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Estimation of Electron Transfer Parameters from AM1 Calculations

Stephen F. Nelsen*,† and Fredrik Blomgren‡

Department of Chemistry, University of Wisconsin—Madison, 1101 University Avenue,
Madison, Wisconsin 53706-1396, and Department of Physical Chemistry, Chalmers University of
Technology, S-41296 Gothenburg, Sweden

nelsen@chem.wisc.edu

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The utility of AM1 calculations for estimation of the electron-transfer parameters λ'_v (the enthalpy part of the Marcus internal reorganization energy) and H_{ab} (the electronic coupling between the charge-bearing units) is considered for some charge-localized intervalence bis(hydrazine) radical cations, for which these parameters have been experimentally determined from optical measurements. The Koopmans estimate of λ'_v that employs the orbital separation for the neutral compound at the radical cation geometry is far from that calculated from the enthalpies of the species involved (eq 1) and is not correct. The eq 1 λ'_v enthalpies estimated by AM1 are reasonably good for compounds with only alkyl substituents but are overestimated by 33−59% for aryl-substituted hydrazines. The Koopmans estimate of H_{ab} as half the orbital separation for the neutral species at the transition state geometry requires adjustment for the twist angles to those of the relaxed ground state to produce useful H_{ab} values. Symmetry breaking occurs for the electron-transfer transition states of the compounds with saturated bridges, and the Koopmans estimate predicts H_{ab} values that are slightly less than half as large as the optical measurements.

Introduction

We have used hydrazines as the charge-bearing units (**M**), to construct organic intervalence compounds of the type **M**−**B**−**M**$^+$, having both saturated[1] and aromatic[2] bridges (**B**). The large vertical vibrational reorganization energies (λ_v) of hydrazine **M** groups allow electron transfer (ET) rate constants to be small enough to measure by ESR, even when the electronic coupling between them (H_{ab}) is large enough that the Hush-type intervalence charge-transfer band[3] is intense enough to observe easily. These studies have provided several systems for which the classical two-state Marcus−Hush theory[4] was tested. Using this theory, parabolic diabatic free energy surfaces (completely characterized by λ) when plotted vs an electron-transfer coordinate that contains both vibrational and solvent effects are employed, and allowed to interact using a 2 × 2 Hamiltonian having H_{ab} as the off-diagonal term. Perhaps surprisingly, this simple model predicts ET rate constants using optically determined λ and H_{ab} more accurately than the much more sophisticated and complex single averaged frequency vibronic coupling theory model for these compounds. Improvement is obtained if the diabatic surfaces are allowed to relax slightly from being perfect parabolas, allowing the observed shape of the absorption bands to be properly fit.[2b] We have recently used AM1 semiempirical calculations[5] to treat the electron transfer distance in an internally consistent manner for both saturated- and aryl-bridged compounds.[6] Using these distances and improved optical band fitting in several solvents has allowed separating the internal vibrational (λ_v) and solvent (λ_s) components of the λ value obtained from optical measurements for several intervalence compounds,[7] including those shown in Table 1 (structures in Chart 1).

Table 1. Experimental ET Parameters (in kcal/mol) Derived from Optical Data in Acetonitrile[7]

compd	λ_s	λ_v	H_{ab}
Hy-PH-Hy$^+$	9.7	28.1	6.3
Hy-BI-Hy$^+$	16.5	27.2	3.1
sBP4T$^+$	15.1	27.0	3.8
aBP6σ^+	21.8	27.9	1.8
Hy-DU-Hy$^+$	11.5	28.9	3.8
aIB6σ^+	22.6	37.5	1.8
22H$^+$	5.7	40.8	4.3

The λ_s values in acetonitrile shown in Table 1 are not ones that would be estimated using simple Marcus

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* To whom correspondence should be addressed. Fax: (608) 265-4534.

† University of Wisconsin—Madison.

‡ Chalmers University of Technology.

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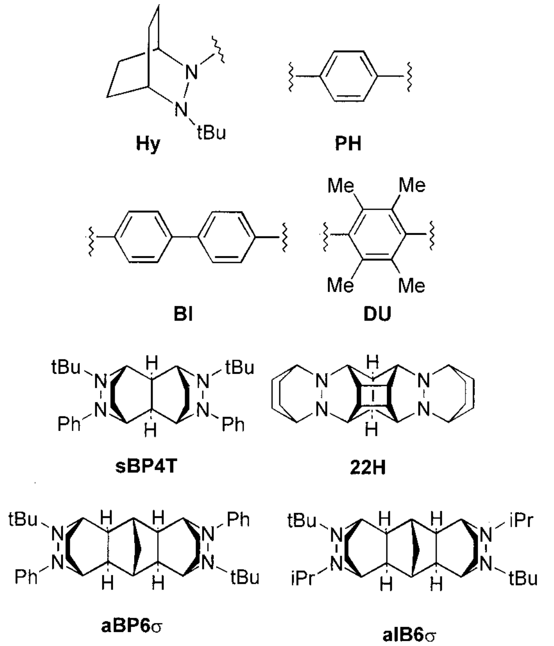
Chart 1. Compounds Studied Optically (Table 1)



theory, because the nature of the bridge clearly affects the size of λ_s, but the λ_v values that result from using these λ_s values are both internally consistent (very similar λ_v values for compounds having different bridges but the same charge-bearing unit) and entirely consistent with intrinsic barriers for intermolecular ET obtained from cross-reaction studies on the related mono(hydrazines).[8] We therefore consider the data of Table 1 to be the best documented ET parameters available for any series of compounds, and in this paper we consider how well AM1 calculations perform for estimating these numbers. It may seem odd to still use semiempirical calculations to estimate ET parameters, but they appear to be the best method that is practically available to us now. The molecules of interest are large enough to cause real difficulties for using sophisticated calculational techniques. Although AM1 calculations do a poor job of calculating bond lengths for hydrazines, they estimate rather well the pyramidality at nitrogen of both the neutral forms and radical cations of some hydrazines for which these quantities are known. AM1 calculations also allow reasonably good estimates of nitrogen inversion barriers for bis(N,N′-bicyclic) hydrazine radical cations,[9] correlating structural effects on nitrogen ESR splittings and π,π^* transition energies in the optical spectra of hydrazine radical cations,[10] and even obtain rather good values for the difference between the vertical and adiabatic ionization potentials of tetraalkylhydrazines.[11] The last number is closely related to λ_v.[12] The intrinsic barriers for intermolecular ET reactions of hydrazines and heteroatom-substituted aromatic systems show a remarkably good correlation with AM1-derived vertical relaxation enthalpies.[8] Much more sophisticated ab initio UHF/6-31G* calculations that take approximately 10^6 times as long to run get much better bond lengths, but the radical cation oxidation states are calculated to be significantly less pyramidal at nitrogen than they actually are. It appears that to obtain the proper pyramidality change upon electron loss using ab initio type methods, one would have to do structural optimizations at calculational levels that are so time-consuming that they are not yet practical for us to carry out on molecules as large as those discussed here. Density functional theory (DFT) methods provide great savings in calculation time compared to available post Hartree−Fock methods for introducing dynamic electron correlation but have been found not to be applicable to the problem of estimating the ET properties of intervalence compounds. They do a fine job on the geometries of both the neutral and radical cation forms of monohydrazines, at no more cost than doing ab initio (U)HF calculations, but we have shown that they do not get appropriately different geometries for the oxidized and neutral units of localized intervalence bis(hydrazines).[13] The inability for present DFT methods to predict the structure of charge-localized intervalence compounds properly is a fundamental problem with these calculations that has been best documented for several small systems[14] but also applies to these larger systems that have extended π interactions.

