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Effects of Bridge Redox State Levels on the Electron Transfer and Optical Properties of Intervalence Compounds with Hydrazine Charge-Bearing Units

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This work concerns zero driving force thermal electron transfer (ET) reactions within charge-localized symmetrical intervalence (SIV) compounds. SIV compounds have different charges on otherwise identical charge-bearing units that are connected by a bridge, and most examples studied have had transition-metal charge-bearing units.[1] SIV compounds show charge-transfer (CT) bands from which two fundamental parameters for ET, the vertical reorganization energy (λ) and the electronic coupling matrix element (V), may be obtained using Marcus−Hush theory.[2] We designate the CT band corresponding to ET between the charge-localized minima, as well as the λ and V associated with this band, with subscript SE (for superexchange).[3] In the Marcus−Hush model (see Figure 1a), the diabatic SE energy surfaces are parabolas centered at 0 and 1, respectively, on an ET coordinate X. Electronic coupling through the bridge, measured by the off-diagonal matrix element (V_{SE}) in a 2 × 2 secular determinant produces a ground-state double-well adiabatic energy surface and a single minimum excited-state surface. Their energy separation at the ground-state minimum is λ_{SE}, which is the transition energy of the CT band at its maximum ($h\nu_{max}$). Hush derived a simple equation for evaluation of V_{SE} from the CT_{SE} band.[2e] The most direct test of ET parameters obtained from a CT_{SE} band is comparing the calculated rate constant for intramolecular ET with that measured experimentally (k_{et}), but this test has not been applied to metal-centered examples because the k_{et} values calculated are too large to measure.[4] Hydrazines have far larger internal vibrational reorganization energies (λ_v) than metal complexes, so their λ_{SE} values are much higher. This allows k_{et} to be in the measurable range even when V_{SE} is rather large,[5] making the CT band intense enough to observe easily. The durene-bridged compound $\mathbf{1}^+$ has $k_{et} = 2.6 \times 10^8$ s^{-1} at −8 °C in CH_3CN, determined by dynamic electron spin resonance (ESR) spectroscopy.[6] It has a large enough V_{SE} to make k_{et} fall in the adiabatic regime, where it is very sensitive only to ΔG^*.[2] A slight modification of the Marcus−Hush analysis of CT_{SE} bands allows accurate calculation of k_{et} from the λ_{SE} and V_{SE} obtained for $\mathbf{1}^+$, its analogue with two fewer methyl groups,[6b] and three bis(hydrazines) with saturated bridges;[5] therefore, the Hush V_{SE} equation[2e] is a rather good approximation.[7]

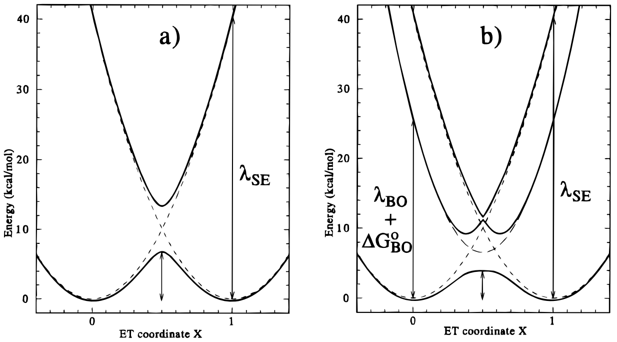
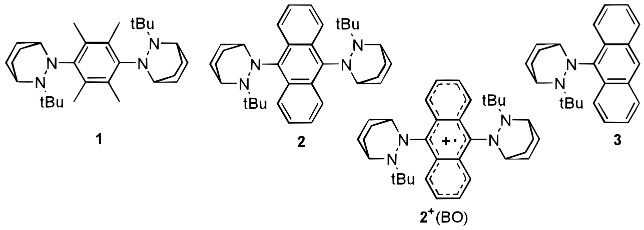


Figure 1. (a) Marcus−Hush plot for $\mathbf{1}^+$ showing the diabatic SE surfaces (broken lines) and the adiabatic surfaces (solid lines) obtained using λ_{SE} = 40.3 kcal/mol and V_{SE} = 3.3 kcal/mol derived from the experimental CT band in acetonitrile. (b) Three-state model[11] plot for $\mathbf{2}^+$ using parameters (kcal/mol) $\lambda_{SE} = 40.3$, $V_{SE}^{eff} = -1.5$, $\lambda_{BO} = 19.2$, $\Delta G^\circ_{BO} = 6.5$, $V'_{BO} = 3.5$, for which $\Delta G^* = 4.2$ kcal/mol. Diabatic surfaces are shown as broken lines and adiabatic ones as solid lines.

