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Estimation of Electron Transfer Distances from AM1 Calculations

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We examine a simple approximate method for calculating the electron transfer (ET) distance suitable for extracting the off-diagonal electronic coupling element (H_{ab}) of Marcus−Hush theory from the optical spectrum of nitrogen-centered organic intervalence radical cations. A very simple estimate of the ET distance on the adiabatic ground-state surface (d_{12}(dm)) is employed. AM1-UHF calculation of the dipole moment component in the long axis direction (μ_1) for the radical cation using the center of mass as the origin gives the estimated d_{12}(dm) (Å) = $2\mu_1$(Debye)/4.8023 (eq 7). Cave and Newton's Generalized Mulliken−Hush theory equation allows calculation of the diabatic counterpart (d_{ab}) in terms of d_{12} and the transition dipole moment (μ_{12}), obtained from the experimental intervalence optical band. These calculations indicate that d_{ab} is significantly smaller than the distance between the nominal sites or charge localization, ratio 0.82−0.85 for the aromatic-bridged bis(hydrazines), 0.76−0.87 for the unsaturated-bridged bis(triarylamines), 0.74−0.79 for the saturated-bridged bis(diazenes), and 0.71−0.85 for the saturated-bridged bis(hydrazines) examined here. Furthermore, d_{ab} is not very different for diastereomers that differ in relative orientation of the oxidized and reduced charge-bearing units for the aromatic-bridged compounds; experimental data corresponds to a superposition of the spectra of such isomers. There appears to be a problem with the trend of calculated ET distances as methyl groups are substituted on a benzene-1,4-diyl bridge. The d_{12}(dm) calculated is smaller for the compound with the tetramethyl-substituted bridge (**DU**) than that with the dimethyl-substituted bridge (**XY**), in contrast to the general trend in d_{12} as twisting increases, and to the dipolar splitting constant for the triplet form of the dication oxidation states of these compounds.

Introduction

Symmetrical, charge localized, intervalence (IV) compounds have two identical charge bearing units (**M**, often metal coordination complexes), symmetrically connected to a bridging unit (**B**).[1] They are at an oxidation level that places different charges on the **M** units, so they may be symbolized as $^{n+1}$**M**−**B**−**M**^{n}. They are the most revealing electron transfer (ET) systems yet devised, because they exhibit a charge-transfer (CT) band from which the ET parameters that allow prediction of the thermal electron-transfer rate constant can be estimated using Marcus−Hush theory.[2−4] When the electronic coupling through the bridge (the off-diagonal matrix coupling element H) is small enough relative to the total vertical reorganization energy upon electron transfer (Marcus's λ), the extra charge is mostly localized on one **M** unit. We will call the diabatic states (those in the hypothetical absence of electronic coupling between the **M**s, that is, at $H = 0$) a and b, and the adiabatic states resulting after inclusion of the electronic coupling 1 and 2. For the Mulliken−Hush model using parabolic diabatic states, the transition energy at the CT band maximum (the energy separation $\tilde{\nu}_{\max}$ between the adiabatic surfaces at the ground-state energy minimum, often called ΔE_{12}), is equal to the vertical energy separation at the minimum for the diabatic surfaces, ΔE_{ab}, and is also equal to λ.[2a,4d] We will use E_{op} to denote this experimental estimate of λ.[2,3] Hush related H_{ab} to E_{op} using the ratio of the transition dipole moment coupling the adiabatic surfaces, μ_{12}, to the change in dipole moment between the ground state and excited state on the diabatic surfaces, $\Delta\mu_{ab}$ (eq 1).[3]

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

Equation 1 is usually written[5] using $|\Delta\mu_{ab}| = e(d_{ab})$, leading to eq 2, where d_{ab} is the effective electron-transfer distance (Å),

$$|H_{ab}| = 2.06 \times 10^{-2}(\epsilon_{\max}\,\Delta\tilde{\nu}_{1/2}\,E_{op})^{1/2}/d_{ab} \tag{2}$$