Calculated Reorganization Enthalpies of Mono(hydrazines)

Calculation of a compound in the gas phase is obviously a much easier task than also considering the interaction of it with its environment, and we only attempt to estimate the internal reorganization energy (λ_v values) here. We shall first consider the mono(hydrazines) that are used as charge-bearing units for the intervalence compounds of Table 1. What is easiest to calculate is the enthalpy contribution to the free energies, which we shall designate by λ'_v and evaluate using eq 1.[12] Designating

$$\lambda'_v = \Delta\Delta H_f(\mathbf{n}^+-\mathbf{c}^+) + \Delta\Delta H_f(\mathbf{c}^0-\mathbf{n}^0) \qquad (1)$$

the optimized geometry as **n**eutral or **c**ation, and showing the charge present as a superscript, λ'_v is the free energy difference between the components having an electron transferred without any relaxation, that is, of $\mathbf{n}^+$ and $\mathbf{c}^0$, and the relaxed forms, $\mathbf{n}^0$ and $\mathbf{c}^+$, which may be written as (1). A principal difficulty in applying eq 1 to many compounds is that more than one minimum often exists for both $\mathbf{n}^0$ and $\mathbf{c}^+$, and significantly different λ'_v values often result for each combination. For the compounds discussed here the radical cations are far more flexible than the neutral forms and it is principally multiple minima of $\mathbf{c}^+$ that cause ambiguity in calculating their λ'_v values. The most important twist angles are indicated in Chart 2, where the arrow points to the bond about which twist is measured. The double N,N′-bicyclic substitution of **22/22** causes each bicyclo[2.2.2]octyl unit to

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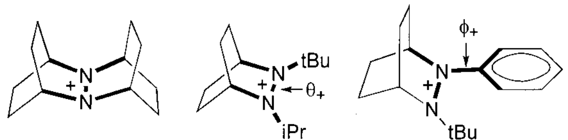
Chart 2. Stereochemical Features of Mono(hydrazines)



22/22$^+$ (*syn*, $\theta_+ = 0$)

Hy-iPr$^+$ (*anti*, θ_+ ~180)

Hy-Ph$^+$

have alkyl groups that are syn in both neutral and radical cation oxidation states: that is, they have lone pair−lone pair twist angles θ that are near 0°. The bonds connecting the six atoms that determine θ are thickened in the structures for **22/22**$^+$ and **Hy-iPr**$^+$ in Chart 2.[15] However, AM1 calculations on **22/22** incorrectly get θ for $\mathbf{n^0}$ (which we will abbreviate as θ_0) to be zero instead of the experimental value of about 13°.[16] This causes the λ'_v value obtained for **22/22**$^{0/+}$ to be too low compared to those of bis(N,N′-bicyclic) hydrazines that actually do have $\theta_0 = 0°$ in their neutral forms, such as ones having bicyclo[2.2.1]heptyl partial structures.[16b] The other compounds considered have only one N,N′-bicyclic group, and all have conformations with anti exocyclic alkyl groups in their neutral forms (for which $\theta_0 \geq 130°$) that are much more stable than syn exocyclic alkyl group conformations, and only this $\mathbf{n^0}$ minimum needs to be considered in calculating λ'_v. However, the nitrogens are much flatter in the radical cations ($\mathbf{c}^+$), resulting in syn and anti forms that are close in enthalpy. The anti $\mathbf{c}^+$ minimum is very slightly lower in enthalpy than the syn one for UHF calculations on **Hy-iPr**$^+$, **Hy-Ph**$^+$, and **Hy-BI-H**$^+$ (by 0.12, 0.06, and 0.20 kcal/mol, respectively), but their λ'_v values differ much more significantly: those for the syn forms are 3.4, 4.4, and 5.1 kcal/mol larger, respectively. This occurs because $\mathbf{c^0}$ is substantially more stable for anti than for syn hydrazine units.

A second geometrical parameter that is very important for the aryl-substituted compounds is the nitrogen lone pair−ring p orbital twist angle φ, and the bonds connecting the atoms that determine it are highlighted on the **Hy-Ph**$^+$ structure in Chart 2. As shown in Table 2, the syn-substituted form is slightly more stable than the anti one for both **Hy-Ph**$^+$ and **Hy-BI-H**$^+$, and syn forms show a substantial increase in both φ_+ and λ'_v. The value of φ_+ represents a balance between nonbonded steric destabilization and stabilization from aryl π−(NN)$^+$ interaction. The radical cations were calculated using the unrestricted Hartree−Fock (UHF) method, which introduces spin contamination, as shown by obtaining $\langle S^2 \rangle$ values larger than the theoretical value of 0.75 for a pure doublet. This means that the structure calculated has the characteristics of the quartet (or higher spin states) as well as the desired doublet, and properties that are sensitive to this will be increasingly incorrectly calculated as spin contamination increases. Spin contamination is only very significant for the aryl-substituted compounds. The VAMP program used for the AM1 calculations[5b] allows annihilation of quartet contaminant after every SCF cycle during optimization, and using this option (we call these AUHF calculations) produces $\langle S^2 \rangle$ values of 0.7500 for the compounds discussed here, demonstrating that essentially only quartet contamination was present, and is eliminated by this technique. These AM1/AUHF calculations successfully negotiate what Bally and Borden call "The Scylla of Spin Contamination" in their review on calculations of open-shell systems.[17] $\Delta H_f(\mathbf{c^0})$ only changes slightly upon going from UHF to AUHF calculations ($\Delta H_f(\mathbf{n^0})$ is the same because $\mathbf{n^0}$ is a closed-shell system that is not calculated using UHF), and the $\Delta\Delta H_f(\mathbf{c}^+ - \mathbf{n^0})$ term dominates the change. The principal changes introduced by eliminating the spin contamination of the UHF calculations are that the syn-alkylated $\mathbf{c}^+$ conformations become slightly more stable than anti ones, and there is an increase in φ_+ for both conformations for the AUHF calculations. Figure 1 demonstrates that the variation of λ'_v is principally controlled by $\varphi_+(\mathbf{c}^+)$, consistent with the small variation found for the neutral oxidation state relaxation enthalpy component ($\Delta\Delta H_f(\mathbf{c^0} - \mathbf{n^0})$; see eq 1). It will be noted that the λ'_v values for both AUHF and UHF calculations of both syn- and anti-alkylated conformations fall near the same line when plotted vs $\varphi_+(\mathbf{c}^+)$. The λ'_v values of **Hy-Ph**$^+$,