This paper principally concerns $\mathbf{2}^+$, which we expected to have a k_{et} value no larger than that of $\mathbf{1}^+$ because the N_{Ar} lone pair, aryl π system twist angle ϕ, and, hence, λ_{SE} should be nearly the same. The ϕ values of crystalline $\mathbf{1}^+$ average 50.5° at the neutral hydrazine unit and 66.2° at the cationic hydrazine unit.[6b] X-ray data for neutral **3** ($\phi = 53.2°$) and $\mathbf{3}^+$ ($\phi = 66.7°$) provide models for the twist of the hydrazine units of $\mathbf{2}^+$ (their structures are reported in the Supporting Information). V_{SE} depends on overlap at the bonds connecting the charge-bearing units to the bridge, so it depends on cos ϕ and the orbital coefficients at the atoms involved. The larger π system of the bridge for $\mathbf{2}^+$ should lower its V_{SE} relative to that for $\mathbf{1}^+$, so smaller k_{et} for $\mathbf{2}^+$ than for $\mathbf{1}^+$ might be expected. However, k_{et} of $\mathbf{2}^+$ is far larger than that of $\mathbf{1}^+$. The ESR spectrum of $\mathbf{2}^+$ is that of a rapidly exchanging hydrazine-centered species at all accessible temperatures in CH_3CN and CH_2Cl_2, but a dynamic alternating line width effect was observed in acetone, allowing determination of k_{et} at −105, −100, and −95 °C as 1.6, 2.1, and 2.9 × 10^8 s^{-1}, respectively. ESR data for $\mathbf{1}^+$ in CH_3CN give rate ratios for $\mathbf{2}^+$:$\mathbf{1}^+$ of 173, 148, and 135 at these temperatures, corresponding to a $\Delta G^\ddagger$ decrease of 1.7 kcal/mol. The ET barrier ΔG^* for $\mathbf{2}^+$ in acetonitrile is estimated at 1.7 kcal/mol less than for $\mathbf{1}^+$ in acetonitrile,[6b] or ∼4.2 kcal/mol.



1 **2** **3** $\mathbf{2}^+$**(BO)**

The principal effect of changing from the durene bridge of $\mathbf{1}^+$ to the anthracene bridge of $\mathbf{2}^+$ is lowering the energy of bridge redox intermediates for $\mathbf{2}^+$. The optical spectrum of $\mathbf{2}^+$ is complex, and we use the spectra of the monohydrazine analogues **3** and $\mathbf{3}^+$ to help understand those of **2** and $\mathbf{2}^+$ (these spectra are shown in the Supporting Information). We attribute the visible

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

(2) (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (b) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (c) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135. (d) The solutions to the secular equation are given in ref 3b, eq 33. The minimum separation of the E_2 and E_1 surfaces occurs at X = 0.5 and is $2V_{SE}$, and the ET barrier ($\Delta G^*_{SE} = E_1(X = 0.5) - E_1(\min)$) is $\lambda_{SE}/4 - V_{SE} + V_{SE}^2/\lambda_{SE}$. (e) We used Hush's familiar formula,[2a−c] $V_H = (0.0206/d)(h\nu_{max}\,\Delta\nu_{1/2}\epsilon_{max})^{1/2}$, for calculating V values, where ϵ_{max} is the maximum extinction coefficient, $h\nu_{1/2}$ is the band width at half-height, and d is the electron-transfer distance. (f) The solutions[2d] are valid for for all values of V_{SE}: Creutz, C.; Newton, M. D.; Sutin, N. *J. Photochem. Photobiol. A.: Chem.* **1994**, *82*, 47.

(3) (a) "The term superexchange in the ET literature is generally meant to imply the mixing of donor and acceptor states by a virtual electronic state of the bridging species. In particular, usage of the term generally implies that neither electron nor hole is ever vibronically localized on the bridge" (ref 3b, p 46). (b) Kosloff, R.; Ratner, M. A. *Isr. J. Chem.* **1990**, *30*, 45.