$\Delta\tilde{\nu}_{1/2}$ the bandwidth at half-height (cm^{-1}), and $\epsilon_{\max}$ the extinction coefficient at the band maximum (cm^{-1} M^{-1}). More sophisticated versions of eqs 1−2 derived using vibronic coupling theory (VCT)[6] are available.[7] They require accurate separation of λ into its classically treated solvent (λ_s) and quantum mechanically treated internal vibrational (λ_v) components (their sum, λ, is slightly larger than E_{op}) and also a weighted average energy of the vibrations responsible for ET ($\tilde{\nu}_v$). Using VCT the observed IV−CT band is a superposition of transitions to each vibrational level of the excited state, weighted by the Franck−Condon factors, so the expression for bandwidth is complex. Nevertheless, a VCT treatment applied to dinitrogen-centered IV compounds produces H_{ab} values that are quite close to those using eq 2 when the same ET distances are employed,[8,9] except for a refractive index (n) correction to $\epsilon_{\max}$ that was not used in obtaining eq 2. The correction corresponds to a factor in H_{ab} of $\geq n^{-1/2}$, i.e., a factor of ≥ 0.86 in acetonitrile at 25 °C, depending on the form of the refractive index correction used.[7]

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Electron-Transfer Distances. This work is concerned with how to estimate the size of d_{ab} that is appropriate to use in eq 2 applied to nitrogen-centered IV compounds. The metal−metal distance has been commonly used as d_{ab} for IV compounds with metal-centered **M**, because the distance in Hush's eq 2 refers to that for the diabatic surfaces (at $H_{ab} = 0$), and if the ligands were all the same, the metal obviously would be the center of charge. However, some charge is delocalized onto the ligands, and the bridge is a ligand that is different from the others, usually more easily oxidized or reduced, so the effective d_{ab} might be argued to be somewhat smaller than the metal−metal distance. Experimental estimates of the effective d from independent measurements of $\Delta\mu$ pertain to the real system, which has a nonzero H_{ab}, and will thus be measures of $d_{12} \equiv \Delta\mu_{12}/\mathrm{e}$, although this distinction has often not been made in the literature (cf. refs 4 and 10). Charge separation distances for the excited states obtained by photoexcitation of neutral organic donor-bridge-acceptor systems in nonpolar solvents have been estimated using time-resolved microwave conductivity experiments, as for Paddon−Row's dimethoxynaphthalene, dicyanoolefin compounds linked by saturated polycyclic alkyl groups.[11] Experimental evaluation of the dipole moment change upon excitation of IV compounds, and hence of their d_{12} values, have employed electroabsorption (Stark effect) spectroscopy.[12−14] The effect of an applied electric field on the position of the absorption maximum of an IV compound frozen in a matrix is analyzed. These studies have shown that d_{12}(Stark) may be considerably smaller than metal−metal distances, even approaching zero for strongly coupled systems.[12,13] Organic charge-bearing units obviously have delocalized charges, but for convenience, the distances between the centers or edges of these units (the atoms attached to the bridge) have often been used as the d_{ab} values required to apply eq 2 for evaluation of H_{ab}.[11] In their generalized Mulliken−Hush theory,[4] Newton and Cave point out that eq 3 gives the relationship between the

$$|\Delta\mu_{ab}| = [(\Delta\mu_{12})^2 + 4(\mu_{12})^2]^{1/2} \tag{3}$$

diabatic and adiabatic $\Delta\mu$ values. Analogous to the comments made in connection with eq 1,[5] eq 3 in general refers to dipole components along the charge-transfer direction. In the present study (except as noted otherwise) the latter direction corresponds to that of $\Delta\vec{\mu}_{12}$.

The ratio of d_{12} to d_{ab} is the ratio between the positions of the adiabatic and diabatic minima on the ET coordinate X using the simple two state model, which is $1 - 2X_{\min} = (1 - 4H^2/E_{\mathrm{op}}^2)^{1/2}$.[2a] This relationship makes it easy to see that d_{12} approaches 0 as H approaches $E_{\mathrm{op}}/2$ and the system changes from an instantaneously charge-localized one to one that is delocalized. The expression for μ_{12} obtained from eq 1 and 2 is shown in eq 4. Equation 3 may be written in terms of the ET

$$\mu_{12} = (2.06 \times 10^{-2})\mathrm{e}(\epsilon_{\max}\,\Delta\tilde{\nu}_{1/2}/E_{\mathrm{op}})^{1/2} \tag{4}$$

distances as eq 5, which is convenient for converting d_{12} to d_{ab} from experimental parameters for the observed IV−CT band.