Table 2. Geometric Parameters and λ'_v Calculated by AM1 for Mono(hydrazines)

couple	$\Delta\Delta H_f$[a]	type[b]	$\langle S^2 \rangle$[b]	θ_+[c]	θ_0	φ_+	φ_0	λ'_v[d]
22/22$^{0/+}$		UHF	0.757	[0]	[0]			33.2
Hy-iPr$^{0/+}$	0	UHF	0.757	161	130			42.0
	+0.12	UHF	0.757	8	130			45.4
Hy-Ph$^{0/+}$	0	UHF	0.929	160	131	59	48	38.1
	+0.06	UHF	0.848	8	131	81	48	42.5
	0	**AUHF**	**0.750**	**8**	131	**83**	48	**43.3**
	+0.09	**AUHF**	**0.750**	**161**	131	**70**	48	**40.2**
Hy-BI-H$^{0/+}$	0	UHF	1.309	158	134	56	49	36.3
	+0.20	UHF	1.238	9	134	79	49	41.4
	0	**AUHF**	**0.750**	**7**	134	**84**	49	**42.2**
	+0.12	**AUHF**	**0.750**	**161**	134	**70**	49	**38.8**
Hy-DU-H$^{0/+}$		UHF	1.032	164	146	72	59	36.3
		AUHF	**0.750**	**165**	146	**74**	59	**37.1**

[a] Relative enthalpy when both anti and syn alkyl minima were obtained for $\mathbf{c}^+$ of a compound. [b] For $\mathbf{c}^+$. [c] Oxidized hydrazine units having syn alkyl groups have θ_+ near 0° and those with *anti* alkyl groups have θ_+ approaching 180°. [d] Calculated using eq 1.

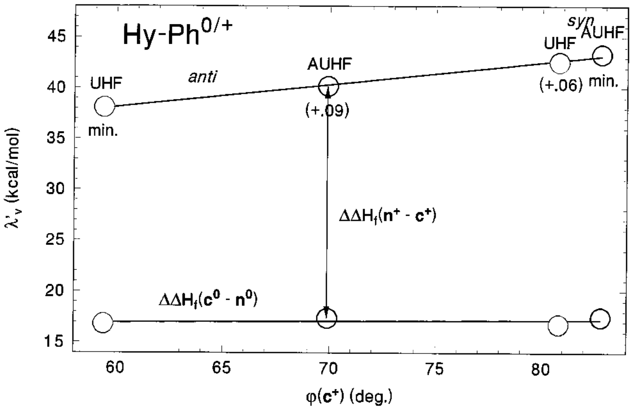


Figure 1. Plot of λ' and its $\Delta\Delta H_f(\mathbf{c^0} - \mathbf{n^0})$ component vs $\varphi(\mathbf{c}^+)$ for **Hy-Ph**$^{0/+}$.

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[15] Lone-pair geometries do not explicitly appear in quantum-mechanical calculations. For these compounds θ is the average of the two bridgehead carbon (C_{br})−nitrogen−nitrogen−alkyl group α-carbon twist angles, which have opposite signs for syn substitution and the same signs for anti substitution. Because the aryl carbon substituted by nitrogen (C_{Ar}) is essentially planar, φ is the average of the smaller $C_{Br}-N_{Ar}-C_{Ar}-C_{ortho}$ and $N'-N-C_{Ar}-C_{ortho}'$ twist angles.

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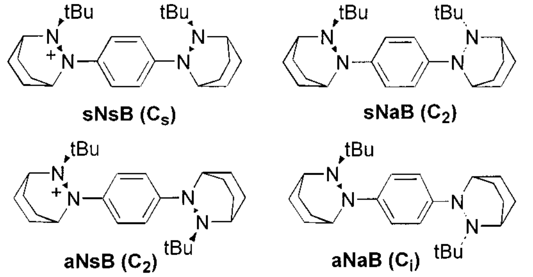
Table 3. ET Parameters Calculated by AM1 for Aromatic-Bridged Diastereomeric Conformations[a]

	-PH-, UHF				**-PH-**, AUHF				**-BI-**, UHF	**-BI-**, AUHF
	aNsB	sNsB	aNaB	aNsB	aNsB	sNsB	aNaB	aNsB	aNsB	aNsB
$\theta(\mathbf{c}^+)$	158	158	158	157	5.7	6.5	7.0	6.8	157.7	6.9
$\varphi(\mathbf{c}^+)$	55.4	55.8	55.1	54.8	88.3	84.7	83.7	84.7	54.6	86.1
$\varphi(\mathbf{c}^0)$	32.7	32.8	32.6	32.5	32.7	32.5	32.0	32.4	36.3	36.5
$\langle S^2\rangle(\mathbf{c}^+)$	0.96	0.96	0.97	0.97	0.7500	0.7500	0.7500	0.7500	1.37	0.7500
λ'_v[b]	37.4	37.3	37.8	37.5	43.9	43.8	43.9	43.9	36.9	42.9
$\varphi(\mathbf{t}^0)$	25.4	25.7	25.6	25.5	24.6	24.8	24.7	24.6	25.5	25.0
$\mathbf{t}^0$ sym	C_2	C_s	C_i	C_2	C_2	C_s	C_i	C_2	C_2	C_2
$\Delta\Delta H_f(\mathbf{t}^+-\mathbf{c}^+)$	4.1	3.9	4.2	3.7	7.6	7.4	7.7	7.1	9.5	12.1
H'_{ab}(second)	6.3	6.7	6.3	7.0	[3.7]	[3.9]	[3.6]	[4.3]	−0.3	[−1.3]
$\Delta E_K(\mathbf{t}^0)/2$	16.1	16.6	15.9	16.7	16.4	17.0	17.3	17.0	11.3	11.3
$H_{ab}(\varphi\text{-adj})$[c]	9.4	9.7	9.4	10.1	6.3	6.1	6.4	6.1	6.5	3.8

[a] Energies in kcal/mol and angles in deg. For comparison, the optical values are as follows: **-PH-**, $\lambda_v = 28.1$, $H_{ab} = 6.3$; **-BI-**, $\lambda_v = 27.2$, $H_{ab} = 3.1$ kcal/mol. [b] Calculated using eq 1. [c] Calculated using eq 4. For the AUHF calculations, the smaller φ_+ twist anti conformations of $\mathbf{c}^+$ ($\varphi_+ = 68-72°$) have been used (see text).

Chart 3. Diastereomeric Conformations of Hy-PH-Hy[a]



[a] Highest symmetry shown in parentheses.

Hy-DU-H$^+$, and **Hy-BI-H**$^+$ are better than (closer to the optically determined values of λ'_v for intervalence bis(hydrazines) having these charge-bearing units) those obtained using (U)HF/3-21G ab initio methods but not as good as the (U)B3LYP/6-31G* values,[13] which are 3.4 and 6.4 kcal/mol higher than Table 1 values for the first two compounds and 2.6 kcal/mol smaller for the third. **Hy-DU-H** is more twisted at its hydrazine−aryl bonds because of the substitution of the ortho positions by methyl groups. It has more degrees of freedom, and we might have not found all of the minima, but we have not found syn hydrazine minima for $\mathbf{c}^+$; our attempts at finding them by inverting at nitrogen only led to spontaneous inversion back to the minima shown when the last geometry restraint is removed.

