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Solvent Effects on Charge Transfer Bands of Nitrogen-Centered Intervalence Compounds

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Abstract: Electron transfer parameters are extracted from the optical spectra of intervalence bis(hydrazine) radical cations. Compounds with 2-*tert*-butyl-3-phenyl-2,3-diazabicyclo[2.2.2]octyl-containing charge-bearing units that are doubly linked by 4-σ-bond and by 6-σ-bond saturated bridges are compared with ones having *tert*-butylisopropyl- and diphenyl-substituted charge bearing units and others having the aromatic units functioning as the bridge. Solvent effect studies show that the optical transition energy (E_{op}) does not behave as dielectric continuum theory predicts but that solvent reorganization energy may be usefully separated from the vibrational reorganization energy by including linear terms in both the Pekar factor (γ) and the Gutmann donor number (DN) in correlating the solvent effect. Solvation of the bridge for these compounds is too large to ignore, which makes dielectric continuum theory fail to properly predict solvent effects on either E_{op} or the free energy for comproportionation.

Introduction

Symmetrical, localized intervalence (IV) compounds have the same two charge-bearing units (**M**) attached symmetrically to a bridge (**B**) and are at an oxidation level that places different charges on the **M** units, so they may be symbolized as $^{n}\mathbf{MBM}^{n+1}$. They are the simplest electron transfer (ET) systems ever devised and have played a major role in the development of ET theory.[1] Hush developed a remarkably simple theory for extracting the two most important ET parameters, the vertical reorganization energy (λ) and the electronic matrix coupling element (H_{ab}), by analysis of the lowest energy **M**-to-**M** intramolecular charge transfer (CT) band.[2] Briefly, the adiabatic ground- and excited-state energy surfaces are obtained from a simple two-state model. Parabolic diabatic ground-state initial ($E_{in} = \lambda X^2$) and final ($E_{fi} = \lambda(1\text{-}X)^2$) energy surfaces on the ET coordinate X are allowed to interact with energy H_{ab}, which represents electronic coupling between the **M** units through the bridge. Using this Marcus−Hush two-state model, the energy minima on the resulting adiabatic ground-state surface are stabilized by $H_{ab}{}^2/\lambda$ from the diabatic minima and are slightly closer to the $X = 0.5$ position of the transition state than the diabatic minima, which occur at $X = 0$ and 1, respectively. The transition state energy is $E^{\ddagger} = \lambda/4 - H_{ab}$.[1] The IV−CT band transition energy at the absorption maximum, $E_{op} = \tilde{\nu}_{max}$, is the energy separation between the ground- and excited-state adiabatic surfaces at the adiabatic minima, and equal to λ. Hush evaluated H_{ab} using the ratio of the transition dipole moment in the ET direction for the IV−CT band ($|\mu_{12}|$) to the change in dipole moment upon ET in the ET direction on the diabatic surfaces ($|\Delta\mu_{ab}|$) multiplied by E_{op}, eq 1, and pointed out that for a Gaussian-shaped band $|\mu_{12}|$ (Debye) can be evaluated from eq 2,

$$H_{ab} = (|\mu_{12}|/|\Delta\mu_{ab}|)E_{op} \tag{1}$$

$$\mu_{12} = (0.0206)\mathrm{e}(\epsilon_{max}\Delta\tilde{\nu}_{1/2}/E_{op})^{1/2} \tag{2}$$

where ϵ_{max} is the extinction coefficient at the band maximum ($\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) and $\Delta\tilde{\nu}_{1/2}$ is the bandwidth at half-height (cm^{-1}), when H_{ab} and E_{op} are in cm^{-1}. Using $|\Delta\mu_{ab}|$ (Debye) $= ed_{ab}$ (where $e = 4.8032$ and the electron-transfer distance on the diabatic surfaces, d_{ab}, is in Å) produces the familiar Hush eq 3, where the (Hush) is included to distinguish H_{ab} values obtained using eq 3 from those estimated by other means.

$$H_{ab}(\mathrm{Hush}) = (0.0206/d_{ab})(E_{op}\epsilon_{max}\Delta\tilde{\nu}_{1/2})^{1/2} \tag{3}$$

The **M** groups of the great majority of IV compounds studied have been transition metal coordination complexes, especially of ruthenium,[3] but the **M** groups may also be organic. We have used the much larger internal reorganization energies of dinitrogen compounds than of ruthenium coordination complexes to construct IV compounds that have the rate constant for intramolecular ET (k_{ET}) near $10^8\ \mathrm{s}^{-1}$, which allows measurement of k_{ET} by ESR.[4−7] These compounds have rather large

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(1) 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.

(2) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.

(3) (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Crutchley, R. J. *Prog. Inorg. Chem.* **1994**, *41*, 273.

(4) (a) Nelsen, S. F.; Ismagilov, R. F.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 10213. (b) Nelsen, S. F.; Ismagilov, R. F.; Trieber, D. A.; II *Science* **1997**, *278*, 846. (c) Nelsen, S. F.; Ismagilov, R. F.; Gentile, K. E.; Powell, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 7108.

(5) Nelsen, S. F.; Adamus, J.; Wolff, J. J. *J. Am. Chem. Soc.* **1994**, *116*, 1589.

(6) Nelsen, S. F.; Ramm, M. T.; Wolff, J. J.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 6863.

(7) Nelsen, S. F.; Trieber, D. W.; II.; Wolff, J. J.; Powell, D. R.; Rogers-Crowley, S. *J. Am. Chem. Soc.* **1997**, *119*, 6873.

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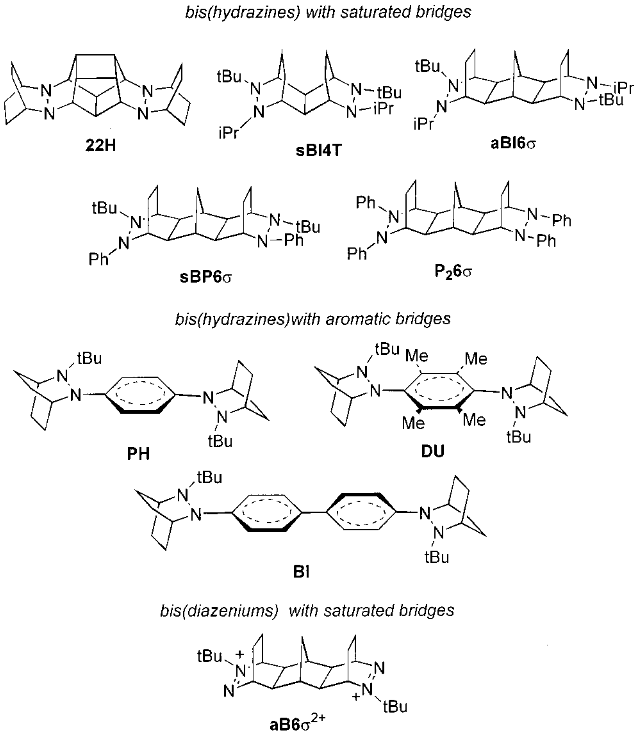
H_{ab}(Hush), ca. 400−1400 cm^{-1}, so the CT band has a large enough $\epsilon_{\max}$ to measure accurately. They provide the most straightforward test of the utility of Hush theory, comparing rate constants calculated from the optical parameters (k_{opt}) with independently measured k_{ET}. We found excellent agreement between k_{ET} and k_{opt} calculated using adiabatic theory, when the diabatic surfaces used fit the observed CT band shape.[4,6,7]

In this work we consider solvent effects on the optical spectra and electron-transfer equilibria of nitrogen-centered IV compounds having both saturated and aromatic bridges. The principal goals of this work have been to find out how to separate the solvent (λ_s) and internal vibrational (λ_v) components of λ by examining how λ is affected by solvent and to address the question of whether H_{ab} for nitrogen-centered IV compounds is sensitive to solvent, as has been found for the extensive series of ruthenium-centered IV compounds having dicyd (1,4-dicyanoamidobenzene derivative) bridges by Crutchley and coworkers.[8] They argue for far more accurate evaluation of H_{ab} using the thermodynamic method introduced by Taube and coworkers[9] than by using eq 3.[10] This method analyzes the free energy for comproportionation (ΔG_c) of the higher and lower oxidation states to two molecules of the IV oxidation state: **^{n}MBM^{n}** + **$^{n+1}$MBM^{n+1}** → 2**^{n}MBM^{n+1}**. Experimentally, ΔG_c is the difference in $E°$ values for the **^{n}MBM^{n+1}** $\rightleftharpoons$ **$^{n+1}$MBM^{n+1}** and the **^{n}MBM^{n}** $\rightleftharpoons$ **^{n}MBM^{n+1}** electron transfers, available from cyclic voltammetry (CV) studies. It has traditionally been assumed that the dielectric continuum theory (DCT) equation (4) introduced by Marcus is at least semiquantitatively correct

$$\lambda_s = e^2 g(r,d)\gamma \tag{4}$$

for IV complexes.[1−3] Equation 4 makes λ_s directly proportional to the Pekar factor, $\gamma = 1/n^2 - 1/\epsilon_S$, where n is the refractive index at the sodium D line, ϵ_s is the static dielectric constant, and ($g(r,d)$) is a distance factor that depends on the radius (r) of the charge-bearing units and the distance apart that the bridge holds their charge centers (d). The simplest form, $g(r,d) = 1/r - 1/d$, requires that $d > 2r$, which is often not the case, and an ellipsoidal correction to account for the nonspherical shape of real molecules has been employed.[11] It is known that specific solvent effects (taken here to mean deviations from DCT predictions) are not always negligible for ET reactions. Specific solvent effects have been observed on various types of ET reactions, especially for ruthenium-centered systems with NH_3 ligands, including metal-to-ligand and metal-to-metal optical charge transfer,[12,13] heterogeneous ET to an electrode,[14] and intermolecular self-ET.[15] The effects seen have been an increase in E_{op}[12,13] and decrease in rate constant[14,15] in more donating solvents. The Gutmann donicity number (DN)[16] has been used as the criterion for solvent donicity, and we also use it in this work.

Scheme 1



Results

The structures of the diamagnetic oxidation states of the IV compounds discussed here appear in Scheme 1, although only one diastereomer is illustrated for each saturated-bridged compound, but for the **6**σ-bridged compounds both *syn* and *anti*-substituted compounds were studied. The syntheses are parallel to previous work and will not be discussed. **sBP4T** shows 11 of the 12 carbon signals expected for one phenyl being "out" and the other "in" with slow rotation about the N−aryl CN bond; the unpaired aromatic carbon signal is approximately double intensity, representing an overlapping pair. This indicates that as for previously studied **4T** derivatives this compound exists mostly in the "opposite corners *syn*" conformations that are made more stable than others by torsion in the tetracyclic core.[7] The conformational mixtures for the **BP6**σ and **BI6**σ isomers are complex and both "opposite corners *syn*" and *-anti* conformations are occupied; the limited amount known is discussed in Trieber's Ph.D thesis and will not appear here because the neutral compound conformations present are not important for the principal thrust of this paper.