$$d_{ab}^{\ 2} = d_{12}^{\ 2} + 4\,(2.06 \times 10^{-2})^2\,\epsilon_{\max}\,\Delta\tilde{\nu}_{1/2}/E_{\mathrm{op}} \tag{5}$$

Cave and Newton showed how d_{ab} may be fully determined using either experimental (spectroscopic) or calculated data. For example, they estimated d_{ab} using eq 3 with semiempirically calculated $\Delta\mu_{12}$ and μ_{12} values, employing the INDO method of Zerner and co-workers,[15] at the configuration interaction (CI) level to describe the initial and final states.

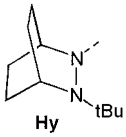
Nelsen's group has used the relatively high internal reorganization energy of nitrogen-centered charge-bearing units to increase E_{op} enough to allow the rate for intramolecular ET (k_{ET}) to be sufficiently slow to measure by ESR even when H_{ab} is large enough to make the IV−CT band clearly visible.[8,16] The nitrogen ESR splitting constant for hydrazine radical cations and hydrazyl radicals is in the range 11−13 G, which makes the ESR spectrum of their IV radical cations very sensitive to intramolecular electron exchange when k_{ET} is near 10^8 s^{-1}. We will call k_{ET} values measured by this method k_{ESR}. The k_{ESR} value provides a sensitive check on the accuracy of the optically determined H_{ab} value. Using Hush theory with parabolic diabatic surfaces, eq 6 with $A = 1$ is the expression for the thermal ET

$$\Delta G^* = AE_{\mathrm{op}}/4 - H_{ab} + H_{ab}^{\ 2}/E_{\mathrm{op}} \tag{6}$$

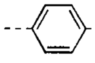
barrier, ΔG^*.[2] Parabolic diabatic surfaces used with the simple classical two state model of Marcus−Hush theory produce an IV−CT band having a width at half-height of $\Delta\tilde{\nu}_{1/2}^{HTL} = (16\,RT\ln(2)\,E_{\mathrm{op}})^{1/2}$. Many of our compounds show broader bands than this. The conventional way of handling this problem is to employ VCT using a single mean harmonic mode,[6] but this procedure is insufficient for our compounds, we believe, because their high λ_{v} values require assuming harmonic energy surfaces to unreasonably high vibrational levels. We therefore assumed that the IV−CT band reveals the effective adiabatic surfaces. Using the simple two state model to relate diabatic to adiabatic surfaces requires that the diabatic surfaces are not prefect parabolas unless $\Delta\tilde{\nu}_{1/2} = \Delta\tilde{\nu}_{1/2}^{HTL}$. Good fit to the observed band shape for all our compounds is obtained using a quartic term in the diabatic surfaces, that is, using $H_{aa} = \lambda/(1 + C)(X^2 + C\,X^4)$ and similarly for H_{bb}, with X replaced by $(1 - X)$ (Marcus−Hush theory uses $C = 0$). This produces an increasingly smaller value of A in eq 4 as C increases. We used the ΔG^* values from eq 4 in an adiabatic rate expression to obtain the rate constant for thermal ET estimated from the optical parameters of the IV−CT band, k_{opt}.[16b,c,17] There is no particular physical significance to using an X^4 term in fitting the optical spectrum, and other functions fit as well.[16c]

For compounds having saturated bridges doubly linking charge-bearing dinitrogen units (discussed later), the dinitrogen units are oriented nearly perpendicular to the electron transfer axis of the molecule. The shortest distances between the nitrogen atoms and the distance between the midpoints of the NN bonds, which ought to be very close to the centers of charge for these tri- and tetraalkyl dinitrogen systems, are nearly the same. For these compounds, using the distance between the dinitrogen units (d_{NN}) as d_{ab} in eq 2 gives k_{opt} values that are rather close to k_{ESR}.[8,9,16]