Estimates of λ_v for Aromatic-Bridged Intervalence Bis(hydrazines)

Consideration of ET within an intervalence radical cation is simpler than that of intermolecular ET because the bridge controls the relative geometry between the charge-bearing units. The λ'_v value calculated by eq 1 should give a better number than using the related mono(hydrazine) as a model, because coupling through the bridge should affect λ'_v. However, having two hydrazine units in the intervalence compound raises the issue of the relative orientation of one with respect to the other, and these stereochemical features are illustrated for **Hy-PH-Hy** in Chart 3. The aromatic-bridged hydrazines can have the NN bonds either syn to each other (NN−N′N′ twist angle $\omega < 90°$) or anti ($\omega > 90°$), and the *tert*-butyl groups can be either on the same or opposite sides of the aryl plane, leading to four diastereomeric conformations related by double nitrogen inversions and N−Ar rotations.[2a,6] All four diastereomers of **Hy-PH-Hy** have been calculated to test how sensitive the ET parameters are expected to be to this type of isomerism, as summarized in Table 3. The calculated enthalpies of both the $\mathbf{n}^0$ and $\mathbf{c}^+$ diastereomers only range over 0.1 kcal/mol each, and the range in λ'_v calculated from the most stable $\mathbf{n}^0$ and $\mathbf{c}^+$ found is 0.5 kcal/mol; therefore, this ET parameter is quite insensitive to which diastereomer is employed for the calculation, which is a significant point for interpreting the experimental numbers because the compound measured ought to be a mixture of all four diasteromers. The **Hy** units interact through the **PH** bridge, slightly mixing the character of the oxidized unit into the neutral one and vice versa. This effect can be seen in the X-ray structural parameters found for **Hy-PH-Hy**$^+$, but not for **Hy-DU-Hy**$^+$, which has a significantly smaller H_{ab} value.[2a] The average λ'_v for **Hy-PH-Hy**$^+$ is 0.6 kcal/mol smaller than that calculated for the mono(hydrazine) **Hy-Ph**, consistent with an expected slight mixing of the characters of the charge-bearing units. Only calculations referring to the lowest enthalpy $\mathbf{c}^+$ minimum found for each diastereomer are shown in Table 3, but the energy surfaces for changes about $\mathbf{c}^+$ are complex, as for the mono(hydrazines). For the **aNsB** stereoisomer, two $\mathbf{c}^+$ minima having a syn oxidized hydrazine unit (which we will abbreviate as $(\mathrm{NN})^+$) having only 0.09 and 0.11 kcal/mol higher enthalpy than the anti-$(\mathrm{NN})^+$ conformation shown were also located, but they have larger λ'_v values by 5.2 and 5.6 kcal/mol, presumably because they are significantly more twisted (φ_+ 83° and 89°) than the $\varphi_+ = 55°$ *anti*-$(\mathrm{NN})^+$ conformation shown. As for the mono(hydrazines), AUHF optimizations get *syn*-$(\mathrm{NN})^+$ units to be more stable than their anti isomers; therefore, the AUHF entries in Table 3 all have θ_+ values near 7° instead of near 158°, like the UHF minima. The λ'_v values for the AUHF calculations are about 0.6 kcal/mol higher than that for **Hy-Ph**$^{0/+}$, instead of slightly smaller as they are for the UHF calculations. The λ'_v values for the higher enthalpy AUHF *anti*-NN^+ forms are even larger: for example, 45.9 kcal/mol for the **aNsB** *anti*-NN^+ isomer, which is 0.10 kcal/mol higher in enthalpy than the *syn*-$(\mathrm{NN})^+$ minimum. This occurs because the vertical neutral ($\mathbf{n}^0$) from *anti*-NN^+ has significantly lower enthalpy than that from *syn*-NN^+. It will be noted that the λ'_v values are too high for the UHF calculations and are even higher for the AUHF calculations. Better λ'_v values could doubtless be obtained using ab initio calculations; especially the $(\mathrm{NN})^0$ bond length is rather poor by AM1. The principal advantage of using AM1 calculations is that it

Table 4. Comparison of λ'_v (from Eq 1) with $\Delta E_K(\mathbf{c^0})$ Values (both in kcal/mol)

bridge	conf	diaster	λ'_v	$\Delta E_K(\mathbf{c^0})$	diff[a]
-PH-	aNsB	UHF	37.4	28.0	10.1
	aNsB	AUHF	43.9	32.5	7.7
-BI-	aNsB	UHF	36.9	24.1	12.2
	aNsB	AUHF	42.9	30.1	7.7

[a] Difference between λ'_v for the related mono(hydrazine) (see Table 2) and $\Delta E_K(\mathbf{c^0})$.

can be established far more rapidly what geometrical features must be controlled to obtain the smallest λ_v values; ET does not have to proceed through the global minimum conformation and will select conformations that give the smallest barriers.

Discussion

Failure of the Koopmans Estimate of λ'_v. Because the transition energy for a localized intervalence compound should be λ, one might expect that the Koopmans estimate of this energy, the orbital energy difference for the neutral compound at the geometry of the radical cation, $\Delta E_K(\mathbf{c^0})$, would be an estimate of λ'_v. This is, however, not the case, as is shown by comparing λ'_v (calculated using eq 1) with $\Delta E_K(\mathbf{c^0})$ in Table 4. Very similar results are obtained for all four diastereomers of the **PH**-bridged compound (only one is shown), and comparable results are obtained for all of the other compounds examined. Note also that $\Delta E_K(\mathbf{c^0})$ is much smaller than the λ'_v value obtained for the related mono(hydrazine) (last column of Table 4). $\Delta E_K(\mathbf{c^0})$ is clearly not a useful estimate of λ'_v for these compounds. We suggest that this happens because the intervalence charge-transfer absorption for a localized intervalence compound does not involve the direct promotion of an electron from the $(NN)^0$ HOMO to the $(NN)^+$ SOMO. If only these orbitals were involved, the nature of the bridge would not matter, but it is clear that the bridge is crucial. The intensity of the transition is governed by the interaction of both charge-bearing units with the bridge.[18] We suggest that because the intervalence transition involves "superexchange", simultaneous ET from the bridge to $(NN)^+$ and from $(NN)^0$ to the bridge, it does not involve a single promotion of an electron from one filled orbital to another half-filled one. We suggest that Koopmans' theorem, which is only accurate because of fortunate cancellation of errors,[19] does not apply to such a double excitation. Transitions that are not simple promotions of single electrons are not uncommon in the absorption spectra of radical ions, and the transition energies for such transitions cannot be predicted by using Koopmans' theorem.[19]