The optical and cyclic voltammetric (CV) data at room temperature are summarized in Table 1. We note that *anti* and *syn* diastereomers give data that are usually within statistical error of being the same, and principally provide a check on nonsystematic errors. Significant overlap of the 0,1+ and 1+,2+ oxidation waves is present in the cyclic voltammograms for all compounds, and formal oxidation potential ($E°'$) values were

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[8] (a) Evans, C. E. G.; Naklicki, M. L.; Rezvani, A. R.; White, C. A.; Kondratiev, V. V.; Crutchley, R. J. *J. Am. Chem. Soc.* **1998**, *120*, 13096−103. (b) dicyd = 1,4-($^{-}$N═CN)$_2$C$_6$R$_4$, where R$_4$ was H$_4$;, (CH$_3$)$_4$, 2,5-Cl$_2$-3,6-H$_2$, or Cl$_4$.

[9] Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

[10] Problems with eq 1−3 arise for IV compounds having very small ET barriers, as discussed in detail separately: Nelsen, S. F. *Chem. Eur. J.* **2000**, *6*, 581.

[11] Grampp, G.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 325 and references therein.

[12] Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.

[13] (a) Hupp, J. T.; Liu, H. Y.; Farmer, J. K.; Gennet, T.; Weaver, M. J. *J. Electroanal. Chem.* **1984**, *168*, 313. (b) Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 1601.

[14] (a) Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233. (b) Lau, K. W.; Hu. A. M.; Yen, M. H.; Fung, E. Y.; Grzybicki, S.; Matramoros, R.; Curtis, J. C. *Inorg. Chem. Acta* **1994**, *226*, 137.

[15] Mao, W.; Qian, Z.; Yen, H.-J.; Curtis, J. C. *J. Am. Chem. Soc.* **1996**, *118*, 3247.

[16] (a) Gutmann, V. *Coord. Chem. Rev.* **1976**, *18*, 225. (b) Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions*; Plenum: New York, 1980. (c) DN is the absolute value of the heat of mixing of a solution of SbCl$_5$ in 1,2-dichloroethane with another solvent, so DN ≡ 0 for 1,2-dichloroethane (abbreviated here as DCE), and increases with the heat of mixing.

Table 1. Room Temperature (296 K) Optical Band and ΔG_c Values

compound	$d_{N,N}$,[a] Å	d_{12},[a] Å	solv	E_{op}, cm^{-1}	Q	μ_{12}, D	d_{ab},[a] Å	H_{ab},[a] cm^{-1}	ΔG_c, cm^{-1}
Bis(hydrazines) with Saturated Bridges									
22H^{+}[b]	4.91	3.98	AN	16300		1.95	4.06	1490	1450
			NM	16200		2.03	4.07	1520	
			PrCN	16100		1.98	4.06	1480	
			DMF	15900		2.02	4.07	1460	
			DMSO	15900		2.14	4.08	1520	
			CH_2Cl_2	15400	-	2.14	4.08	1490	1200
sBI4T^{+}[c]	4.88	3.99	AN	18000	0.19	1.73	4.05	1460	1650
			PrCN	17900		1.69	4.05	1400	
			DMF	18600		1.68	4.05	1420	
			CH_2Cl_2	16400	0.23	1.76	4.06	1320	1700
aBI6σ^{+}[d]	7.22	5.92	AN	21100	0.19	0.95	5.93	640	650
			PrCN	20700	0.19	0.97	5.93	630	600
			DMF	21600	0.18	0.89	5.93	600	650
			PhCN	20000	0.19	1.10	5.94	670	600
			CH_2Cl_2	18000	0.18	0.97	5.93	550	500
sBI6σ^{+}[d]	7.22	5.92	AN	21100	0.19	0.94	5.94	630	650
			PrCN	20700	0.19	0.95	5.94	620	500
			DMF	21700	0.19	0.89	5.94	600	550
			PhCN	20000	0.19	1.07	5.94	660	550
			CH_2Cl_2	18200	0.18	0.96	5.94	540	500
sBP4T^{+}[d]	4.86	3.85	AN	14700	0.19	1.86	3.93	1320	1450
			Acet	14700	0.19	1.90	3.93	1350	1100
			PrCN	14500	0.19	1.82	3.93	1260	1200
			DMF	15000	0.19	1.82	3.93	1280	1150
			CH_2Cl_2	13200	0.19	1.79	3.92	1120	1350
aBP6σ^{+}[d]	7.19	6.02	AN	17400	0.18	1.14	6.04	620	600
			PrCN	17200	0.18	1.12	6.04	600	400
			DMF	17800	0.18	1.09	6.04	590	500
			DMSO	17800	0.18	1.07	6.04	580	500
			CH_2Cl_2	14800	0.19	1.28	6.05	580	300
sBP6σ^{+}[d]	7.19	6.02	AN	17900	0.17	1.11	6.04	630	550
			PrCN	17400	0.17	1.13	6.04	610	350
			DMF	18100	0.17	1.12	6.04	620	550
			DMSO	18500	0.18	1.06	6.03	590	500
			CH_2Cl_2	15200	0.18	1.27	6.04	590	400
**P$_2$6**σ^{+}[d]	7.20	6.52	AN	11200	0.20	1.12	6.53	370	550
			Acet	11100	0.19	1.16	6.54	370	500
			PrCN	11100	0.19	1.20	6.54	380	500
			DMF	11500	0.19	1.09	6.53	350	600
			CH_2Cl_2	10200	0.19	1.25	6.54	360	450
Bis(hydrazines) with Aromatic Bridges									
PH^{+}[e]	5.70	4.47	AN	13200	0.11	4.19	4.80	2200	2250
			CH_2Cl_2	11100	0.14	6.33	4.80	2480	3000
DU^{+}[d]	5.70	4.58	AN	14100	0.20	2.30	4.68	1320	2450
			Acet	14400	0.20	2.29	4.68	1340	2100
			PrCN	14000	0.21	2.28	4.68	1280	2150
			DMF	14700	0.19	2.20	4.67	1280	1900
			DMSO	14700	0.20	2.14	4.67	1220	1950
			CH_2Cl_2	*12400*[g]		*2.48*	*4.70*	*1210*	*2800*
BI^{+}[d]	9.99	8.41	AN	15200	0.02	3.18	8.51	1080	750
			Acet	15300	0.02	3.57	8.54	1210	800
			PrCN	15000	0.03	3.04	8.50	1010	900
			DMF	15500	0.02	2.98	8.50	1000	800
			DMSO	15600	0.03	3.01	8.50	1000	800
			CH_2Cl_2	*12900*[g]		*3.57*	*8.54*	*1000*	
Bis(diazeniums) with Saturated Bridges									
aB6σ^{+}[d,f]	7.16	5.62	AN	13100	0.32	1.26	5.64	560	950
			PrCN	12800	0.35	1.23	5.64	520	800
			DMF	13400	0.34	1.14	5.64	500	850
			DMSO	13400	0.35	1.23	5.64	530	900
			CH_2Cl_2	11500	0.36	1.27	5.64	480	750
sB6σ^{+}[d,f]	7.16	5.62	AN	13100	0.31	1.30	5.65	580	950
			PrCN	12800	0.35	1.19	5.64	520	-[h]
			DMF	13400	0.37	1.12	5.64	490	900
			DMSO	13400	0.35	1.16	5.64	500	900
			CH_2Cl_2	11500	0.40	1.25	5.64	470	780

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[a] N,N distance and d_{12} calculated by AM1 and combined with the experimental μ_{12} value shown to calculate d_{ab} using eq 5. The H_{ab} values reported here are refractive index corrected using $H_{ab}(n) = 3n^{1/2}/(n^2+2)H_{ab}(\text{Hush})$: for MeCN at room temperature, $3n^{1/2}/(n^2 + 2)$ at 296 $K = 0.914$; see the Supporting Information for other solvents. Although we doubt that the H_{ab} values are more precise than 100 cm^{-1}, the extra place has been written to emphasize the small decrease that is observed as solvent polarity is reduced (see text). The ΔG_c values are rounded to 50 cm^{-1}, although their actual precision is probably closer to about 80 cm^{-1}. [b] Data from ref 5. [c] Data from ref 6. [d] This work. [e] Data from ref 4a. [f] Data reanalyzed and two solvents added since ref 7. [g] Values from fit to ion pairing equation, extrapolated to free ion values, from ref 20.

determined by simulation of the experimental curves, although only the free energy for comproportionation (ΔG_c) appears in Table 1. The $E°'$ values, comproportionation equilibrium constants, and the fraction of total bis(hydrazine) present as

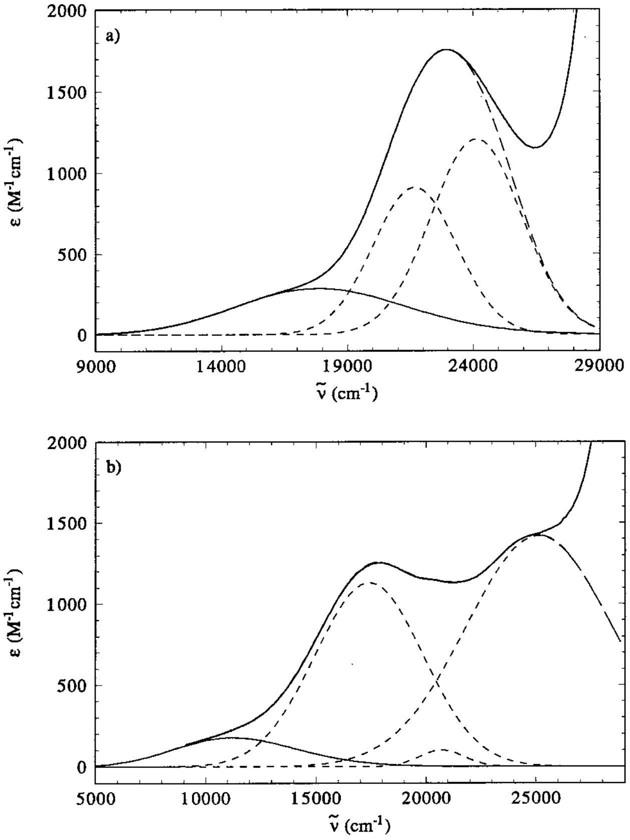

Figure 1. Sample fits to optical data at 296 K in acetonitrile. Solid lines: observed spectrum, and quartic-enhanced IV−CT band. Dashed lines, Gaussian fitting curves. Long-dashed line (only apparent when deviation from experimental becomes significant), sum of the calculated bands. (a) **sBP6**σ^+. (b) $\mathbf{P_26}\sigma^+$.

radical cation because of disproportionation to the adjacent oxidation states appear in the Supporting Information. Although the previously studied 4-σ-bond bridged saturated compounds have large enough comproportionation constants (fractions of bis(hydrazine) present as radical cation close enough to 1.0) that the stoichiometric concentrations of IV radical cation could be employed in calculating $\epsilon_{\max}$, the $\Delta G°_c$ values are small enough for **sBP4T**$^+$ and all of the 6-σ-bond bridged compounds that significant amounts of 0 and +2 oxidation states are present in a solution that is formally at the +1 oxidation state because of disproportionation. The stoichiometric +1 oxidation state concentration was corrected using the fractions shown in the Supporting Information in calculation of $\epsilon_{\max}$, and hence of μ_{12} and H_{ab}.

