest CT states, $\mathbf{Hy}^{2+}$-$\mathbf{B}$-$\mathbf{Hy}^0$ and $\mathbf{Hy}^0$-$\mathbf{B}$-$\mathbf{Hy}^{2+}$. Numerical solution of the 3 × 3 Hamiltonian by using as diabatic surfaces $H_{AA} = \lambda X^2$ and $H_{BB} = \lambda(1 - X)^2 + \Delta G^\circ$, $H_{CC} = \lambda(1 + X)^2 + \Delta G^\circ$ (X is the ET coordinate),[4] with $V_{AB} = V_{AC}$ and $V_{BC} = 0$, gives a lowest energy surface, predominantly H_{AA} in character, having a minimum at $X = 0$. Making the same assumption as Okamura that only the singlet is stabilized, this gives eq 3 to an excellent approximation

$$|E(\text{singlet}) - E(\text{triplet})| = 2\,V(\mathbf{1}^{2+})^2/(\lambda + \Delta G^\circ) \qquad (3)$$

for the sizes of V and $\lambda + \Delta G^\circ$ appropriate for $\mathbf{1}^{2+}$.[14] $\mathbf{1}^{2+}$ in acetonitrile has a CT band with $\lambda_{max} = 446$ nm ($h\nu_{CT} = \lambda + \Delta G^\circ = 64.1$ kcal/mol), bandwidth at half-height of 5500 cm^{-1}, and ϵ_{max} of 2100 M^{-1} cm^{-1}. Hush's (2) gives $V(\mathbf{1}^{2+})$ as 3.81 kcal/mol.[15] The $-J$ value predicted from the optical spectrum of $\mathbf{1}^{2+}$ by using (3) is 0.23 kcal/mol, in excellent agreement with the experimental measurements. $V(\mathbf{1}^{2+}) = 1.15\ V(\mathbf{1}^+)$ when the same d value is used. The presence of two CT states for the bis(cation) and only one for the radical cation leads to a prediction of a $\sqrt{2}$ larger V for the bis(cation), but quantitating the ratio expected for **1** is complicated by the probable difference in nitrogen lone pair, aryl ring twist angles (ϕ). V should be roughly proportional to cos ϕ at each ring, N bond. In crystals, $\phi = 63.6°$ for $\mathbf{1}^{2+}$ and 66.2° at the oxidized unit of $\mathbf{1}^+$, but averages to 50.5° at the disordered reduced unit.[8a] The ϕ values might also be different in solution than in the crystals.

The relationships demonstrated here between the optical properties of a bis-radical dication and its magnetic properties and between the V values of an intervalence compound and its oxidation product suggest new ways to estimate both J and V. We are currently studying related systems to see whether these suggestions will prove to be useful.

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[13] We used $\chi_{mol} = \{(1 - x)(2Ng^2\mu^2/k_BT)/(3 + \exp(2J/k_BT))\} + x(C/(T - \theta))$, where x is the fraction of monoradical impurity (ca. 3%). The first term corresponds to the dimer (ST) model and the second to the Curie−Weiss model: see Carlin, R. L. *Magneto-Chemistry*; Springer-Verlag: Weinheim 1985; pp 75−77.

[14] (a) Okamura and others used perturbation arguments in deriving relations such as (1), which means that they might become inaccurate at high V values. As pointed out by Creutz and co-workers,[14b] these relationships are not limited to small V, as can be obtained by solution of the Hamiltonian. Solution of the 2 × 2 Hamiltonian for Okamura's case does indeed produce (1). (b) Creutz, C.; Newton, M. D.; Sutin, N. *J. Photochem. Photobiol. A: Chem.* **1994**, *82*, 47.

[15] (a) Because $\mathbf{1}^{2+}$ is symmetrical, excitation at both hydrazine units will give absorption, so ϵ_{max} if the V values were the same would be twice as large as for the unsymmetrical $\mathbf{1}^+$, where only one hydrazine unit can be excited. We therefore used $\epsilon_{max}/2$ in (2) for calculating $V(\mathbf{1}^{2+})$. Leaving out this statistical factor of 2 would make $V(\mathbf{1}^{2+})$ a factor of $\sqrt{2}$ larger, and $V(\mathbf{1}^{2+})^2/(\lambda + \Delta G^\circ)$ a factor of 2 larger than the numbers quoted in the text. (b) The band shape for bis-hydrazine dications is significantly broader at the base than is that of the intervalence oxidation state. We applied (2) despite this difference. Partial overlap with a higher energy band also required estimating $\Delta\nu_{1/2}$ for $\mathbf{1}^{2+}$ as twice the band half-width on the low-energy side. (c) Another factor complicating analysis is that using the SQUID J of -0.205 kcal/mol, the $\mathbf{1}^{2+}$ sample examined is about 2/3 singlet and 1/3 triplet, and both species might contribute to the 446 nm absorption.