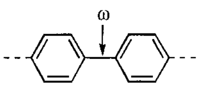
We have also studied several examples of $^+$**Hy**−**Ar**−**Hy**, where **Hy** is the 2-*tert*-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl unit, and **Ar** is a symmetrical aromatic diyl such as the ones shown below. For these compounds the NN bond axes lie at about a 120° angle to the ET axis, and the aromatic bridge is considerably different electronically from the other three (saturated alkyl) substituents at each dinitrogen unit. For $^+$**Hy**−**Ar**−**Hy**, we found good agreement of k_{opt} with k_{ESR} when we employed



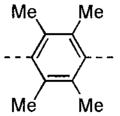
Hy



PH



BI



DU

TABLE 1: Comparison of Various Distances (Å) Calculated for Simple Aryl-Bridged IV Bis(hydrazines)

compound	$d_{N,N}$ [a]	$2r$(pc) [b]	μ_{12} [c]	d_{ab}(pc) [d]	d_{12}(ESR) [e]
$^+$Hy−PH−H	—	6.14	—	—	—
$^+$Hy−PH−Hy	5.70	4.56	4.30	4.90	4.6−4.8
$^+$Hy−DU−Hy	5.70	4.59	2.30	4.69	5.67
$^+$Hy−BI−Hy	9.99	8.42	3.18	8.52	8.0

[a] Distance between the nitrogens bonded to the aryl bridge, from the AM1-UHF energy minimum structure (the **sNsB** diastereomers of these compounds). [b] Twice the distance from the center of charge to the center of the aryl bridge. [c] Transition dipole moment, in Debye. Calculated using eq 4 and the experimental optical parameters in acetonitrile: (see ref 13c) $^+$**Hy−PH−Hy** $E_{op} = 13\,000$ cm^{-1}, $\epsilon_{max} = 3800$ M^{-1} cm^{-1}, $\Delta\tilde{\nu}_{1/2} = 6460$ cm^{-1}; $^+$**Hy−DU−Hy** $E_{op} = 14\,100$ cm^{-1}, $\epsilon_{max} = 970$ M^{-1} cm^{-1}, $\Delta\tilde{\nu}_{1/2} = 7890$ cm^{-1}; $^+$**Hy−BI−Hy** $E_{op} = 15\,210$ cm^{-1}, $\epsilon_{max} = 2600$ M^{-1} cm^{-1}, $\Delta\tilde{\nu}_{1/2} = 6040$ cm^{-1}. [d] Calculated from μ_{12} in acetonitrile using eq 5, with $2r$(pc) as d_{12}. [e] Estimated from the dipolar splitting of the +2 oxidation state ESR spectrum. (See refs 16b,c.)

distances obtained from the dipolar splitting of the triplet form of the dication diradical (d(ESR), Å $= 30.3/D^{1/3}$, where D is the dipolar splitting in Gauss) in making H_{ab} value estimates from the optical spectra.[16b,c,17] However, because d(ESR) arises from an experimental measurement which refers to adiabatic energy surfaces, it is an experimental estimate of d_{12}. To the extent that d_{ab} and d_{12} differ, what we did departs from the general practice of using d_{ab} estimates for the ET distance since 1967. This paper considers how different these two quantities are predicted to be, and how much they differ from the traditional estimates of charge center separation, employing semiempirical AM1 calculations[18] (at the unrestricted Hartree−Fock (UHF) level) to estimate d_{12} for several types of nitrogen-centered IV compounds.