The intervalence radical cation oxidation states of all of these compounds have significant charge localization, so E_{op} should be λ, and eq 3 should give H_{ab}. However, overlap of the IV−CT band with other bands is appreciable on the high-energy side of the band for the **6**σ-bridged bis(hydrazines), especially those with phenyl substituents. The ET parameters for their IV−CT bands were obtained by fitting one to three Gaussian bands at higher energy plus the IV−CT band to the experimental spectrum. This process allowed good fit to the observed spectrum in the range of the IV−CT band. Examples of the type of fit obtained are shown for **sBP6**σ^+ in Figure 1a, where two Gaussians in addition to the IV charge transfer band allowed fit to about 23 000 cm^{-1}, and for $\mathbf{P_26}\sigma^+$ in Figure 1b, where three Gaussians were used, allowing fit to within experimental error up to 25 000 cm^{-1}. In all cases, fit to the experimental spectrum well beyond $\tilde{\nu}$ values for which the IV−CT band had significant absorption was achieved, and the $\lambda_{\max}$ for the IV−CT band, and hence E_{op}, was insensitive to fitting to slightly smaller $\tilde{\nu}$ values, so we believe the E_{op} values extracted are reliable. As described previously,[4] most organic IV−CT bands are broader than that which would occur for the simple two-state model if the diabatic surfaces were exactly parabolas, but these bands are well fit using an initial diabatic surface given by $E_{in} = [\lambda X^2/(1 + Q)][1 + Q X^2]$ and a final surface that has the X of E_{in} replaced by $(1 - X)$. Using a quartic term to do the fitting is not significant; other functions serve as well.[4c] Plots of Q vs the difference between the observed $\Delta\tilde{\nu}_{1/2}$ value and that calculated using parabolic diabatic surfaces, $(16RT\ln(2)E_{op})^{1/2}$, are quite linear, indicating that Q essentially only represents the increase in broadening over that predicted for parabolic diabatic surfaces. The Q values are nearly independent of solvent, and they are rather independent of other substituents for the **6**σ-bridged bis(hydrazines) having **BI**, **BP**, and $\mathbf{P_2}$ substitution and **sBI4T**$^+$, falling in the range 0.17−0.20 (except 0.23 for **sBI4T**$^+$ in CH_2Cl_2). Nevertheless, data for the aromatic-bridged bis(hydrazines) and the bis(diazeniums) show that both the structure of the bridge and of the charge-bearing units can affect Q substantially. We do not yet know what structural features control Q, but the band broadening is not principally determined by the effective barrier crossing frequency, as Hush suggested,[17] because quite different Q values can arise when only the bridge is changed, as shown by the data for **PH**$^+$, **DU**$^+$, and **BI**$^+$.

Two changes have been made in Table 1 from the optical band analyses previously published for **PH**$^+$, **DU**$^+$, and the compounds with saturated bridges, **22H**$^+$, **sBI4T**$^+$, and both diastereomers of **B6**σ^+. The first change involves inclusion of a solvent refractive index (n) correction to $\epsilon_{\max}$, pointed out to be necessary by Young and co-workers.[18] The largest such correction that we have seen makes $H_{ab} = (n^{-1/2})H_{ab}(\text{Hush})$.[18a] We shall use here the intermediate correction to $\epsilon_{\max}$ proposed by Chacko that Young and co-workers used later,[18b] eq 3a. The $[3n^{1/2}/(n^2 + 2)]$ factor is 0.91 at room temperature in acetonitrile (MeCN, see Supplementary Information for the values in other solvents). Equation 3a has been used to calculate the μ_{12} and

$$H_{ab}(n) = [3n^{1/2}/(n^2 + 2)]H_{ab}(\text{Hush}) \tag{3a}$$

$H_{ab}(n)$ values that appear in Table 1. The second change involves how the ET distance has been treated. Although the distinction frequently has not been made in the literature, the distance d_{ab} required for eq 3 is on the diabatic surfaces, so it cannot in principle be directly measured, because compounds exist on their adiabatic surfaces. However, the Generalized Mulliken−Hush theory of Cave and Newton[19] allows one to relate adiabatic d_{12} values to d_{ab} through eq 5. In this work we combine d_{12} values

$$d_{ab}^{\ 2} = d_{12}^{\ 2} + 4(|\mu_{12}|/e)^2 \tag{5}$$

calculated using AM1 semiempirical calculations as described

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[17] Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135.

[18] (a) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.* **1993**, *176*, 439. (b) Gould, I. R.; Young, R. H.; Mueller, L. J.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8176. (c) Gould, I. R.; Young, R. H.; Mueller, L. J.; Albrecht, A. C.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8188. (d) Gould, I. R.; Farid, S. *Acct. Chem. Res.* **1996**, *29*, 522.

[19] (a) Newton, M. D.; Cave, R. J. *Molecular Electronics*; Jortner, J., Ratner, M., Eds.; Blackwell Science: Oxford, 1997; p 73. (b) Cave, R. J.; Newton, M. D. *Chem. Phys. Lett.* **1996**, *249*, 15. (c) Cave, R. J.; Newton, M. D. *J. Chem. Phys.* **1997**, *106*, 9213. (d) Newton, M. D. *Adv. Chem. Phys.* **1999**, *106*, Pt. 1, 303.

Table 2. Comparison of d_{12}(ESR) and d_{12}(AM1) Values (in Å)

compound	d_{12}(ESR)[a] (2+ ox. state)	d_{12}(AM1)[b] (1+ ox. state)	change[c]
sBI6σ	6.88	5.93	−14%
sBP6σ	6.88	6.02	−13%
aBP6σ	6.91	6.02	−13%
DU	5.58	4.58	−18%
BI	7.99 (7.49)[d]	8.41	+5% (+12%)

[a] Calculated as $d_{12}(\mathrm{ESR}) = 0.650\, g^2/(D')^{1/3}$, where D' is the dipolar splitting of the triplet form of the triplet for of the dication (in cm^{-1}). [b] Calculated as $2\mu_{12}(\mathrm{ET})/e$ for the most stable diastereomer of the radical cation, where μ_{12}(et) is the largest component of the dipole moment calculated using the center of mass as the origin. See ref 19 for details. [c] Calculated as $100 \times [d_{12}(\mathrm{AM1}) - d_{12}(\mathrm{ESR})/d_{12}(\mathrm{ESR})]$. The presence of two species, possibly diastereomers, was detected. See ref 4a.

in detail elsewhere[20] with optically determined μ_{12} values to generate the d_{ab} values using eq 5. For comparison, Table 1 also shows $d_{\mathrm{N,N}}$, the average *N,N* distance for the saturated-bridged compounds, and the distance between the nitrogens attached to the aromatic ring for the aryl-bridged compounds (both calculated by AM1).[21a] It may be noted that the d_{ab} values obtained are almost completely determined by the d_{12} value employed: d_{ab} is about 2% larger than d_{12}(AM1) for the 4-σ-bond bridged saturated compounds but it is less than 0.4% larger for the 6-σ-bond bridged ones. It is not obvious how accurate the AM1-calculated d_{12} values actually are.[21b] For the aryl-bridged compounds, we previously used a d_{12} estimate from the dipolar splitting of the triplet form of the diradical 2+ oxidation state, d_{12}(ESR), in calculating the H_{ab}(Hush) values (without changing it to a d_{ab} value). An obvious drawback to using d_{12}(ESR) is that N,aryl twist angles (ϕ) are known from X-ray crystallography to be slightly different for the 1+ and 2+ oxidation states and H_{ab} should be proportional to cos(ϕ).[4] From ESR work done in Osaka[22] on the 2+ oxidation states of three 6σ-bridged bis(hydrazine) dications, **sBI6**σ^{2+} and **s-** and **aBP6**σ^{2+}, d_{12}(ESR) values for saturated-bridged compounds have become available and are compared with calculated d_{12}(AM1) values in Table 2.[21c] The changes of including the $\epsilon_{\max}$ correction and calculating the ET distance differently have opposite effects on the H_{ab} obtained for the saturated-bridged compounds, the *n* correction lowering it and using d_{ab} estimated using eq 5 instead of using the distance between the dinitrogen units raising it.

To properly consider the effect of solvent on λ, one must account for ion pairing, if it is present. Ion pairing effects for aromatic-bridged bis(hydrazine) IV compounds, including **DU**$^+$ and **BI**$^+$, have recently been discussed in detail.[23] In this work we carried out exactly analogous dilution studies for **aBI6**σ^+SbF$_6^-$ and **aBP6**σ^+PF$_6^-$. The concentration dependence of E_{op} for both compounds follows that expected for the simple ion pairing equilibrium of eq 6, that is, eq 7,

$$[\mathbf{A}^+] + [\mathbf{X}^-] \underset{}{\overset{K_{\mathrm{IP}}}{\rightleftharpoons}} [\mathbf{AX}] \tag{6}$$

$$E_{\mathrm{op}} = (E_{\mathrm{op}}{}^{\mathrm{free}} + K_{\mathrm{IP}}[\mathbf{X}^-]E_{\mathrm{op}}{}^{\mathrm{IP}})/(1 + K_{\mathrm{IP}}[\mathbf{X}^-]) \tag{7}$$

where [**AX**] is the concentration of ion paired material, [**A**$^+$] and [**X**$^-$] are the concentrations of the individually solvated ions, and $E_{\mathrm{op}}{}^{\mathrm{free}}$ and $E_{\mathrm{op}}{}^{\mathrm{IP}}$ are for **A**$^+$ and **AX**, respectively. Equation 6 assumes that the observed band maximum is a weighted average of the free and ion paired value and has been shown to be sufficient to describe the behavior of **DU**$^+$ and **BI**$^+$. The experimental data were fit to eqs 8 and 9, as in the previous work.[23]

$$[\mathbf{AX}] = [\mathbf{A}^{\mathrm{tot}}] - [\mathbf{A}^+] \tag{8}$$

$$E_{\mathrm{op}} = \{2E_{\mathrm{op}}{}^{\mathrm{free}} + [(1 + 4K_{\mathrm{IP}}[\mathbf{A}^{\mathrm{tot}}])^{1/2} - 1]E_{\mathrm{op}}\mathrm{IP}\}/ \{1 + (1 + 4K_{\mathrm{IP}}[\mathbf{A}^{\mathrm{tot}}])^{1/2}\} \tag{9}$$