Estimates of H_{ab} for Aromatic-Bridged Intervalence Bis(hydrazines). According to classical Marcus theory, ET can only occur when the geometries of the charge-bearing units have become the same. In contrast to all other localized intervalence compounds of which we are aware, including the saturated-bridged compounds considered here, when proper symmetry is imposed to make the **M** groups identical (shown for each diastereomer in Chart 3), **Hy-PH-Hy**$^+$ and its close analogues are optimized with delocalized charge. Vibrational spectrum calculations show that each has one imaginary vibrational frequency; therefore, these are the calculated transition states for ET within these compounds, and we call structures having such imposed symmetry $\mathbf{t^+}$. The crudest way of estimating H_{ab} from calculations would appear to be to base the estimate on the enthalpy difference between the relaxed ground state ($\mathbf{c^+}$) and the transition state ($\mathbf{t^+}$), shown in Table 3 as $\Delta\Delta H_f(\mathbf{t^+}-\mathbf{c^+}) = \Delta H_f(\mathbf{t^+}) - \Delta H_f(\mathbf{c^+})$. For the two-state model with parabolic surfaces, the free energy of activation for ET, ΔG^*, is determined by λ and H_{ab} as shown in eq 2.[4] Our calculations are for gas-phase species;

$$\Delta G^* = \lambda/4 - H_{ab} + (H_{ab})^2/\lambda \qquad (2)$$

therefore, only λ_v is present. Experiments demonstrate that the Marcus−Hush two-state model works well[1,2,4] and that H_{ab} has so little sensitivity to solvent that the small effects observed lie within probable experimental error.[7] Because we do not expect H_{ab} to be significantly solvent sensitive for these compounds, we use eq 3

$$\Delta H^* = \Delta\Delta H_f(\mathbf{t^+}-\mathbf{c^+}) = \lambda'_v/4 - H'_{ab}(\text{second}) + (H'_{ab}(\text{second}))^2/\lambda'_v \qquad (3)$$

to provide an enthalpy-based estimate of electronic coupling in these systems. Equation 3 assumes that the energies of eq 2 may be replaced by enthalpies, and we use the calculated λ'_v, $\Delta H_f(\mathbf{t^+})$, and $\Delta H_f(\mathbf{c^+})$ to allow an estimate of the electronic coupling, which we call H'_{ab}(second). The H'_{ab}(second) estimate obtained using eq 3 is independent of Koopmans' theorem. Small errors in the ΔH_f values will cause large errors in ΔH^* and hence in H'_{ab}(second) when H'_{ab} is small; therefore, using eq 3 must be inaccurate for small coupling cases. Nevertheless, we list the H'_{ab}(second) values obtained in Table 3. The UHF H'_{ab}(second) values are very close to optically derived experimental H_{ab} values (Table 1), although the corresponding λ'_v values are about one-third larger than the optically derived λ_v value. However, we note that the AUHF calculations optimizing to the higher φ_+ syn-alkylated conformations appear to cause a problem for using eq 3 to estimate H'_{ab}(second). The entries shown in brackets for the AUHF calculations are for the enthalpy minimum syn conformation. As noted above, because H_{ab} is proportional to $\cos \varphi_+$, ET should be faster for the less twisted but slightly higher enthalpy anti conformation. However, $\Delta\Delta H_f(\mathbf{t^+}-\mathbf{c^+})$ is almost the same for syn and anti conformations because of the small enthalpy gap between the $\mathbf{c^+}$ minima, but λ'_v is significantly smaller for the anti conformations (see Figure 1). Using eq 3 makes H'_{ab}(second) smaller for the anti conformations than for the syn ones, which is not what should happen. Although this result is presumably incorrect, because it occurs eq 3 does not give internally consistent results for the AUHF calculations. There are other problems with the enthalpies of the AUHF calculations. λ'_v is even larger for the AUHF calculations than it is for the UHF ones, and $\Delta\Delta H_f(\mathbf{t^+}-\mathbf{c^+})$ is also unreasonably large. This leads to the unsatisfying result that, for these AM1 calculations, the spin-contaminated UHF calculations give results closer to experiment than do the

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[18] Bally, T. In *Radical Ionic Systems*; Lund, A., Shiotoni, M., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; p 3.

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

AUHF calculations using eq 3. We conclude that the enthalpy-based method of extracting H_{ab} from these calculations does not work very well.

A potentially more accurate way of estimating H_{ab} for these compounds would be to use the special properties of intervalence charge-transfer bands. Calculation of the intervalence band transition dipole moment that is necessary to directly calculate H_{ab} is inherently rather difficult, although especially Newton and Cave[20] have used Zerner's specially parametrized INDO semiempirical calculations[21] at the configuration interaction level for this purpose. AM1 calculations are not parametrized for accurate calculation of transition dipoles, nor do the programs available to us have such calculations implemented. However, the transition energy for a delocalized intervalence compound is $2H_{ab}$ according to Hush theory; therefore, the transition dipole does not need to be estimated to obtain H_{ab} if the transition energy can be estimated independently. The Koopmans method for obtaining H_{ab} is to use half the energy gap between the hydrazine-centered orbitals in the neutral compound calculated at the geometry of the transition state, which we will call $\Delta E_K(\mathbf{t^0})/2$. For several delocalized intervalence compounds, including *p*-phenylenediamine derivatives, AM1 calculations have been shown to give $\Delta E_K(\mathbf{t^0})/2$ values that are close to the observed transition energies, and hence according to Hush theory, $\Delta E_K(\mathbf{t^0})/2$ is close to H_{ab}.[21] Although the localized *p*-phenylene-bridged bis(hydrazines) being discussed also have benzene rings bearing para-substituted nitrogen-centered charge-bearing units, $\Delta E_K(\mathbf{t^0})/2$ is much larger than their optically determined H_{ab} values. For these compounds $\Delta E_K(\mathbf{t^0})/2$ is also significantly larger than a value consistent with the calculated difference in enthalpies between $\mathbf{t}^+$ and $\mathbf{c}^+$: using $\Delta E_K(\mathbf{t^0})/2$ as H'_{ab}(second) and λ'_v with eq 3 produces ΔH^* values that are 0.2 kcal/mol or less for the UHF calculations and 0.7 or less for the AUHF calculations.