(4) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148.

(5) (a) Nelsen, S. F.; Chang, H.; Wolff, J. J.; Adamus, J. *J. Am. Chem. Soc.* **1993**, *115*, 12276. (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.

(6) (a) Nelsen, S. F.; Ismagilov, R. F.; Powell, D. R. *J. Am. Chem. Soc.* **1996**, *118*, 6313. (b) Nelsen, S. F.; Ismagilov, R. F.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 10213.

(7) Nelsen, S. F.; Ismagilov, R. F.; Trieber, D. W., II *Science* **1997**, *278*, 846.

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absorption for the neutral compounds to bridge reduction charge transfer (CT_{BR}), $Hy^0{-}B^0 \rightarrow Hy^+{-}B^-$, where Hy is the hydrazine unit and B is the bridge. The CT_{BR} bands in methylene chloride have the following parameters: **3**, $h\nu_{max} = 21\,500$ cm^{-1} ($\lambda_{max} = 465$ nm), $\epsilon_{max} = 3800$ M^{-1} cm^{-1} (all ϵ values are reported using these units); **2**, $h\nu_{max} = 19\,600$ cm^{-1} ($\lambda_{max} = 510$ nm), $\epsilon_{max} = 6000$.[8] Local excitations of the anthracene ring are also observed. That corresponding to the Clar *p* band shows vibrational fine structure, and the 0,0 band occurs at 1200 cm^{-1} lower energy for **2** than **3**. The Clar β bands are very broad: **3**, ~34 800 cm^{-1} ($\epsilon_{max} = 7300$); **2**, ~34 300 ($\epsilon_{max} = 11\,000$). Species $\mathbf{3}^+$ in acetonitrile shows two visible bands at 12 900 cm^{-1} (755 nm) $\epsilon_{max} = 450$ and 19 000 cm^{-1} (526 nm) $\epsilon_{max} = 2000$. We assign them as bridge oxidation bands, BO_1 and BO_2, respectively, corresponding to $Hy^+{-}B^0 \rightarrow Hy^0{-}B^+$ CT, from the highest occupied molecular orbital (HOMO) and either HOMO-1 of anthracene or a band of more complex origin, respectively. CT bands from orbitals below the HOMO have been reported for transition-metal-centered compounds.[4] The BO_1 band of $\mathbf{2}^+$ in acetonitrile has $h\nu_{max,BO} = 9000$ cm^{-1} (1110 nm), $\epsilon_{max} = 1400$, $\Delta\nu_{1/2} = 4300$ cm^{-1} (estimated from the low-energy side because of band overlap on the high-energy side) and has nearly the same parameters in acetone. Both BO bands are much lower in energy for $\mathbf{2}^+$ than those for $\mathbf{3}^+$, presumably because the anthracene ring of $\mathbf{2}^+$ has an electron-releasing neutral hydrazine substituent. Species $\mathbf{2}^+$ shows the optical bands expected for both oxidized and reduced hydrazine units, as required for a localized system. The CT_{SE} band expected for $\mathbf{2}^+$ near 14 100 cm^{-1} is probably present but is not resolved from the BO_2 band.

The striking feature of the absorption spectrum of $\mathbf{2}^+$ is that a CT_{BO} band occurs at significantly lower energy than its Hush-type CT_{SE} band, indicating that the anthracene ring oxidized state, $\mathbf{2}^+$(**BO**), cannot lie far above the hydrazine-centered $\mathbf{2}^+$ ground state. The BO_1 transition energy, $h\nu_{max,BO} = 25.7$ kcal/mol $= \lambda_{BO} + \Delta G°_{BO}$ for $\mathbf{2}^+$, making it unlikely that $\Delta G°_{BO}$ is larger than about 6 kcal/mol.[9]