Obviously, experimental data would not necessarily be described by these relatively simple equations, but in practice, it is for **aBI6**σ^+SbF$_6^-$ and **aBP6**σ^+PF$_6^-$ under the conditions examined (CH$_2$Cl$_2$ solutions, at 296 K, under 3 mM), as indicated graphically in Figure 2. Ion pairing data for bis(hydrazines) are compared in Table 3. As expected, the change in vertical reorganization energy that occurs upon ion pairing, $\Delta G°_{\mathrm{ET,IP}} = E_{\mathrm{op}}{}^{\mathrm{IP}} - E_{\mathrm{op}}{}^{\mathrm{free}}$, is smaller than the negative of the free energy for ion pairing, $\Delta G°_{\mathrm{IP}} = -RT \ln(K_{\mathrm{IP}})$. Their values would only approach each other as the difference in distance between the anion and the center of cationic charge of the two ET forms of the IV compound became very large. As can be seen in Table 3, $\Delta G°_{\mathrm{IP}}$ is quite insensitive to which bis(hydrazine) was studied and is 4.7 ± 0.2 kcal/mol for all four compounds. $\Delta G°_{\mathrm{ET,IP}}$ is also not particularly sensitive to structure, falling in the range 1.6−2.6 kcal/mol, with the larger value for the compound with larger *N,N* distance and the smaller one for the compound with all saturated bridges. From the rather similar sizes of their $\Delta G°_{\mathrm{ET,IP}}$ values, it seems likely that the average position of the counterion lies not very far from the axis between the hydrazine units in the saturated-bridged systems as well as the aromatic-bridged ones, where the counterion position is presumably similar to that in the crystal. For this work, the most important result of the ion pairing study is to establish $E_{\mathrm{op}}{}^{\mathrm{free}}$ in dichlormethane for these compounds, allowing the E_{op} value for this solvent to be used in correlations with the more polar solvents, where ion pairing is not a problem at the concentrations studied (on the order of mM). As will be seen by comparing the CH$_2$Cl$_2$ E_{op} values from Table 1 with the values in Table 3, partial ion pairing is clearly present for the data recorded in dichloromethane. We have not been able to experimentally detect concentration effects on E_{op} values for the compounds studied in acetonitrile ($\gamma = 0.528$) or DMSO ($\gamma = 0.437$), and we do not believe that ion pairing effects are significant at 1 mM concentration in solvents having γ larger than 0.43.

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(20) Nelsen, S. F.; Newton, M. D. *J. Phys. Chem. A* **2000**, *104*, 10023.

(21) (a) The literature optical data for **22H**$^+$, **sBIT**$^+$, and **PH**$^+$ are repeated but have been reanalyzed to extract $H_{ab}(n)$ using d_{ab} values calculated from the d_{12}(AM1) values shown in Table 1. Trial resimulations using the Gaussian superposition technique showed that significant changes from the published values of E_{op} and do not occur for these compounds; there is not serious enough band overlap for these compounds to require such analysis. (b) We previously used (by default) the average of the smaller nonbonded N,N distances (which is the separation of the midpoints of the NN bonds) as d_{ab} in calculating H_{ab}(Hush) for the saturated-bridged compounds. We note that these distances are significantly larger than d_{ab}(AM1). (c) Although it is not obvious which are the better d_{12} values to use to correlate the optical data, experimental d_{12}(ESR) values are not available for many compounds, and we use d_{12}(AM1) values here. The 2+ oxidation state must be both long-lived and have a low-enough lying triplet form for the dipolar splitting to be measured, which we have not yet succeeded in doing for any of the 4-σ-bond bridged systems. An advantage of using d_{12}(AM1) over distances between atoms is that it allows consistent estimations of d_{12} for compounds that have the axis of the delocalized π system both nearly perpendicular to the electron-transfer direction (as for the σ-bond bridged systems, which for the examples studied, the “center-to-center” distance is the same as the “edge-to-edge” distance between the charge-bearing units) and at a larger angle (ca. 120° for the aromatic-bridged systems, for which the “edge-to-edge” distance, the $d_{\mathrm{N,N}}$ distances quoted in Table 2 are smaller than the “center-to-center” distance.[20]

(22) (a) Nelsen, S. F.; Ismagilov, R. F.; Teki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 2200. (b) Teki, Y.; Ismagilov, R. F.; Nelsen, S. F. *Mol. Cryst. Liq. Cryst. A* **1999**, *334*, 313.

(23) Nelsen, S. F.; Ismagilov, R. F. *J. Phys. Chem. A* **1999**, *103*, 5373.

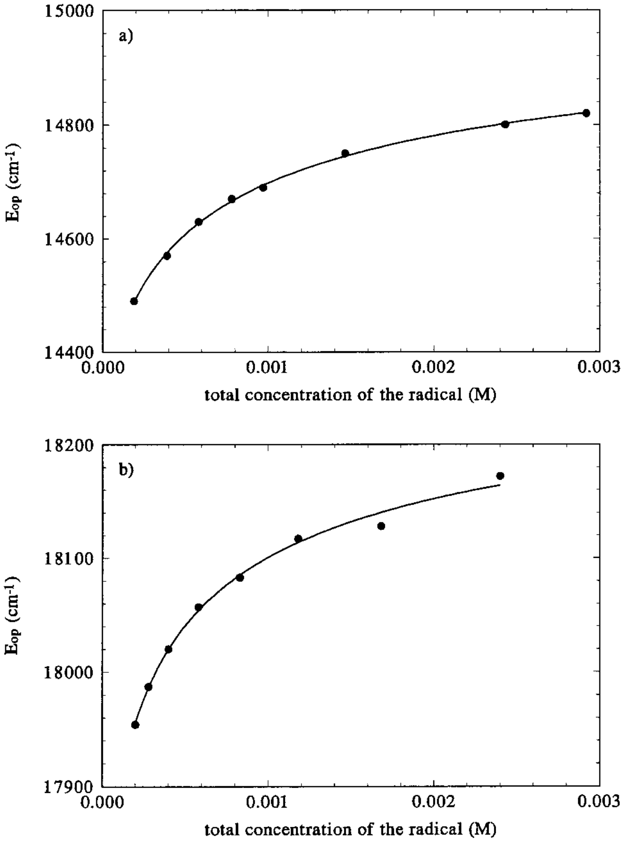


Figure 2. Fits of observed E_{op} to eq 9 using the best fit parameters of Table 3. (a) **aBP6**σ^+SbF$_6^-$. (b) **aBI6**σ^+SbF$_6^-$.

Table 3. Ion Pairing Data at 296 K in Dichloromethane

species	K_{IP}, M^{-1}	$\Delta G°_{IP}$, kcal/mol	$E_{op}{}^{free}$, cm^{-1}	$E_{op}{}^{IP}$, cm^{-1}	$\Delta G°_{ET,IP}$, kcal/mol
aBI6σ^+SbF$_6^-$	3800	−4.9	17 800	18 300	1.6
aBP6σ^+PF$_6^-$	2200	−4.6	14 300	15 100	2.2
DU$^+$PF$_6^-$	3100	−4.7	12 400	13 100	2.0
BI$^+$PF$_6^-$	3100	−4.7	12 900	13 800	2.6

Variable temperature optical studies were also carried out for **aBI6**σ^+, **sBI6**σ^+, **aBP6**σ^+, and **sBP6**σ^+ in acetonitrile, butyronitrile (PrCN), dimethylformamide (DMF), and methylene chloride, but dimethyl sulfoxide (DMSO) was used instead of butyronitrile for the **BP6**σ^+ diastereomers. The full results appear in the Supporting Information, along with the data for **DU**$^+$ and **BI**$^+$ in acetonitrile[4c] that have been refit using the methodology of this paper. The Q values for the σ-bridged compounds were all 0.21−0.22 at 260 K and dropped linearly within experimental error, with temperature to 0.15−0.17 at 322 K. The H_{ab} values obtained also decrease slightly as temperature is increased, −0.26 to −0.36 cm^{-1}/K for MeCN, −0.13 to −0.25 for PrCN, −0.07 to −0.22 for DMF, and −0.11 to −0.24 for CH$_2$Cl$_2$ (the −0.23 and −0.42 cm^{-1}/K values for the **BP6**σ^+ diastereomers in DMSO are unlikely to be very accurate because only a 26° temperature range was available; see Supporting Information). The E_{op} values also decrease slightly as the temperature is increased; see the Discussion section.

Of the saturated-bridged compounds discussed here, only the 6-σ-bond bridged bis(hydrazyls)[7] and the 4-σ-bond bridged bis(hydrazines) **22H**$^+$ [5] and **BI4T**$^+$ [6] have the electron-transfer rate constant k_{ET} near 10^8 at convenient temperature, allowing accurate measuring of the electron-transfer rate constant by ESR. The ESR spectra of **aBP6**σ^+ were examined in MeCN, PrCN, and CH$_2$Cl$_2$ between 250 and 350 K, but the spectra were indistinguishable from localized ones (as predicted from the optical spectra), and k_{ET} would be even smaller for **BI6**σ^+. The k_{ET} predicted even for **P$_2$6**σ^+ is slightly too slow for accurate measurement by ESR. These compounds were selected for study of their optical spectra even though ET rate constant data cannot be obtained for them using ESR.

Discussion

Separation of λ_v from λ_s. Only compound **22H**$^+$ of those considered here follows the DCT prediction that E_{op} will correlate with γ.[5] As pointed out previously,[4,6,7] there is a distinct tendency for higher E_{op} than the DCT prediction for solvents with greater donicity (higher DN) for the other compounds. It is not obvious why **22H**$^+$ is the only compound studied that is insensitive to solvent donicity effects, but structurally it is the only compound that has all of its NC−H substituents directed *anti* to the NN bond and might have the most hindered approach for solvent to the nitrogens. Even though we know k_{ET} from ESR studies for several of the compounds studied, this information does not help to separate λ_v from λ_s because these reactions are nearly adiabatic and k_{ET} is only sensitive to their sum. Accurate separation of λ_v from λ_s is, however, required for application of modern vibronic coupling ET theory to these compounds and for comparison of inter- and intramolecular ET (see below). Attempted separation of λ_s from λ_v using the usual averaged single frequency version of vibronic coupling theory fails for these compounds because of great sensitivity of the result to the value of the parameter $\tilde{\nu}_v$, and the fact that λ_v must be unreasonably temperature dependent is observed if a constant $\tilde{\nu}_v$ is employed.[4,6,7] Matyushov's molecular solvent theory[24] that includes both dielectric continuum and density variation effect rationalizes the observed decrease in E_{op} (and therefore in λ_s) as temperature is decreased (for all compounds studied in all solvents, see ref 4c and the Supporting Information). Matyushov's solvent theory, like that Marcus used, assumes that the only effect of changing the bridge is to change the distance between the charge-bearing units and does not accommodate specific solvent, solute interactions such as DN dependence that we observe.