$\mathbf{c}^+$ vs $\mathbf{t}^+$ Twist Angle for Evaluation of H_{ab} and Symmetry Breaking. Why does $\Delta E_K(\mathbf{t^0})/2$ not give a reasonable value of H_{ab} for these localized intervalence compounds? The problem does not appear to be the level of the calculation. The UB3LYP/6-31G* calculations gave $\Delta E_K(\mathbf{t^0})/2 = 11.9$ kcal/mol, and λ'_v was estimated from mono(hydrazine) models at 31.5 kcal/mol, giving a ΔH^* value of 0.5 kcal/mol.[13] Thus, even a considerably more sophisticated calculation produces too large a $\Delta E_K(\mathbf{t^0})/2$ value for it to be a reasonable H_{ab} estimate. It appears to us that the principal problem is not in the assumption that $\Delta E_K(\mathbf{t^0})/2$ is a good estimate of H_{ab} but in the substantially smaller twist angles φ for $\mathbf{t}^+$ than for $\mathbf{c}^+$ (see Table 3).[13] Changing an **M**−**B** twist angle for nearly p-hybridized atoms has always been expected to cause H_{ab} to vary as cos φ.[3,4] This prediction can be tested for $\Delta E_K(\mathbf{t^0})/2$ of **-PH-** using the C_2 **sNaB** and **aNsB** $\mathbf{t}^+$ species (the C_s **sNsB**$^+$ and C_i **aNaB** $\mathbf{t}^+$ structures have their NN−NN twist angles fixed at 0 and 180°, respectively, and if φ is changed, the symmetry is broken and the charge localizes). Figure 2 shows a plot of $\Delta E_K(\mathbf{t^0})/2$ for **aNsB** $\mathbf{t}^+$ calculations that have the angle φ varied by changing the NN−C=C twist angle, compared with $\cos^2 \varphi$ multiplied by a constant to make the curves the same at $\varphi = 0°$ (note that φ is not the same as the NN−C=C twist angle shown because the nitrogen is not quite planar). The twist angle for greatest stability is indicated, along with the range in twist angle corresponding to an *RT* increase in enthalpy at room temperature (the energy−twist angle plot is shown in the Supporting Information). Increasing the twist angle very far past the enthalpy minimum starts to cause the charge to become unsymmetrical, despite the C_2 symmetry imposed on the geometry. The dipole moment calculated along the long axis of the molecule using the center of mass as the origin, shown as μ_{ET} (D) in Figure 2, must be zero for a symmetrical charge distribution. It may be seen that μ_{ET} starts to increase as the NN−C=C twist angle gets above about 10° and that substantial charge localization occurs quite suddenly at twist angles above about 25°. As this charge localization occurs, the $\Delta E_K(\mathbf{t^0})/2$ value calculated is obviously affected, drifting back from the somewhat less than the $\cos^2 \varphi$ dependence calculated for the truly delocalized structures to nearly the position predicted by the idealized $\cos^2 \varphi$ dependence.

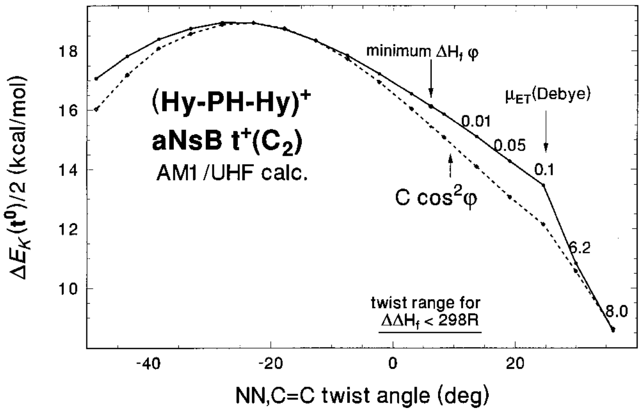

Figure 2. Plot of $\Delta E_K(\mathbf{t^0})/2$ vs the NN−aryl ring twist angle for the **-PH-** bridged compound in the aNsB geometry, optimized using C_2 symmetry. The dashed line compares the result with a scaled $\cos^2 \varphi$ curve.

It is not surprising when charge localization occurs, even though symmetry is imposed. Although this "should not happen", it usually does for quantum-mechanical calculations on open-shell systems. This effect has been discussed as the "Charybdis of Symmetry Breaking" by Bally and Borden.[22] Symmetry breaking appears to occur even for the especially well-behaved aromatic-bridged cations under discussion when they are far from their optimum geometry, and it can have a large effect on the enthalpy obtained, as is found for the cations vertical from the neutrals. The $\mathbf{n}^+$ cation (vertical from $\mathbf{n^0}$) for **Hy-PH-Hy** and many of its analogues is calculated to have significantly different enthalpy, depending upon whether the $\mathbf{n^0}$ calculation used has exact symmetry imposed. Although imposing exact symmetry during the optimization of the neutral oxidation state hardly affects $\Delta H_f(\mathbf{n^0})$ (the largest change obtained was a 0.017 kcal/mol stabilization for removing symmetry during optimization of the **sNaB** diastereomer), it has a large effect upon the charge distribution and the enthalpy of $\mathbf{n}^+$. When calculated from the not-quite-symmetrical structures, unsymmetrical charge distributions that are significantly more stable (by 3.2−3.6 kcal/mol) are obtained

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[20] Zerner, M. C.; Loew, G. J.; Kirchner, R. F.; Meuller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589.

[21] Nelsen, S. F.; Tran, H. Q. *J. Am. Chem. Soc.* **1998**, *120*, 298.

[22] Bally, T.; Borden, W. T. *Rev. Comput. Chem.* **1999**, *13*, 1.

than the symmetrical charge distribution $\mathbf{n}^+$ that arise from the symmetry-constrained neutrals. The higher enthalpy obtained for $\mathbf{n}^+$ using these symmetrical charge distribution calculations does not give λ'_v values that are expected from calculations on the related monohydrazines. The values thus obtained are larger than those of **Hy-Ph**$^{\mathbf{0/+}}$, which is not expected, while using the lower ΔH_f unsymmetrical charge distribution solution gives the expected λ'_v values, slightly smaller than the mono(hydrazine) calculation. Starting from the exactly symmetrical structures, very similar enthalpies and unsymmetrical charge distributions result when the density matrix from the symmetrical transition state ($\mathbf{t}^+$) is employed instead of using the default orbital-filling built into the program. We therefore believe that obtaining the symmetrical charge distribution and higher enthalpy solution is an incorrect result and that the unsymmetrical charge distribution results are the proper ones to use in calculation of λ'_v, as we have in Table 3.

Changing the φ twist angles from those of the transition state to those of the ground state leads to a smaller calculated H_{ab} value that is more consistent with the experimental optically derived H_{ab}. To test this quantitatively, we include values for a φ-adjusted H_{ab} estimate that we call $H_{ab}(\varphi\text{-adj})$ in Table 3, employing the $\mathbf{c}^+$ twist angles and using cos φ dependence at each **M**−**B** bond, as shown in eq 4. For the AUHF calculations, the

$$H_{ab}(\varphi\text{-adj}) = [\cos \varphi_+(\mathbf{c}^+) \cos \varphi_0(\mathbf{c}^+)/\cos^2 \varphi(\mathbf{t}^+)]\Delta E_K(\mathbf{t^0})/2 \quad (4)$$

enthalpy-minimum syn alkyl group (NN)$^+$ conformation gives a significantly smaller $H_{ab}(\varphi\text{-adj})$ value than the slightly higher enthalpy anti alkyl group conformation, from which the ET should proceed because of the larger electronic splitting. The entries for the AUHF calculations in Table 3 employ the latter value, and we note that they are significantly closer to the optical H_{ab} values than are the UHF values.