Does such a low-lying $\mathbf{2}^+$(**BO**) surface mean that it will be an intermediate for ET between the hydrazine units of $\mathbf{2}^+$? Extensive theoretical work on how coupling of charge-bearing units with the orbitals of the bridge affects V_{SE} has been discussed by Newton.[10] The assumption of a small $V_{SE}/\Delta G°$ ratio is clearly not valid for the anthracene HOMO of $\mathbf{2}^+$, so a different approach is required. We suggest that it is useful to consider $\mathbf{2}^+$ as a three-state system having Marcus−Hush parabolic diabatic surfaces corresponding to charge localized on each hydrazine unit and a third parabolic energy surface corresponding to $\mathbf{2}^+$(**BO**) centered between them (see Figure 1b).[11] Whether $\mathbf{2}^+$(**BO**) is a minimum on the ground-state surface depends on the relative sizes of the matrix elements V_{BO} and $V_{SE}{}^{eff}$.[11b] Hush analysis of the CT_{BO} band of $\mathbf{2}^+$ in acetonitrile gives $V_{BO} = 4726/d_{BO}$ cm^{-1}.[2e] We believe that d_{BO} should be larger than half the distance between the nitrogens because charge in $\mathbf{2}^+$(**BO**) is delocalized over the 14-atom π system of the aryl ring; $V_{BO} = 4.5$ kcal/mol (using d_{BO} of 3.0 Å) and 3.9 kcal/mol (using 3.5 Å). *V* values evaluated from optical spectra which are smaller than Hush ones by a factor of $n_D{}^{-1/2} = 0.86$ for acetonitrile (n_D is the solvent refractive index) have been suggested by Young and co-workers,[12] and these lower *V* values better fit the observed k_{et} values for five bis(hydrazine) radical cations.[7] This would lower the V_{BO} estimated from the optical spectrum to 3.9 kcal/mol (using $d_{BO} = 3.0$ Å) and 3.3 kcal/mol (using 3.5 Å). At $V_{BO} = 3.5$ kcal/mol, the three-state model fits $\lambda_{BO} + \Delta G_{BO} = 25.7$ and $\Delta G^* = 4.2$ kcal/mol for $\Delta G°_{BO}$ rising from 6.3 (at $V_{SE}{}^{eff} = 1.0$) to 7.3 (at $V_{SE}{}^{eff} = 3.0$) kcal/mol, and the ground-state surface is very flat-topped, but $\mathbf{4}^+$(**BO**) is not an intermediate (see Figure 1b). At $V_{BO} = 2.5$ kcal/mol, fit is obtained for $\Delta G°_{BO} = 5.1$ kcal/mol (at $V_{SE}{}^{eff} = 1.0$) and 5.8 (at $V_{SE}{}^{eff} = 3.0$) kcal/mol and there is a minimum on the ground-state surface at $X = 0.5$ that is less than *RT* kcal/mol deep (0.13 kcal/mol at $V_{SE}{}^{eff} = 1.0$, falling to zero at $V_{SE}{}^{eff} = 1.0$) (see Supporting Information for more details). It appears from this modeling that $\mathbf{2}^+$ is near the borderline for which $\mathbf{2}^+$(**BO**) becomes a very shallow dip on the ground-state energy surface and that the barrier for ET between the hydrazine units is affected little by whether $\mathbf{2}^+$(**BO**) is an intermediate or not.

This approximate analysis[13] indicates how much information about ET reactions involving the bridge is present in the rich absorption spectrum of $\mathbf{2}^+$. Its ground state has charge localized on one hydrazine unit, but the bridge-oxidized state $\mathbf{2}^+$(**BO**) only lies a few kcal/mol higher in energy. $\Delta G°_{BO}$ is small enough to significantly lower the ET barrier, although if $\mathbf{2}^+$(**BO**) is an intermediate on the ground-state energy surface, the energy gap to the transition state for ET is very small. The bridge-reduced state lies too high in energy to affect the adiabatic ET surface for $\mathbf{2}^+$ significantly.

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Supporting Information Available: Preparation of **2** and **3** and their radical cations, and crystallographic data for **3** and $\mathbf{3}^+Ph_4B^-$ and their absorption spectra; plot of $\Delta G°_{BO}$ vs $V_{SE}{}^{eff}$ for three-state fits to $\mathbf{2}^+$ for V_{BO} 1.5, 2.5, 3.5, and 4.5 kcal/mol (15 pages). An X-ray crystallographic CIF format file is available on the Web only. See any current masthead page for ordering information and Web access instructions.