Estimates of Electron-Transfer Distances from AM1 Point Charge Distributions. We shall first consider very simple estimates of d_{12} for the three $^+$**Hy−Ar−Hy** examples shown above (see Table 1). For these monocations, we first employ the centroid of atomic point charges (which we will call the center of charge)[19] relative to the **PH** midpoint (r(pc), for point charge) as the basis for estimating d_{12}. Direct calculation of d_{ab} does not seem achievable because the bridge obviously interacts with the hydrazine units, and we see no simple way to turn off this interaction in a calculation on an IV compound. An estimate of d_{ab} in the spirit of using the metal−metal distance for metal-centered compounds would be to use distance between the midpoints of the NN bonds as d_{ab}, using the assumption that the center of charge for the oxidized hydrazine unit lies at the midpoint of the NN bond. However, the aryl bridge has quite different electronic properties from saturated alkyl groups, so it ought to be a better assumption to include the bridge as well as the **Hy** unit in calculating the center of charge. We therefore consider the center of charge for a monohydrazine model, $^+$**Hy−PH−H**. It has no H_{ab} because it lacks the second **Hy** unit, but it can delocalize the positive charge onto the phenyl group as well as the alkyl groups. The center of charge for the AM1-UHF optimized structure lies 0.21 Å from the midpoint of the NN bond and corresponds to r(pc) = 3.07 Å. We therefore estimate d_{ab} for $^+$**Hy−PH−Hy** using this model compound as $2r$(pc) = 6.14 Å. However, 6.14 Å does not yield a realistic H_{ab} for $^+$**Hy−PH−Hy** using eq 2. When the H_{ab} it produces is used in eq 4, the calculated k_{opt} is 7.5 to 5.5-fold smaller than that using the 4.6−4.8 Å estimate based on d(ESR). We only know k_{ESR} approximately for $^+$**Hy−PH−Hy** because it is inconveniently large on the ESR time scale for very accurate measurement, but it is a few times larger than that estimated using $2r$(pc) as d_{ab} in eq 2. k_{ESR} approximately agrees with the k_{opt} calculated using d_{12}(ESR).[16b] Perhaps a better model compound for $^+$**Hy−PH−Hy** than $^+$**Hy−PH−H** could be found, but if a substituent is included at the para position of the bridge of a model system, this system will have an H_{ab} value for electronic interaction of the substituent with $^+$**Hy** through the bridge. Figure 1 compares the r(pc) values for $^+$**Hy−PH−NH$_2$** having enforced twisting at the C$_{Ar}$−NH$_2$ bond with those for $^+$**Hy−PH−H** and $^+$**Hy−PH−Hy**. When the NH$_2$, aryl ring twist angle $\phi = 90°$ and through-ring electronic coupling is lost, r(pc) is nearly as large as for $^+$**Hy−PH−H**, but as this coupling becomes larger when the NH$_2$,Ar overlap is increased, r(pc) drops, following the expected cosϕ relationship. Coupling of NH$_2$ with $^+$**Hy** never becomes as effective as that of **Hy** because the energy gap is larger for NH$_2$. Figure 1 indicates that estimating the electron-transfer distance from the geometric distance between the charge centers of organic **M** units is not a good way to proceed. Structural changes five bonds away from the aryl nitrogen cause large changes in the calculated distance, and there appears to be no good way to choose a compound to use as the model that would produce the distance required. The geometric distance between the charge centers of the **M** groups has almost always been used in calculating H_{ab} using eq 2, but there are apparently problems.

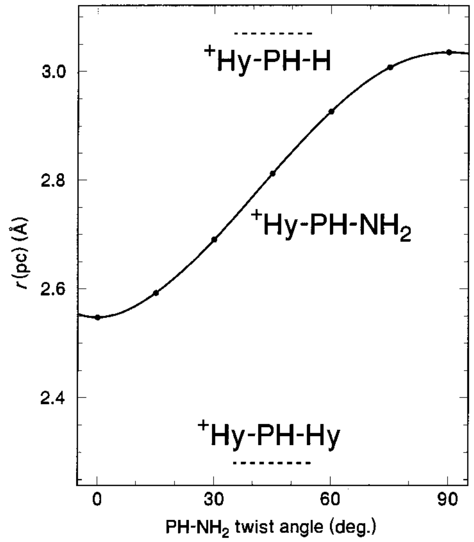
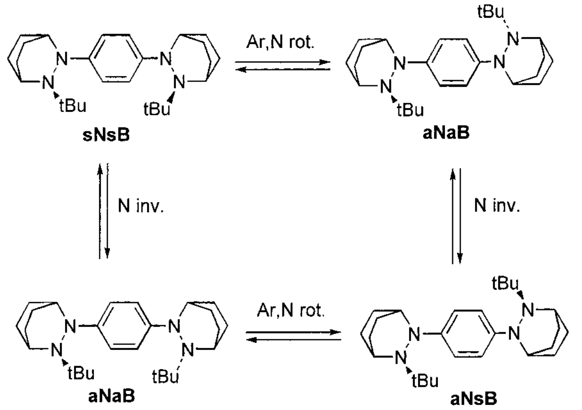


Figure 1. Plot of r(pc) versus the Ar−NH$_2$ twist of $^+$**Hy−PH−NH$_2$**, and for comparison, r(pc) values for $^+$**Hy−PH−H** and $^+$**Hy−PH−Hy**. The r(pc) values are given in Å.