Data for only the **aNsB** form of **Hy-BI-Hy**$^+$ are also included in Table 3. This was the only conformation examined because of the small difference for different conformations of the **-PH-** bridged compound, and because $\mathbf{t}^+$ for it can only be calculated properly for C_2 symmetry diastereomers because that is the inherent symmetry of the bridge; if other diastereomers are constrained to C_s or C_i symmetry, this arbitrarily forces the twist angle at the central C−C bond connecting the *p*-phenylene rings to 0°, artificially destabilizing them. The geometric parameters at the hydrazine units are seen to be very similar, but λ'_v is calculated to be slightly smaller for the **-BI-** than the **-PH-** bridged compound, as expected from the related mono(hydrazines). The behavior of $H'_{ab}(\varphi\text{-adj})$ is quite similar for the two compounds, although the drop-off calculated for increasing the ET distance by inserting a second phenylene ring in the bridge, 6.3 → 3.8 kcal/mol, is not quite as large as that observed optically, 6.3 → 3.1 kcal/mol (Table 1). There are obvious problems in estimating H'_{ab}(second), which incorrectly comes out negative for **Hy-BI-HY**$^+$ possibly because the electronic coupling is small.

Thus, these calculations verify that H_{ab} depends significantly upon twist angle and that the twist angle is sensitive to position on the reaction coordinate, being significantly larger at the relaxed $\mathbf{c}^+$ geometry than it is at the geometry of $\mathbf{t}^+$. Nevertheless, the classical two-state Marcus−Hush model, which assumes that H_{ab} is a constant on the electron-transfer coordinate, has been shown to work well for these compounds. The treatment of Talaga and Zink appears to us to explain this contradiction.[23] Talaga and Zink point out that the same adiabatic surfaces can arise from different diabatic surfaces, in particular that using the same λ and H_{ab}, a model having diabatic surfaces that are superimposed on the electron-transfer coordinate but that have H_{ab} that increases as the geometry deviates from the minimum energy geometry (their model 3, which is qualitatively what happens for **-PH-** and its analogues because φ_+ decreases as the transition state is approached) and the Marcus−Hush model (their model 1)[24] give the same double-well adiabatic ET surface. Thus, there is in fact no inconsistency for the Marcus−Hush two-state model working for systems that have an H_{ab} increase as the classical ET transition state is approached, but H_{ab} needs to be evaluated at the geometry of $\mathbf{c}^+$ and not at that of $\mathbf{t}^+$ for such cases. This is a change from the Marcus−Hush theoretical treatment, which assumes that H_{ab} is independent of where on the ET surface H_{ab} is evaluated, but not from the practical analysis of an observed spectrum, which is by necessity done at the geometry of $\mathbf{c}^+$. We also note that using vibronic coupling theory makes ET a tunneling process that occurs at the ground state geometry; using it, the “electron transfer coordinate” region of the classical transition state is never significantly populated anyway.

Results

Intervalence Compounds That Produce Charge-Localized $\mathbf{t}^+$. Experiments indicate that saturated-bridged compounds having the *tert*-butyl substituents at the farthest apart nitrogens of the parallel bis(hydrazine) systems (anti) and those having them on the closer nonbonded nitrogens (syn) give data within experimental error of each other.[1] We have only calculated the anti diastereomers in the nitrogen inversion forms that make imposition of C_2 symmetry necessary to calculate transition states (see Chart 4), where the **i**nner and **o**uter notation refers to whether the substituents are directed on the face of the nitrogens that lies toward the center of the molecule, **i** (down in the views of Chart 4) or away from it, **o** (up). The results are summarized in Table 5. The *N*-phenyl saturated-bridged compounds **aBP4T**$^+$ and **aBP6**$\boldsymbol{\sigma}^+$ have lowest enthalpy as *syn*-(NN)$^+$ forms. Because they have larger φ_+ values than the *anti*-(NN)$^+$ forms, higher λ'_v values are obtained than for the aryl-bridged compounds.[25,26] The $\Delta E_K(\mathbf{t^0})/2$ values for **aBP4T**$^+$, **aBP6**$\boldsymbol{\sigma}^+$, and **aIP6**$\boldsymbol{\sigma}^+$are slightly smaller than half (42−47%) the size of their H_{ab}(opt) values. Because the bridge of these compounds is saturated, the size of φ_+ should not affect H_{ab} significantly.

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(23) Talaga, D. S.; Zink, J. I. *J. Phys. Chem.* **1996**, *100*, 8712.

(24) Talaga and Zink (TZ) use modified vibronic coupling theory (VCT) notation. Marcus−Hush theory uses diabatic parabolas $E_a = \lambda X^2$ and $E_b = \lambda(1 - X)^2$ that make the zero of energy the diabatic minima and the crossover point occur at $X = 0.5$. VCT theory makes the zero of both energy and the ET axis (Q) the parabola crossover point. TZ model 1 only has nomenclature changed from simplest Marcus−Hush theory: the diabatic parabolas are given by $E = {}^1/_2 k(Q \pm \Delta Q)^2$. What TZ calls ΔQ is usually written as V/k, where V is the vibronic coupling constant and k is the force constant. Their ϵ is the same as the Marcus−Hush H_{ab}. Although not explicitly used in VCT, $\lambda = 2k(\Delta Q)^2 = 2V^2/k$. TZ model 3 parabolas are both $E = {}^1/_2 kQ^2$, and the off-diagonal matrix element is $[((\Delta Q)kQ)^2 + \epsilon^2]^{1/2}$.

Table 5. ET Parameters Calculated by AM1-UHF for Bis(hydrazine) Cations with Charge-Localized t^+ [a]

	aBP4T$^+$, iPoB	**aBP6**σ^+, iPoB	**aIB6**σ^+, iIoB	**22H**$^+$, oo,ii	**Hy-DU-Hy**$^+$, aNaB
θ_+	12	10	17	0, 0	171
φ_+	77	78			84
$\langle S^2\rangle(\mathbf{c}^+)$	1.02	1.02	0.76	0.76 ,0.76	1.07
λ'_v	40.7	41.2	41.6	34.3, 32.7	40.1
$\Delta E_K(\mathbf{t^0})/2$	1.6	0.85	0.8	0.2, 6.5	4.5
$\Delta H^*(\mathbf{c}^+ - \mathbf{t}^+)$	10.1	9.6	10.0	7.9, 7.0	9.5
H'_{ab}(second)	0.1	0.7	0.3	0.7, 1.2	0.5

[a] Energies in kcal/mol and angles in deg.