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[8] Because replacing a hydrogen by a hydrazine unit presumably makes the ring harder to reduce, we would expect $\Delta G°_{BR}$ for **2** to be larger than for **3**. The transition energy $h\nu_{max,BR} = \lambda_{BR} + \Delta G°_{BR}$. It is not obvious to us why λ_{BR} would be smaller for **2** than for **3**, which is what the experimental result appears to imply.

[9] (a) With similar ϕ values and identical charge-bearing units, $\mathbf{1}^+$ ($h\nu_{max,SE}$) $= 14\,100$ cm^{-1} $= 40.1$ kcal/mol in acetonitrile) should be a good model for λ_{SE} of $\mathbf{2}^+$, but λ_{BO} will be smaller than λ_{SE} because significantly smaller reorganization energy is involved. Estimating $\lambda_s \approx 13{-}15$ kcal/mol for $\mathbf{1}^+$ in acetonitrile, λ_v, involving two hydrazine units, is ~25−27 kcal/mol. $\lambda_{v,BO}$ for $\mathbf{2}^+$ should be the average of that for its hydrazine unit and the bridge. The estimate for λ_v for anthracene itself calculated by the published method[9b] is 6.5 kcal/mol, resulting in a $\lambda_{v,BO}$ estimate for $\mathbf{2}^+$ of ~16.3 ± 0.5 kcal/mol. We estimate $\Delta G°_{BO}$ as $\sim(9.4 - \lambda_{s,BO})$ kcal/mol. $\lambda_{s,BO}$ will be smaller than that for the SE ET, but we have no way of estimating its size accurately. Because $h\nu_{max,BO}$ is 3.4 kcal/mol larger in acetonitrile than it is in methylene chloride, it seems likely that $\lambda_{s,BO}$ in acetonitrile is at least 3.4 kcal/mol, although $\Delta G°_{BO}$ could change too. Using this number, $\Delta G°_{BO}$ is estimated at no more than 6 kcal/mol. However, substantial mixing between the hydrazine and the bridge might be argued to lower $\lambda_{v,BO}$ from the value assumed above. (b) Nelsen, S. F.; Blackstock, S. C.; Kim, Y. *J. Am. Chem. Soc.* **1987**, *109*, 677.

[10] Newton, M. D. *Chem. Rev.* **1991**, *91*, 767.

[11] (a) The three-state secular determinate is shown in eq 1:

$$\begin{vmatrix} H_{AA} - E & V_{SE}{}^{eff} & V'_{BO} \\ V_{SE}{}^{eff} & H_{BB} - E & V'_{BO} \\ V'_{BO} & V'_{BO} & H_{CC} - E \end{vmatrix} = 0$$

$H_{AA} = \lambda_{SE}X^2$, $H_{BB} = \lambda_{SE}(1 - X)^2$, and $\lambda_{SE} = 40.3$ kcal/mol (that for $\mathbf{1}^+$) are employed. $H_{CC} = \lambda_{BO}(1 - 2X)^2 + \Delta G°_{BO}$, giving $H_{CC} = \lambda_{BO} + \Delta G°_{BO}$ at $X = 0$ and 1, as required to give $h\nu_{max,BO}$. (b) Hush *V* values[2e] are for two-state systems and require statistical correction for use in a three-state system because V'_{BO} appears four times in eq 1 but only twice in a two-state equation. $V'_{BO} = -V_{BO}/\sqrt{2}$ when Hush theory is used to calculate *V*. This may be seen by consideration of an alternative, double two-state treatment. Here E_1, the double-well ground surface calculated using the usual two-state Marcus−Hush secular determinate with $V_{SE}{}^{eff}$ as the off-diagonal term is mixed with the H_{CC} energy surface as the second state in a second two-state perturbation, using the equations published by Creutz and co-workers.[2f] Use of V_{BO} in this two-state treatment gives close to the same results as use of $V'_{BO} = -V_{BO}/\sqrt{2}$ in the three-state treatment of eq 1. The ground-state energies at $X = 0.5$ are identical, but the energies at other *X* values differ; the double two-state treatment ignores significant mixings. We quote the two state V_{BO} in the text (to correspond to Hush *V* values which are traditionally used), but the calculations use V'_{BO}.

[12] Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.* **1993**, *176*, 439.

[13] It is not clear how realistic it is to represent BO and SE processes with a single *X* value, as we have done.