One might expect to obtain d_{12} from r(pc) calculated in the same manner for the IV compound (d_{12}(pc) = $2r$(pc)). The charge center calculated for $^+$**Hy−PH−Hy** lies nearer the midpoint of the N−C$_{Ar}$ bond, and r(pc) = 2.28 Å. There are four nearly isoenergetic diastereomers calculated for $^+$**Hy−PH−Hy**. For the **sNsB** isomer (see Scheme 1 below) we obtain d_{12}(pc) = 4.56 Å. Use of this estimate together with eq 5 and the optical data yields a d_{ab} estimate of 4.90 Å, rather close to the d(ESR) of 4.6−4.8 Å obtained from a compound, and also compatible with the rather imprecisely known k_{ESR} for $^+$**Hy−PH−Hy**. Figure 1 includes the r_{12}(pc) value for $^+$**Hy−PH−Hy**, which is seen to be considerably smaller than the value obtained for $^+$**Hy−PH−H**. These calculations indicate that when there is a substantial electronic interaction through a bridge as in this compound, using the center of charge in the $^+$**M−B** unit as a model to estimate the electron-transfer distance is inadequate.

SCHEME 1: Diastereomers of Hy-PH-Hy



Increasing the number of bonds in the bridge to nine in $^{+}$**Hy**−**BI**−**Hy** increases r(pc) to 4.21 Å, so a maximum d_{12} estimate is 8.42 Å, while the distance between the NN bond midpoints is 10.7 Å, and the edge-to-edge N_{Ar}−N_{Ar} distance is 9.99 Å for the minimum energy diastereomer. Once again, a d_{ab} value estimated from the centers of the NN bonds or the edges of the charge bearing unit is larger than d_{ab}(pc) estimated from the charge and ring centers and the observed optical spectrum. The difference between d_{ab}(pc) and $2r_{12}$(pc) is significantly smaller (1.2%) for the smaller H_{ab} **BI**-bridged compound than it is for the **PH**-bridged one (7.5%). The observed k_{ESR} is compatible with H_{ab} obtained from eq 2 when the experimental d_{ESR} estimate from the dipolar splitting of the dication, 8.0 Å, is used, but this is not very different from using d_{ab}(pc). The effect of decreasing H_{ab} by increasing twist at the aryl ring hydrazine units upon methylating the *p*-phenylene bridge, which does not change d_{NArNAr}, is apparently not predicted properly by AM1 calculations. The AM1 value of $2r$(pc) for $^{+}$**Hy**−**DU**−**Hy** is only 0.03 Å larger than for the less twisted, higher H_{ab} $^{+}$**Hy**−**PH**−**Hy**. Equation 5 predicts a smaller d_{ab}(pc) value for $^{+}$**Hy**−**DU**−**Hy** than for $^{+}$**Hy**−**PH**−**Hy** because μ_{12} is significantly smaller. Using the d(ESR) values with eq 2 for both $^{+}$**Hy**−**PH**−**Hy** and for $^{+}$**Hy**−**DU**−**Hy** does produce agreement with the experimental k_{opt} values.[16b]

Estimates of d_{12} for Aryl-Bridged Bis(hydrazines) from Dipole Moment Changes. The interpretation of the charge-center estimations of d_{12} using $2r$(pc) as discussed above is based on an assumed relationship between a point charge representation of charge densities and the effective ET distance. A more direct approach is to calculate the change in dipole moment, $\Delta\mu_{12}$. Cave and Newton used CI to describe the relevant states,[4,20] but here we investigate an approximate computational shortcut.[21] If the dipole simply switches sign as the charge centroid switches from one end of the molecule to the other upon excitation, which is qualitatively what happens in the symmetrical IV compounds under discussion, eq 7 might be

$$d_{12}(\mathrm{dm}) = 2\,\mu_1(\mathrm{Debye})/4.8032 \qquad (7)$$

expected to be a reasonable approximation for d_{12} (in Å), where μ_1 is the calculated AM1-UHF dipole moment (dm) for the ground state of the IV compound. Using eq 7 is quite similar to using the point charge approach, but accounts for the slightly nonspherical distribution of electrons about the heavy atoms. The dipole moment of an ion depends on the choice of the origin for the calculation, and we have used the center of mass as the origin for the dipole moment calculation. Equation 7 is an approximation because the geometries are slightly different at the oxidized and reduced **M** units, but the approximation appears to be quite a good one (see the section on bis(hydrazines) with saturated bridges).