A simpler method that is more closely related to classical Marcus theory seems desirable in separating λ_s and λ_v. The problem in fitting experimental data for IV compounds to equations containing γ for the purpose of separating λ_s from λ_v has always been that to get a large enough range in γ to obtain a reasonably accurate slope and hence intercept, it is necessary to include relatively nonpolar solvents, but as solvent polarity drops, ion pairing that will make photoinduced electron transfer endoergonic occurs, increasing E_{op} without necessarily changing λ. In an attempt to get a more useful expression for correlating solvent changes upon E_{op}, but keep as close to the Marcus framework as possible, we use fits to an empirical expression having both γ and DN terms,[25] eq 10. It may be noted that the

$$E_{cor} = A + B(\gamma) + C(\mathrm{DN}) \qquad (10)$$

A term in eq 10 is the only solvent-independent term, so A ought to be the internal vibrational component of λ, λ_v. Best fits to eq 10 are included in Table 4. Figure 3 shows graphically using the data for **DU**$^+$ that including the C(DN) term greatly improves the correlation and hence the presumed reliability of the solvent-independent component of λ. The average root mean square (rms) deviations from the best fit lines (shown in the rms fit column of Table 4) are mostly well under the ca. 100 cm^{-1}

Table 4. Fits of E_{op}(cm^{-1}) to Eq 10 To Separate λ_v from λ_s (given in kcal/mol)^a

ion	A	B fit^b	C	rms	λ_v^{c}	λ_s(MeCN)^d	%DN
			Bis(hydrazines) with Saturated Bridges				
22H$^+$	14 300	3800	−3	41	40.8	5.7	−2
sBI4T$^+$	13 050	6810	93	60	37.3	14.1	27
aBI6$\boldsymbol{\sigma}^+$	13 110	12 150	107	60	37.5	22.6	19
sBI6$\boldsymbol{\sigma}^+$	13 130	12 100	109	71	37.5	22.7	19
sBP4T$^+$	9450	8180	68	52	27.0	15.1	18
aBP6$\boldsymbol{\sigma}^+$	9770	11 870	97	45	27.9	21.8	18
sBP6$\boldsymbol{\sigma}^+$	9330	12 970	113	98	26.7	24.1	19
P$_2$**6**$\boldsymbol{\sigma}^+$	6960	6530	58	24	19.9	12.1	19
			Bis(hydrazines) with Aromatic Bridges				
PH$^+$	9810	5600	32	21	28.1	9.7	13
DU$^+$	10 100	5800	69	65	28.9	11.5	24
BI$^+$	9500	9100	70	55	27.2	16.5	17
			Bis(diazeniums) with Saturated Bridges				
aB6$\boldsymbol{\sigma}^+$	5610	11 960	86	29	16.0	21.5	16
sB6$\boldsymbol{\sigma}^+$	5530	12 080	87	25	15.8	21.7	16

^{a} Because of ion pairing, methylene chloride was excluded from the correlation except for cases where E_{op}(free) is known from ion pairing studies (**aBI6**σ^+, **aBP6**σ^+, **DU**$^+$, **BI**$^+$), benzonitrile was excluded for **a-** and **sBI6**σ^+ and pyridine for **PH**$^+$. ^{b} rms fit is $[\sum(\mathrm{Dev})^2/n]^{1/2}$, where Dev is E_{op}(eq 10) − (regression line value) and n is the number of solvents used. ^{c} A converted to kcal/mol. ^{d} ($E_{op} - A$) converted to kcal/mol.

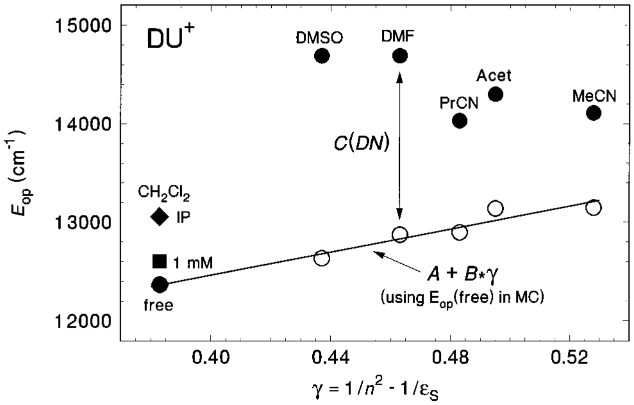
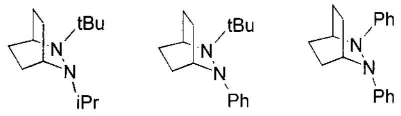


Figure 3. E_{op} data for **DU**$^+$ plotted vs the Pekar factor, γ. Filled circles, experimental data. For CH_2Cl_2 the E_{op} value at 1 mM concentration is shown as a square, and the extrapolated free ion and ion paired values (Table 3) as a circle and diamond, respectively. The open circles show best fit to eq 10 as a plot of $A + B\gamma$ vs γ, so the vertical deviations of the experimental points from the calculated ones is C(DN). Because DN for $CH_2Cl_2 = 0$, the experimental and calculated points fall on top of each other in this plot.

(0.3 kcal/mol) accuracy with which we estimate we can measure E_{op} for these compounds. Simple proportionality with DN may well not accurately describe the entire contribution of non-DCT effects to E_{op}, but including this term unquestionably straightens the correlation lines.

We believe it should be noted that finding fit to an empirical equation such as (10) invites misinterpretation. Perfect fit for any data observed will be obtained for three solvents using a three-parameter fit, and if these solvents are chosen to span the "polarity" and "donicity" ranges (however these terms are defined), and the other solvents have approximately intermediate properties, reasonable fit is likely to be found even if the situation is considerably more complicated. For example, comparable fit is obtained using either ion paired or free ion values for $E_{op}(CH_2Cl_2)$ in Table 4, but changing $E_{op}(CH_2Cl_2)$ this amount causes quite noticeable changes in the fitting constants. The fact that inserting a DN term improves correlation lines for solvent effects on E_{op} does not really indicate that solvent donicity "causes" these changes. Knowing the fitting constants for one compound does not appear to allow predicting them, even for rather similar ones. We suggest that this indicates that changes in E_{op} may not really be principally controlled by bulk solvent parameters such as DN and γ. They instead might be influenced significantly by solvation of the bridge, which would account for the differences observed even when the charge-bearing units **M** are the same. This means that for accurate prediction of E_{op}, one might very well need to be able to estimate the size of specific solvent/counterion, solute interactions, and not just treat an intervalence compound as idealized charged spheres fixed at a given distance. The much more complex finite-difference method solution to the Poisson−Boltzmann equations for the entire system being studied, developed by Honig and co-workers,[26] has become extremely popular for estimating solvation energies of proteins and is starting to be applied to some ET problems.[27]

Scheme 2



22/tBuiPr **22/tBuPh** **22/Ph**$_2$

The only significance that we hope to attach to the empirical fits to eq 10 shown in Table 4 is the ability to extract useful λ_v values, which we equate with the A fitting parameter. This assumes that changing solvent affects λ_s but does not affect λ_v. λ_v is sensitive to the conformations of both oxidation states, and it is certainly conceivable that solvent might affect the conformations. However, the most easily affected significant conformational parameter appears to us to be the N,aryl twist angle ϕ for the aryl-bridged systems, and since H_{ab} is proportional to cos ϕ at each N,aryl bond and has been found to be solvent independent within experimental error (see below), we doubt that very large changes in conformation are occurring as solvent is changed for these compounds. The A values also lie in the expected order for λ_v. The highest λ_v values are known to be for compounds having all four hydrazine substituents saturated, and **22H**$^+$, at 40.8 kcal/mol, has the largest value. We shall consider the other compounds by grouping them according to their monohydrazine charge-bearing units, illustrated in Scheme 2. The three compounds having **22/tBuiPr** charge-bearing units (**sBI4T**$^+$ and **s-** and **aBI6**σ^+), for which flattening has been introduced by including a *tert*-butyl group, have the same λ_v value within experimental error, 37.3−37.5 kcal/mol. The three saturated-bridged compounds having **22/tBuPh** charge bearing units (**sBP4T**$^+$ and **s-** and **aBP6**σ^+) have smaller λ_v in the range 26.7−27.9 kcal/mol. A decrease in λ is

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[24] (a) Matyushov, D. V. *Mol. Phys.* **1993**, *79*, 795. (b) Matyushov, D. V. *Chem. Phys.* **1993**, *174*, 199. (c) Matyushov, D. V.; Schmid, R. *J. Phys. Chem.* **1994**, *98*, 5152. (d) Matyushov, D. V.; Schmidt, R. *Chem. Phys. Lett.* **1994**, *220*, 369. (d) For a recent successful experimental application, see: Vath, P.; Zimmt, M. B. *J. Phys. Chem. A* **2000**, *104*, 2626.

[25] Marcus's commonly used DCT expression for λ_s uses no DN term (that is, $C = 0$) and $B = e^2(r^{-1} - d^{-1})$, where r is the radius of a charge-bearing unit and d is the distance between their centers. This expression cannot be used for our compounds because it assumes that $2r > d$, which is not the case for either the 4- or the 5-bond bridged compounds.

[26] (a) Sharp, K. A.; Honig, B. *Annu. Rev. Biophys. Biophys. Chem.* **1990**, *19*, 301. (b) Sitkoff, D.; Sharp, K. A.; Honig, B. *J. Phys. Chem.* **1994**, *98*, 1978.

[27] (a) Liu, Y.-P.; Newton, M. D. *J. Phys. Chem.* **1995**, *99*, 12382. (b) (b) Kurnikov, I. V.; Zusman, L. D.; Kurnikova, M. G.; Farid, R. S.; Beratan, D. N. *J. Am. Chem. Soc.* **1997**, *119*, 5690. (c) Kumar, K.; Kurnikov, I. V.; Beratan, D. N.; Waldeck, D. H.; Zimmt, M. B. *J. Phys. Chem. A* **1998**, *102*, 5529.

expected because replacing an isopropyl group by phenyl causes more flattening, which makes the pyramidalities at nitrogen of the oxidized and reduced hydrazine units closer. Quite strikingly, λ_v for the aryl-bridged compounds that share the same **22/tBuPh** charge-bearing unit, **PH**$^+$ and **BI**$^+$, are within experimental error of being the same, 27.2−28.1 kcal/mol. The λ_v for **DU**$^+$, for which the additional methyl groups cause twisting of the hydrazine unit even more out of conjugation with the aryl ring, has only a slightly larger λ_v, 28.9 kcal/mol. The single **22/Ph$_2$** charge-bearing unit compound studied, **P$_2$6**σ^+, has another large decrease in λ_v, to 19.9 kcal/mol, while the smallest λ_v values are found for the bis(diazenium) salts **s-** and **aB6**σ^+, at 15.8−16.0 kcal/mol.