Chart 4. Stereochemical Features of Bis(hydrazines) Having Saturated Bridges

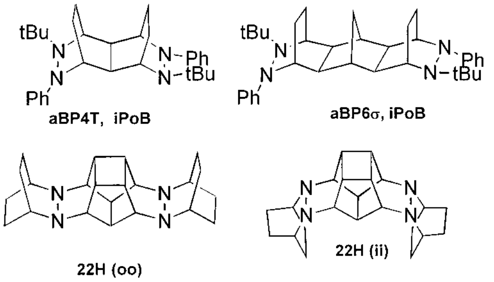
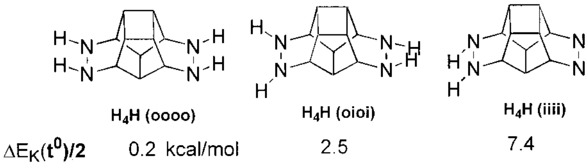


Chart 5. $\Delta E_K(\mathbf{t^0})/2$ Values for Model Bis(hydrazine) Radical Cations



A factor that ought to affect H_{ab} is the alignment of the lone pair orbitals with the intervening σ bonds. We especially note the large difference in predicted coupling for **ii** and **oo** **22H**$^+$, where the ratio of $\Delta E_K(\mathbf{t^0})/2$ values for the all-anti lone pair$-\sigma$-bond alignment **ii** conformation to the nonaligned **oo** is >29. To further examine the large effect of orbital alignment calculated for saturated bridges, we show $\Delta E_K(\mathbf{t^0})/2$ for the three symmetrical isomers of $\mathbf{H_4H}^+$ in Chart 5. The C_2 symmetry **oioi** isomer gives a value intermediate between the large value of the all anti lone pair$-\sigma$-bridge C_{2v} symmetry isomer **iiii** and the all gauche lone pair$-\sigma$-bridge C_{2v} symmetry isomer **oooo**. Important alignment effects on orbital$-$orbital interactions transmitted through σ-bonds were first pointed out by Hoffmann, have been especially studied using photoelectron spectroscopy by the groups of Gleiter and of Paddon-Row, and have been most recently reviewed by Jordan and Paddon-Row.[27] However, such effects on H_{ab} of **22H**$^+$ might not actually be this large. Especially the small temperature effect on the electron-transfer rate constant for **22H**$^{+\ 1b}$ makes it very likely that this compound does not exist in either the **oo** or **ii** conformation but instead exists, like the neutral oxidation state, in an **io** conformation so that the equilibrium constant for formation of a much larger H_{ab} and hence more reactive symmetrical conformation appears in the ET rate expression.[28] If this is true, the relatively large experimental H_{ab}(opt) = 4.3 kcal/mol appears incompatible with the very large orbital alignment effect predicted by these calculations.

The **-DU-** aromatic-bridged system was included in Table 5 instead of Table 3 because, like all the saturated-bridged systems we examined, it gives "symmetry breaking" for $\mathbf{t}^+$, the extra charge being localized on one hydrazine unit, even though the geometry is constrained to be the same at both units.[29] The considerably larger λ'_v value calculated for **Hy-DU-Hy**$^+$ than for the related mono(hydrazine) is inconsistent with the experimental optical spectrum. The conformational surface for this compound may be especially complex because of its very flattened nitrogens, very twisted hydrazine units, and especially large nonbonded interactions. We might well not have found the proper minima. It may be noted from Table 5 that $\Delta E_K(\mathbf{t^0})/2$ for the **-DU-** bridged aromatic system (4.5 kcal/mol) is far smaller than the 15.9$-$16.7 kcal/mol calculated for the **-PH-** bridged diastereomers. The principal reason for this drop in calculated $\Delta E_K(\mathbf{t^0})/2$ is the change in $\varphi(\mathbf{t}^+)$, 59° for the **-DU-** bridged species vs ~25° for **Hy-PH-Hy**$^+$: $[\Delta E_K(\mathbf{t^0})/2]/\cos^2 \varphi(\mathbf{t}^+)$ is 17.4 kcal/mol for **Hy-DU-Hy**$^+$, compared with 20.0 ± 0.5 for the four diastereomers of **Hy-PH-Hy**$^+$. It seems very likely that the $\varphi_+(\mathbf{c}^+)$ value of 84° calculated for **Hy-DU-Hy**$^+$ is too large, given that the X-ray crystallographic φ_+ values are 57° for **Hy-PH-Hy**$^{2+}$ and 64° for **Hy-DU-Hy**$^{2+\ 2a}$ and the relatively large H_{ab}(opt) value of 3.8 kcal/mol for the **-DU-** bridged compound. It seems ironic that this compound, which gives the most accurate experimental ET data, is the most difficult to calculate properly.

Conclusions

AM1 calculations predict that the Ar$-$N bond rotation and double nitrogen inversion diastereomers of aromatic-bridged bis(hydrazine) intervalence compounds should have very similar ET parameters. The Koopmans method for estimating vertical reorganization enthalpy for intervalence bishydrazine cations as being equal to the orbital energy difference for neutral in cation geometry ($\mathbf{c^0}$) is

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[25] For **aBP4T**$^+$ and **aBP6**σ^+ the anti alkyl conformations lie 0.4 and 0.2 kcal/mol higher in enthalpy than the syn ones shown in Table 4; the θ_+ values are both 163° and the φ_+ values 69°. As expected from the smaller φ_+ values, the λ'_v values are smaller than for the syn conformations, 38.9 and 39.5 kcal/mol, respectively.

[26] We do not discuss AUHF calculations for these saturated-bridged compounds because the results are very similar to the UHF ones, as might have been expected because their UHF $\langle S^2\rangle$ values are close to the pure doublet value of 0.75.

[27] (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R. *Acc. Chem. Res.* **1974**, *4*, 1. (c) Gleiter, R. *Angew. Chem., Int. Ed. Engl. 1974, 13*, 69. (d) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245. (e) Jordan, K. D.; Paddon-Row, M. N. *Chem. Rev.* **1992**, *92*, 395.

[28] Nelsen, S. F. *J. Am. Chem. Soc.* **1996**, *118*, 2047.

[29] The charge obtained for these symmetry-broken $\mathbf{t}^+$ species is nearly as localized as in the unsymmetrical, geometry-relaxed $\mathbf{c}^+$. For example, the AUHF calculation on aNaB **Hy-DU-Hy**$^+$ produces μ_{ET} = 10.56 D, 97% of that for relaxed $\mathbf{c}^+$ for this system, although the dipole moment obtained in the long-axis ET direction (μ_{ET}) is constrained by symmetry to be zero if charge is delocalized. Other compounds examined give similar results.

not valid, we suggest because the intervalence transition involves simultaneous double transfer of electrons (**B** → **M**$^+$ and **M** → **B**) and is thus not calculable using Koopmans' theorem. Calculation of λ'_v is complex for these compounds because conformational changes that only raise the enthalpy slightly can have a large effect on λ'_v. As expected from previous work, AM1 does a rather good job at estimating λ_v for saturated hydrazines: λ_v is slightly underestimated for **22**$^+$ and slightly overestimated (11%) for **aIB6**σ^+ compared to optically derived values. However, enthalpy-derived λ'_v values (eq 1) for aryl-substituted intervalence compounds are overestimated substantially (33−59%). The H_{ab} values for aromatic-bridged intervalence bis(hydrazines) clearly depend on N−Ar twist angles. Although AM1 calculations appear to give good estimates of H_{ab} using the Koopmans method (calculating $\Delta E(\mathbf{t^0})/2$), it is important to make the estimation using the relaxed cation (**c**$^+$) twist angles. The $\Delta E(\mathbf{t^0})/2$ method applied to the saturated-bridged compounds studied, all of which show "symmetry breaking", gives values slightly less than half of those determined optically, although it is not clear how important the symmetry breaking is in causing this underestimation.

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Supporting Information Available: Text giving a discussion of the enthalpy change for twisting the transition state of the **-PH-** bridged radical cation. This material is available free of charge via the Internet at http://pubs.acs.org.

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