It is not clear how to define the electron transfer axis rigorously for localized IV compounds, which have no symmetry because the geometries of the charge bearing units differ somewhat. In all cases, the largest component of the dipole moment vector (μ_1) is, as expected, along the long axis of the molecule, which corresponds at least roughly to the electron-transfer axis. Support for adopting the long axis (whose precise definition depends on the detailed structure of the IV system, as indicated in the table footnotes) is provided (for a small sample of the IV systems considered in the present paper) by supplementary CI calculations[22] carried out at the INDO level[15] for both $\Delta\vec{\mu}_{12}$ and $\vec{\mu}_{12}$. These calculations show that $\Delta\vec{\mu}_{12}$ and $\vec{\mu}_{12}$ are nearly collinear and are also essentially collinear with the long axis component of $\vec{\mu}_1$ (as well as $\vec{\mu}_2$, the dipole moment of the final state). They also indicate that the approximation for $\Delta\mu_{12}$ entailed in eq 7 is accurate to 10% or better. Finally, these calculations reveal that in some cases $\vec{\mu}_1$ and $\vec{\mu}_2$ may have appreciable components perpendicular to the long axis that tend to cancel in $\Delta\vec{\mu}_{12}$. Some related examples based on the present AM1-UHF calculations are also noted below, and estimates of the effect are provided in the tables by the parameter R_{μ}, the direction cosine between the long axis component and $\vec{\mu}_1$. We will use the designation d_{ab}(dm) for d_{ab} values obtained using using d_{12}(dm) values obtained from eq 5 using d_{12}(dm) values based on eq 7. These d_{ab}(dm) values appear in the tables, and we believe they constitute a simple, convenient method for extracting electron-transfer distance estimates from a combination of experimental optical measurements and calculations.[23]

Diastereomers of similar energy that interconvert by nitrogen inversions and CN bond rotation exist for most of the compounds studied here, and we are especially interested in finding out whether these diastereomers should have significantly different d values. Carbon NMR has shown that at −50 °C, the neutral species **Hy**−**PH**−**Hy** is present as an equal mixture of four slowly interconverting diastereomers,[16] shown diagrammatically in Scheme 1. There is a most favorable twist angle between the axes of the aryl ring pπ orbital and the lone pair at the nitrogen attached to the aryl ring (ϕ = 33°), but these diastereomers differ in other aspects of the relative orientation of their **Hy** units. Double nitrogen inversion in the **Hy** units (the vertical arrows in Scheme 1) is slow on the NMR time scale even at elevated temperatures (single nitrogen inversions would give cis alkyl groups; such conformations are much less stable than ones having trans alkyls for neutral bicyclic hydrazines). Aryl, N rotation (the horizontal arrows) is slow at −50 °C for **Hy**−**PH**−**Hy**. This causes separation of signals for diastereomers that differ by having the twist angle between their NN bonds (χ) nearer 0° (which we will abbreviate **sN**) or nearer 180° (**aN**), and the *tert*-butyl groups may either be on the same side of the bridge (**sB**) or on opposite sides (**aB**). The nearly equal amounts of these four diastereomers that are present show that the energy of one **Hy** unit is not affected by the relative orientation of the other one. The intervalence radical cation oxidation state diastereomers are calculated to also have very similar enthalpies, total range 0.1 kcal/mol (see Table 2). The charge is principally localized in one hydrazine unit, and the geometries at the cationic and neutral hydrazine units are rather different. A more realistic view of the **sNsB** diastereomer is shown below, with the central bonds for the two types of twist angles (ϕ and θ) indicated. The X-ray structure of crystalline