Comparison of Intra- and Intermolecular ET. The above comparison establishes that the λ_v values in Table 4 are internally consistent, but whether they are correct is a much more difficult question to answer. Even though we know rate constants for intramolecular ET for many of these compounds, this information does not help establish the correctness of the λ_s, λ_v separation made here, because k_{ET} may be accurately calculated for these nearly adiabatic ET reactions without separating the components of λ and because λ_v is so large that use of the single averaged frequency vibronic coupling theory equation introduced by Jortner, which does depend on the λ_s, λ_v separation, is inaccurate for these compounds.[4] However, separation of λ_s from λ_v is certainly required to allow comparison of intermolecular and intramolecular ET because the λ_s values obviously will differ greatly. In collaboration with Jack Pladziewicz (UW-Eau Claire), we have been successfully analyzing intermolecular ET rate constant data between different partners using Marcus cross rate theory to extract intrinsic rate constants and hence Eyring barriers to self-ET that give best fit to cross reactions ($\Delta G^{\ddagger}_{ii}$(fit)).[28] These $\Delta G^{\ddagger}$ values cannot be equated with the ΔG^* values of ET theory; however, it is necessary to know H_{ab} to obtain ΔG^* and hence λ values for these reactions. Recently,[28d] we showed that slightly modified Levich and Dogodnaze theory (eq 11) that employs only λ and H'_{ab} =

$$k_{L\&D} = K_e(2\pi/\hbar)H_{ab}{}^2(4\pi RT\lambda)^{-1/2}\exp[-\Delta G^*/RT] \qquad (11)$$

$(K_e)^{1/2}H_a$[29] successfully analyzes the rate constants in terms of semiclassical ET theory. The conclusions we reached might be considered surprising because they differ from what many workers in the area have assumed controls all ET reactions.[28d] We concluded that for tetra-α-branched hydrazines reacting with a wide variety of compounds, the effective H_{ab} is quite surprisingly constant and has a very small magnitude ("perhaps 10^{-2} kcal/mol"), so that $\lambda/4$ values for these intermolecular ET reactions are numerically the same as ΔG^* values. We also concluded that $\lambda_s/4$ values for intermolecular ET in acetonitrile are not very sensitive to compound size and are slightly less than 2 kcal/mol (because the most reactive compound has a ΔG^* barrier close to 2 kcal/mol).[28d] Table 5 compares the intermolecular intrinsic ΔG^* values obtained for the monohydrazines that are incorporated as **M** units in the IV compounds studied here (Scheme 2) with the $\lambda_v/4$ values obtained from solvent studies of the IV compounds. The intramolecular $\lambda_v/4$ values are seen to be completely compatible with the $\lambda/4$ values obtained from the intermolecular ET data assuming that H'_{ab} is 0.01 kcal/mol. The value included in parentheses for **22/Ph$_2$** is calculated for H'_{ab} = 0.016, to demonstrate how sensitive the ΔG^* values are to the H'_{ab} value employed. The last column shows the intermolecular $\lambda_s/4$ values obtained by combining the inter- and intramolecular data. A constant H'_{ab} value of 0.01 kcal/mol indeed produces a nearly constant $\lambda_s/4$ value just under 2 kcal/mol, and if H'_{ab} actually is slightly larger for **22/Ph$_2$** (which would make the λ_s obtained more constant), it is not very much larger.

Table 5. Comparison of Inter- and Intramolecular ET Barriers (in kcal/mol)

compound	intermol. $\Delta G^{\ddagger}_{ii}$(fit)[a]	intermol. $\Delta G^* = \lambda/4$[b]	intramol. $\lambda_v/4$[c]	intramol. $\lambda_s/4$(MeCN)[d]
22/tBuiPr	15.8	11.1	9.4	1.7
22/tBuPh	13.3	8.7	6.8	1.9
22/Ph$_2$	11.0	6.4 *(6.9)*	5.0	1.4 *(1.9)*

[a] From ref 28d (see its Supporting Information for the **22/tBuiPr** value). [b] Calculated from eq 11 using H'_{ab} = 0.01 kcal/mol *(number in parentheses used H'_{ab} = 0.016 kcal/mol).* [c] Averages of λ_v values for the saturated-bridged compounds of Table 4. [d] Column 3 − column 4.

Table 6. Comparison of Acetonitrile $\lambda_s/4$ Values for IV Compounds Having **22/tBuPh** Charge-Bearing Units

compound	bridge type	bonds[a]	d_{ab}[b]	$\lambda_v/4$[c]	$\lambda_s/4$(MeCN)[c]
sBP4T$^+$	sat.	4	3.93	6.7	3.8
sBP6σ^+	sat.	6	6.04	7.0	5.5
aBP6σ^+	sat.	6	6.64	6.7	6.0
PH$^+$	aryl	5	4.83	7.0	2.4
BI$^+$	aryl	9	8.51	6.8	4.1

[a] Number of bonds (by the shortest path) between the charge-bearing units. [b] From Table 1. [c] From Table 4.

The compatibility of the inter- and intramolecular λ values in Table 5 encourages us to believe that the λ_v values shown in Table 4 are reasonably accurate and therefore that the λ_s values obtained using them need to be considered. We note from the last column of Table 4 that except for the anomalous **22H**$^+$ the C(DN) term of λ_s constitutes a significant contribution, corresponding to 13−27%. This means that DCT calculations of λ_s will not work well for these compounds. Table 6 shows d_{ab} values and $[\lambda_s/4]$(MeCN) values for the IV compounds having **M = 22/tBuPh**, which demonstrates that although λ_s increases significantly as the bridge is enlarged, it is rather sensitive to whether the bridge consists of saturated or aryl hydrocarbon fragments. This demonstrates that sovent theories that estimate λ_s from properties of two **M** units and a distance imposed by the bridge will not work well for these compounds.

Solvent Sensitivity of H_{ab}. We carry an additional place for the accuracy of $H_{ab}(n)$ reported in Table 1 over that we estimate to be significant (about 100 cm^{-1}) to make a point. The $H_{ab}(n)$ values are systematically highest in acetonitrile and lowest in methylene chloride. The decrease corresponds to about 14% for bis(hydrazines) **BI6**σ^+ and **BP4T**$^+$ and bis(diazeniums) **B6**σ^+ and less for all the rest of the data. This solvent sensitivity is quite small compared to what has been argued for dicyd-bridged ruthenium-centered compounds.[8] It is not completely obvious to us that the solvent variation of $H_{ab}(n)$ reported in Table 1 does not arise from some artifact. For example, the $[3n^{1/2}/(n^2 + 2)]$ term of eq 3a may not accurately describe the inherent dependence of ϵ_{max} upon solvent for these compounds. It has been pointed out that solvent as well as substrate in

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(28) (a) Nelsen, S. F.; Ismagilov, R. F.; Chen, L.-J.; Brandt, J. L.; Chen, X.; Pladziewicz, J. R. *J. Am. Chem. Soc.* **1996**, *118*, 1555. (b) 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. (c) Nelsen, S. F.; Ismagilov, R. F.; Gentile, K. E.; Nagy, M. A.; Tran, H. Q.; Qu, Q.; Halfen, D. T.; Oldegard, A. L.; Pladziewicz, J. R. *J. Am. Chem. Soc.* **1998**, *120*, 8230. (d) Nelsen, S. F.; Trieber, D. A., II.; Nagy, M. A.; Konradsson, A.; Halfen, D. T.; Splan, K. A.; Pladziewicz, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 5940.

(29) Because there is no experimental way of evaluating the encounter complex formation constant K_e, one cannot separate effects on it from those on $(H_{ab})^2$, and technically, we can only discuss the size of $H'_{ab} = (K_e)^{1/2}H_{ab}$).

principle affects H_{ab} and that quite large effects rather clearly caused by solvent-coupled H_{ab} increases are seen for intramolecular charge recombination in $\mathbf{D}^{+}{-}\mathbf{B}{-}\mathbf{A}^{-}$ molecules specially constructed to have a very small through-bond coupling, but which hold their charge-bearing units rather close in space but far enough apart to accommodate a solvent molecule.[27c,30] Much smaller effects are shown by organic-centered molecules without this special structural feature. Delocalized IV compounds that show vibrational fine structure in their IV−CT bands so that the 0,0 band position may be accurately located allow far more accurate optical determination of H_{ab} than do any localized compounds, because $E_{op} = 2H_{ab}$ for delocalized compounds, and E_{op} can be determined to about 15 cm^{-1} accuracy. For two tetraalkyl *p*-phenylenediamine derivatives and the tetramethylbenzidine radical cation, the optical H_{ab} value decreases detectably as n increases, but the range is only 1 to 2% between DMSO and MeCN, and there is a lot of scatter in a plot vs $n^{-1/2}$.[31] We conclude that any solvent sensitivity of the H_{ab} values of the compounds under discussion is small enough that experimental errors in obtaining H_{ab} might be responsible for all of the variation seen.

Thermodynamics for Comproportionation. Crutchley and co-workers have provided the most recent and extensive use of the thermodynamics for disproportionation to measure H_{ab}.[8] They used the equivalent of eq 12 for determining H_{ab} values

$$\Delta G_c = RT\ln(4) + 2[H_{ab}(\mathrm{CV})]^2/E_{op} - J + \Delta G_s \quad (12)$$

from ΔG_c values, where the $RT\ln(4)$ term (287 cm^{-1} at 25 °C) and the factor of 2 in the term containing H_{ab}(CV) arise statistically. ΔG_s represents all nonexchange solvation contributions and was evaluated as the sum of an inductive term, ΔG_i (considered to be the same in all solvents for a given intervalence compound), and a DCT term, ΔG_e (see below). The $2[H_{ab}(\mathrm{CV})]^2/E_{op}$ term is the stabilization energy for the two molecules of the IV compound involved in the equilibrium, and $-J$ term (half the singlet, triplet splitting) arises from stabilization of the diradical oxidation state singlet by electron exchange, and had not been included in prior analyses of ΔG_c.[32] The DCT term ΔG_e was evaluated using eq 13, where ϵ_S is the static

$$\Delta G_e = (4\pi\epsilon_S\epsilon_o d)^{-1} = 1.16 \times 10^5(\text{Å cm}^{-1})/d\epsilon_S \quad (13)$$

dielectric constant. Crutchley and co-workers used a constant $d = 13.1$ Å (the Ru,Ru distance) for all dicyd derivatives and assumed that $\Delta G_s(\mathrm{cm}^{-1}) = 120 + 8854(\epsilon_S)^{-1}$ for dicyd derivatives.

This comproportionation method can only be very accurate for larger H_{ab} compounds, because the relatively small H_{ab} values for the 6-σ-bond bridged compounds we studied make ΔG_c not very much larger than the statistical term, making the two oxidation waves overlap badly, and preclude much accuracy in either measuring ΔG_c or estimating H_{ab}(CV) from it. We shall consider the changes in the larger ΔG_c values for $\mathbf{DU}^{+}$ here.[33] The optical measurements show that $H_{ab}(n)$ for $\mathbf{DU}^{+}$ is rather insensitive to solvent, as might be expected because its formally positively charged nitrogens appear to be well protected from direct interaction with the solvent by the bulky groups attached to them. The exchange coupling in $\mathbf{DU}^{2+}$ ($-J$) has also been shown to be rather insensitive to conditions. SQUID measurements on polycrystalline $\mathbf{DU}^{2+}(\mathrm{Ph_4B^-})_2$ gave $-J = 72 \pm 5$ cm^{-1}, while the less accurate method of ESR intensity measurements in a mixed solvent glass (1:1:1 AN,PrCN,MC) gave 63 cm^{-1}.[4a,22] As expected for a strongly trapped compound, $-J$ makes only a small contribution to ΔG_c for $\mathbf{DU}^{+}$, ∼3% in AN. Because H_{ab} does not vary much with solvent and J probably does not and is small anyway, ΔG_s for $\mathbf{DU}^{+}$ can be extracted accurately from the experimental values for $H_{ab}(n)$, $-J$, and ΔG_c using eq 12 with H_{ab}(CV) replaced by $H_{ab}(n)$, and considered independently (see Table 7). The only component of ΔG_s that changes with solvent using DCT is ΔG_e, so this theory predicts that changes in ΔG_s should correlate with changes in ΔG_e. Table 7 shows that this is not the case. Because DMF and MeCN have almost the same ϵ_S, the electrostatic term ΔG_e of eq 13 should be almost the same size for these two solvents, but a large decrease in ΔG_s is found experimentally in DMF, which is a considerably more donating solvent.

Table 7. Comparison of ΔG_s for DU^{+} with Expectation from Dielectric Continuum Theory

solvent	ΔG_s[a]	rel. ΔG_s[b]	rel. ΔG_e[c]
AN	1900	≡1	≡1
acet	1600	0.82	1.75
DMSO	1400	0.73	0.77
DMF	1400	0.72	0.98
PrCN	1400	0.71	1.45
CH_2Cl_2	2300	1.18	4.03

[a] Unit: cm^{-1}. Using eq 12 replacing H_{ab}(CV) by H_{ab}(Hush), and using $-J = 72$ cm^{-1}. [b] ΔG_s(solvent)/ΔG_s(AN). [c] ΔG_e(solvent)/ΔG_e(AN) using eq 13, that is, ϵ_S(AN)/ϵ_S(solvent).

Considering ΔG_c data for other compounds (see Table 1), the DCT expression (13) does not explain the changes with solvent for them either. There is a qualitative difference between bridge types comparing methylene chloride with other solvents. The saturated-bridged compounds show smaller ΔG_c values in MC than in DMF and MeCN, while the aromatic-bridged compounds show larger ones. It will be noted that using eq 12 assumes that changes in ΔG_s with solvent are completely described by DCT, and no provision is made for the solvent donicity effects that rather clearly are important for the compounds under discussion. Solvent stabilization for all three oxidation states (0, 1+, and 2+) contribute to ΔG_c. For the aromatic-bridged compounds, the sum of solvent stabilization by more donating solvents for the 2+ and 0 oxidation state forms is apparently more than double that for the 1+ oxidation state, because more donating solvents tend to lower ΔG_c, but the reverse occurs for the saturated-bridged compounds. As for the solvent effects on E_{op} that are considered above, solely dielectric continuum considerations do not fit the experimental data. Solvent donicity effects fairly obviously need to be included to correlate ΔG_c values for our compounds. Although solvent effects on ΔG_c values can also be correlated with a three-term equation using $(\epsilon_S)^{-1}$ and DN, the correlation coefficients are not useful in the sense that they provide no ability to predict the values for even closely related compounds, and we shall not consider them here. It seems clear that H_{ab}(CV) values obtained using eq 12 are not useful for our compounds, because of specific solvation effects, so eq 13 cannot be used to extract reliable H_{ab} values using eq 12. The E_{op} and the ΔG_c values for these compounds both show large deviations from the behavior predicted by simple DCT. As we discussed else-

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(30) (a) Kumar, K.; Kurnikov, I. V.; Beratan, D. N.; Waldeck, D. H.; Zimmt, M. B. *J. Phys. Chem. A* **1998**, *102*, 5529. (b) Read, I.; Napper, A.; Kaplan, R.; Zimmt, M. B.; Waldeck, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 10976. (c) Roest, M. R.; Verhoeven, J. W.; Schuddeboom, W.; Warman, J. M.; Lawson, J. M.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1996**, *118*, 1762. (d) Jolliffe, K. A.; Bell, T. D. M.; Ghiggino, K. P.; Langford, S. J.; Paddon-Row, M. N. *Angew. Chem., Int. Ed.* **1998**, *37*, 916.

(31) Nelsen, S. F.; Tran, H. Q. *J. Am. Chem. Soc.* **1998**, *120*, 298.

(32) The $-J$ term in eq 12 had not been previously used.[8a]

(33) Although $\mathbf{PH}^{+}$ has a significantly larger H_{ab} and in retrospect might have been a better choice, its ΔG_c was not measured in a variety of solvents.

where,[10] the compounds Crutchley and co-workers studied have such large H_{ab} values relative to λ that there are significant problems using Hush theory to evaluate H_{ab}.

Conclusions

Obtaining useful intervalence charge transfer (IV−CT) band transition energies (E_{op} values) requires computer simulation to deconvolute the IV−CT band for the 6σ-bond linked systems, where overlap of this band with higher energy optical bands is a problem. The E_{op} values for several bis(hydrazine) and bis(hydrazyl) IV radical cations correlate nearly linearly with a three-term empirical equation containing terms linear with the Pekar factor (γ) and the Gutmann donor number (DN). Although these correlations have no predictive value, the solvent-independent term appears to be a useful estimate of λ_{v} when the free ion value is used for solvents in which ion pairing is significant, such as methylene chloride. The λ_{v} values so obtained are nearly constant for intervalence compounds having the same charge-bearing units when the bridge is changed, and using these λ_{v} values with self-exchange λ values obtained for intermolecular ET reactions of the monohydrazines gives self-consistent λ_{s} values for intermolecular ET. The λ_{s} values for intramolecular ET obtained using the λ_{v} values obtained in this work depend significantly upon the bridge structure, so physical modeling of λ_{s} for these compounds assuming that the bridge is inert is not sufficient. The present work shows that the DCT assumption that the static dielectric constant and refractive index of the solvent will adequately explain both vertical solvation energies and the solvent effect on the free energy of comproportionation simply is not true for most of our compounds. Obviously, the organic-centered monocations studied here differ a great deal in structure from transition metal-centered coordination compounds.

Experimental Section

4,10-Di-*tert*-butyl-5,9-diphenyl-4,5,9,10-tetraazatetracyclo$[6.2.2.2^{3,6}.0^{2,7}]$tetradecane (**sBP4T**). Phenyllithium (3.3 mL, 1.8 M in 2:1 cyclohexane−ether, 5.9 mmol) was added dropwise to a stirring, ice cold suspension of the *syn* di-*tert*-butyldiazenium bis(tetrafluoroborate),[34] and after stirring for 2 h, a 1:1 water−methanol mixture (30 mL) was carefully added. The aqueous layer was acidified to pH 1 with concentrated HCl and washed with pentane (2 × 20 mL). The aqueous layer was basicified using solid KOH and extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried with anhydrous Na_2CO_3 and the solvent evaporated, giving 0.6 g of brownish solid. Column chromatography on basic alumina with dichloromethane as eluant followed by sublimation (0.01 mmHg, 135 °C) gave 0.59 g (80%) **sBP4T** as a white solid, mp 191−192 °C. ^{1}H NMR ($CDCl_3$): δ 7.87 (m, 4H), 7.20 (m, 4H), 7.05 (d, 1H), 6.88 (m, 3H), 3.91 (m 1H), 3.48 (m, 2H), 3.35 (br s, 2H), 2.60 (m, 2H), 2.32 (m, 1H), 1.96 (m, 5H), 1.22 (s, 9H) 0.94 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 156.07, 155.17, 127.90, 127.84, 127.55, 120.89, 120.59, 120.42, 120.21, 120.11, 119.51, 59.09, 58.40, 57.17, 56.90, 49.30, 48.87, 36.90, 35.50, 29.31, 28.93, 25.35, 23.57, 19.21, 18.51. Empirical formula $C_{30}H_{42}N_4$ established by high-resolution mass spectrometry.

4,5,11,12-Tetraphenyl-4,5,11,12-tetraazahexacyclo$[6.6.1.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]$nonadecane (**$P_2$6**$\sigma$). A suspension of the **6**σ bis-azo compound[7] (0.27 g, 1.0 mmol) in THF (10 mL) was deaerated with an argon stream for 15 min and cooled to −10 °C in an ice−ethanol bath. Phenyllithium (1.2 mL, 1.7 M in 2:1 cyclohexane−ether, 2.04 mmol) was added dropwise. After the orange solution was stirred at −10 °C for 1 h and at room temperature for 1 h, the solution was cooled in an ice bath and transferred by cannula into an ice-cold solution of iodine (0.53 g., 2.1 mmol) in ether (50 mL). After 30 min of stirring at room temperature, the suspension was filtered and the red-brown solid residue was washed with ether. The solid was dissolved in 10 mL of acetonitrile, precipitated by dropwise addition of ether (100 mL), and dried. The mixture of diphenyldiazeniumdication diiodides obtained as a red-brown powder (0.58 g) was suspended in 10 mL of THF and cooled in an ice bath, and phenyllithium (1.2 mL, 1.7 M in 2:1 cyclohexane−ether, 2.04 mmol) was added dropwise. The mixture was quenched with 30 mL of a 1:1 methanol−water mixture after stirring at room temperature for 2 h. Workup as for **sBP4T** followed by recrystallization from dichloromethane−acetonitrile after chromatography gave **$P_2$6**σ as a white microcrystalline powder, 0.41 g (59% from the azo compound), mp 288−290 °C (dec). ^{1}H NMR ($CDCl_3$, two conformations): δ 7.15 (m, 8H), 6.70 (m, 4H), 6.890 (m, 8H), 4.03 (m, 2H), 3.99 (m, 1H), 3.95 (m, 1H), 2.10 (m, 2H, 1.77−2.02 (m, 10H), 1.55 (m, 3H), 1.21 (m, 1H). ^{13}C NMR ($CDCl_3$, 2 conformations): δ 150.38, 149.5, 128.88, 128.79, 120.13, 119.26, 117.22, 117.04, 115.67, 115.61, 54.68, 54.40, 52.16, 46.03, 45.91, 43.31, 43.14, 39.71, 39.65, 30.74, 22.54, 18.92, 18.77. Empirical formula $C_{39}H_{40}N_4$ established by high-resolution mass spectrometry.

4,11-Di-*tert*-butyl-5,12-diphenyl-4,5,11,12-tetraazahexacyclo$[6.6.1.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]$nonadecane (**aBP6**$\sigma$). Using **aB6**$\sigma^{2+}(BF_4^-)_2$ (1.19 g, 2.2 mmol),[7] **aBP6**σ was prepared by the same method as **sBP4T**. After column chromatography (basic alumina, CH_2Cl_2, R_f = 0.9), the residue was recrystallized from dichloromethane−acetonitrile, producing the product as a white, microcrystalline solid (0.71 g, 62%), mp 231−233 °C (dec). ^{1}H NMR ($CDCl_3$, three conformations): δ 7.82 (m, 1H), 7.60 (d, 1H), 7.16 (m, 4H), 6.83 (m, 4H), 3.37 (m, 2H), 3.13 (m, 2H), 1.42−2.33 (m, 16H), 1.13 (s, 3H), 1.07 (s, 3H), 1.00 (s, 9H), 0.89 (s, 3H). ^{13}C NMR ($CDCl_3$, three conformations): δ 156.32, 156.11, 127.96, 127.50, 122.53, 122.34, 121.60, 121.38, 120.93, 120.83, 118.57, 59.15, 58.84, 58.17, 49.56, 49.44, 48.82, 48.61, 47.32, 44.23, 43.40, 42.33, 39.48, 37.97, 31.31, 31.20, 29.28, 24.09, 23.41, 23.26, 19.14, 17.88, 17.79. Empirical formula $C_{35}H_{48}N_4$ established by high-resolution mass spectrometry.

4,12-Di-*tert*-butyl-5,11-diphenyl-4,5,11,12-tetraazahexacyclo$[6.6.1.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]$nonadecane (**sBP6**$\sigma$). Starting with **sB6**$\sigma^{2+}$-$(BF_4^-)_2$ (1.10 g, 2.0 mmol),[7] **sBP6**σ was prepared by the same method as **sBP4T**. The product was recrystallized as a white, microcrystalline solid (0.83 g, 78%), mp 224−226 °C (dec). ^{1}H NMR ($CDCl_3$, two conformations): δ 7.80 (m, 2H), 7.20 (m, 4H), 6.82 (m, 4H), 3.45 (bs, 1H), 3.33 (bs, 1H), 3.28 (m, 2H), 1.41−2.34 (m, 16H), 1.09 (s, 3H), 1.11 (s, 6H), 1.04 (s, 9H). ^{13}C NMR ($CDCl_3$, two conformations): δ 156.26, 156.04, 128.05, 127.92, 127.58, 127.45, 127.27, 122.43, 122.39, 122.06, 121.53, 121.39, 121.10, 120.90, 120.85, 119.50, 59.27, 59.11, 58.95, 58.62, 58.09, 50.13, 49.66, 49.52, 49.41, 49.07, 47.13, 47.06, 44.19, 42.31, 42.10, 40.12, 39.37, 31.31, 29.34, 24.19, 24.18, 23.30, 23.11, 19.29, 17.69. Empirical formula $C_{35}H_{48}N_4$ established by high-resolution mass spectrometry.

4,11-Di-*tert*-butyl-5,12-diisopropyl-4,5,11,12-tetraazahexacyclo$[6.6.1.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]$nonadecane (**aBI6**$\sigma$). Isopropylmagnesium chloride (5.0 mL, 2.0 M in THF, 10.0 mmol) was added dropwise to a stirring, ice cold suspension of **aB6**$\sigma^{2+}(BF_4^-)_2$ (0.27 g, 0.50 mmol)[7] in THF (5 mL). After stirring at room temperature for 2 h, water (20 mL) was carefully added to the reaction solution. The aqueous solution was then extracted with CH_2Cl_2 (4 × 10 mL), the combined organic layers were dried with anhydrous Na_2CO_3, and the solvent was evaporated, leaving 0.36 g of red-brown oil. Column chromatography (basic alumina, CH_2Cl_2, R_f = 0.9), followed by recrystallization from CH_3CN, gave the product as a white, microcrystalline solid (0.29 g, 84%), mp 227−229 °C. ^{1}H NMR ($CDCl_3$, three conformations): δ 3.27 (septet, 2H), 3.08 (bs, 2H), 2.92 (bs, 2H), 1.54−1.94 (m, 14H), 1.36 (m, 2H), 1.22 (d, 6H), 1.18 (s, 9H), 1.17 (s, 9H), 1.09 (two overlapping doublets, 6H). ^{13}C NMR ($CDCl_3$, three conformations): δ 57.92, 57.83, 57.69, 54.46, 50.51, 50.41, 50.19, 50.10, 49.52, 48.99, 48.42, 45.79, 44.62, 41.76, 39.98, 39.86, 38.12, 31.08, 31.00, 30.30, 24.66, 23.85, 20.45, 20.05, 19.93, 19.69. Empirical formula $C_{29}H_{52}N_4$ established by high-resolution mass spectrometry.

4,12-Di-*tert*-butyl-5,11-diisopropyl-4,5,11,12-tetraazahexacyclo$[6.6.1.2^{3,6}.2^{10,13}0^{2,7}.0^{9,14}]$nonadecane (**sBI6**$\sigma$) was prepared and purified by the same method as the *anti* isomer but using **sB6**$\sigma^{2+}(BF_4^-)_2$ (0.51 g, 0.94 mmol).[7] The product was obtained as a white microcrystalline

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(34) Nelsen, S. F.; Wolff, J. J.; Chang, H.; Powell, D. R. *J. Org. Chem.* **1991**, *113*, 7882.

solid (0.27 g, 59%), mp 223−225 °C. ^{1}H NMR (CDCl$_3$, two conformations): δ 3.27 (septet, 2H), 3.10 (bs, 2H), 2.95 (bs, 2H), 1.31−2.03 (m, 16H), 1.22 (d, 6H), 1.18 (s, 18H), 1.09 (two overlapping doublets, 6H). ^{13}C NMR (CDCl$_3$, two conformations): δ 57.95, 57.72, 54.47, 50.51, 50.46, 50.21, 50.10, 49.53, 48.44, 45.81, 44.58, 40.00, 39.86, 38.14, 36.72, 31.06, 30.30, 24.66, 23.88, 20.46, 20.08, 19.93, 19.69. Empirical formula $C_{29}H_{52}N_4$ established by high-resolution mass spectrometry.

4,10-Di-*tert*-butyl-5,9-diphenyl-4,5,9,10-tetraazatetracyclo-[6.2.2.2^{3,6}.0^{2,7}]tetradecyl Dication Bishexafluoroantimonate (sBP4T^{2+}-(SbF$_6^-$)$_2$). **sBP4T** (21 mg, 0.046 mmol) and AgSbF$_6$ (30 mg, 0.087 mmol) were placed in a test tube under nitrogen and cooled to −20 °C. Acetone (1.5 mL) was cooled to −20 °C and added via cannula to the stirring solids. The mixture was stirred at −20 °C for 15 min and then at room temperature for 1 h. The solution was filtered through Celite, and the silver solid was washed with acetone. The red-orange filtrate was concentrated to 0.5 mL with a stream of nitrogen, and diethyl ether (10 mL) was added dropwise, precipitating a dark red-orange solid (36 mg, 87%). UV−vis: λ_{max} = 464 nm (ϵ_{max} = 6478 M^{-1} cm^{-1}), 325 (10800), 275 (5780), 233 (4780).

4,5,11,12-Tetraphenyl-4,5,11,12-tetraazahexacyclo-[6.6.1.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]nonadecyl Dication Bishexafluoroantimonate (P$_2$6σ^{2+}(SbF$_6^-$)$_2$). Following the same procedure, **P$_2$6**σ (21 mg, 0.038 mmol) was oxidized with AgSbF$_6$ (24 mg, 0.070 mmol). A dark blue solid (27 mg, 75%) was precipitated by dropwise addition of 1:1 diethyl ether−pentane (10 mL). UV−vis: λ_{max} = 568 nm (ϵ_{max} = 5569 M^{-1} cm^{-1}), 399 (3422), 327 (13500), 264 (15800).

4,11-Di-*tert*-butyl-5,12-diphenyl-4,5,11,12-tetraazahexacyclo-[6.6.1.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]nonadecyl Dication Bishexafluoroantimonate (aBP6σ^{2+}(SbF$_6^-$)$_2$). Following the procedure for **sBP4T^{2+}**(SbF$_6^-$)$_2$, **aBP6**σ (60 mg, 0.11 mmol) was oxidized with AgSbF$_6$ (72 mg, 0.21 mmol). A red-orange solid (60 mg, 5%) was obtained after precipitation. UV−Vis: λ_{max} = 434 nm (ϵ_{max} = 3384 M^{-1} cm^{-1}), 327 (9410), 279 (5790), 234 (4480).

4,12-Di-*tert*-butyl-5,11-diphenyl-4,5,11,12-tetraazahexacyclo-[6.6.1.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]nonadecyl Dication Bishexafluorophosphate (sBP6σ^{2+}(PF$_6^-$)$_2$. Following the same procedure, **sBP6**σ (37 mg, 0.071 mmol) was oxidized with AgPF$_6$ (35 mg, 0.14 mmol). A red-orange solid (35 mg, 62%) was obtained after precipitation. UV−vis: λ_{max} = 434 nm (ϵ_{max} = 3424 M^{-1} cm^{-1}), 329 (9110), 277 (5350), 233 (4300).

4,11-Di-*tert*-butyl-5,12-diisopropyl-4,5,11,12-tetraazahexacyclo-[6.6.1.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]nonadecyl Dication Bishexafluoroantimonate (aBI6σ^{2+}(SbF$_6^-$)$_2$). Following the same proceedure, **aBI6**σ (33 mg, 0.072 mmol) was oxidized with AgSbF$_6$ (45 mg, 0.13 mmol). A light yellow solid (54 mg, 90%) was obtained. UV−vis: λ_{max} = 283 nm (ϵ_{max} = 6690 M^{-1} cm^{-1}).

4,12-Di-*tert*-butyl-5,11-diisopropyl-4,5,11,12-tetraazahexacyclo-[6.6.1.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]nonadecyl Dication Bisnitrate (sBI6σ^{2+}(NO$_3^-$)$_2$). Following the same procedure, **sBI6**σ (41 mg, 0.091 mmol) was oxidized with AgNO$_3$ (25 mg, 0.15 mmol). A light yellow solid (31 mg, 70%) was obtained after precipitation. UV−vis: λ_{max} = 283 nm (ϵ_{max} = 6572 M^{-1} cm^{-1}).

Intervalence Bis(hydrazine) Radical Cation Samples for Optical Analysis. Better reproducibility was found when solutions of bis(hydrazine) radical cations were made by comproportionation than by preparing and isolating the radical cations. Equimolar quantities of a neutral bishydrazine and its dication were added to 3−4 mL of the desired solvent in a 10 mL volumetric flask. The solution was sonicated until all the solids dissolved (15−60 min; slow dissolving is a major problem) and was then diluted to 10 mL and filtered through a cotton plug to remove any undissolved solids before optical analysis. One or more Gaussian bands (eq 14) were summed with a simulated IV−CT

$$\epsilon(\tilde{\nu}) = \epsilon_{max}/\exp[((\tilde{\nu} - \tilde{\nu}_{max})^2 \times 4 \log[2]/(\Delta\tilde{\nu}_{1/2})^2] \qquad (14)$$

band to fit the observed spectra. The ϵ values reported were adusted for concentrations calculated from the comproportionation equilibria ($\Delta G°$ values determined by cyclic voltammetry are reported in Table 1). For variable temperature spectra, the solution volume was adjusted for solvent expansion using the temperature coefficient for solvent density, and $H_{ab}(n)$ was calculated using the refractive index calculated at the temperature used employing the temperature coefficient for refractive index. The ϵ_s, n, γ, and temperature coefficients employed here were obtained from the literature[35] and appear in Table 8 of the Supporting Information.

The bis(hydrazyl) radical cation samples were prepared electrochemically, as described previously.[7]

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Supporting Information Available: Tables of solvent parameters employed, cyclic voltammetric data, and variable temperature optical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) Riddick, J. A.; Bunder, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley: New York, 1986.