TABLE 2: AM1-UHF Twist Angles (deg.) and *d* Values (Å) for $^{+}$Hy−PH−Hy Diastereomers

	rel. ΔH_f[a]	χ[b]	θ_+[c]	θ_0	ϕ_+[d]	ϕ_0	$d_{N,N}$	d_{12}(dm)	R_μ[e]
sNsB	0.00	33.0	157.8	130.5	55.8	32.8	5.70	4.47	0.996
sNaB	0.05	50.6	157.6	130.6	55.1	32.6	5.70	4.48	0.993
aNsB	0.02	129.1	157.7	130.4	55.4	32.4	5.70	4.48	0.983
aNaB	0.10	150.9	157.5	130.5	54.7	32.7	5.70	4.47	0.980
•*(sNsB)x-ray*[f]		23.6	142.4	147.3	47.6	32.6	5.66	—	—

[a] Unit: kcal/mol. [b] χ is the twist angle between the two NN bonds. [c] θ is the twist angle between the nitrogen lone pair axes, calculated assuming the axes bisect the CNC bond angle in a projection down the NN bond. The + and 0 subscripts refer to the radical cation and neutral hydrazine. [d] ϕ is the twist angle of the nitrogen lone pair axis, aromatic carbon p orbital axis at the N−Ar bond. [e] R_μ is the direction cosine between the calculated dipole vector and the charge transfer direction, taken as the vector corresponding to the long axis of the system. The long axis direction was chosen as the line between the aryl nitrogens for the π-bridged systems and that between the midpoints of the NN bonds for the saturated-bridged systems. [f] From the Supporting Information for ref 16a.

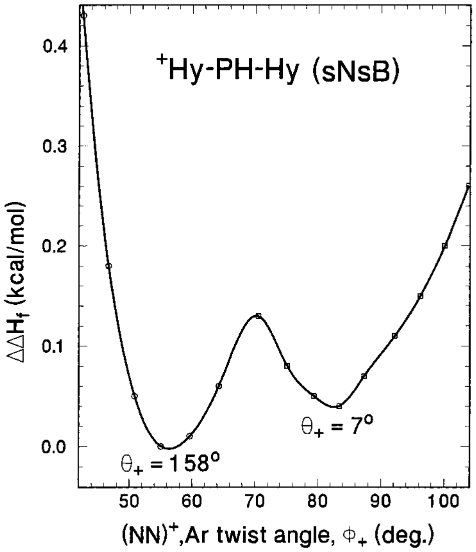
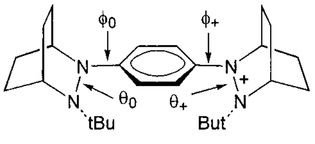


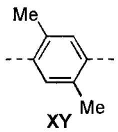
Figure 2. Plot of the change in ΔH_f as a function of forcing an NN$^+$−Ar twist angle (ϕ_+) to change. A very small increase in ΔH_f is calculated because N_{Ar}, which is nearly planar, inverts without changing the steric interaction of the *tert*-butyl group with the ring significantly.

$^{+}$**Hy−PH−Hy** Ph_4B^- shows it to be in the **sNsB** diastereomer, to have ϕ_0 and $d_{N,N}$ quite similar to the calculated values, and to have a 16° smaller θ_+, 17° larger θ_0, and 8° smaller ϕ_+ value. However, these compounds are exceptionally flexible at the oxidized **Hy** unit. Figure 2 shows that there is a double minimum in the $\Delta\Delta H_f$ versus ϕ_+ plot, and that the heat of formation (ΔH_f) is calculated to change less than 0.2 kcal/mol for a 60° change in ϕ_+. This occurs because the very flattened N_{Ar} nitrogen has only a very small inversion barrier, and the oxidized hydrazine unit changes from having *tert*-butyl and Ar anti (θ_+ large, 158° at the minimum enthalpy point) to syn (θ_+ small, 7° at the minimum enthalpy point) near the maximum of the curve (about $\phi_+ = 125°$). This flexibility at the oxidized hydrazine unit (NN$^+$) allows the relative position of the bulky *tert*-butyl and aryl groups to change little for rather large changes in ϕ_+. The geometry obtained for the neutral hydrazine unit (NN^0) is rather insensitive to changes at NN$^+$. As shown in Table 2, d_{12}(dm) is quite similar (4.53(4) Å) for all four optimized diastereomers. Furthermore, it is also insensitive to changes in ϕ_+, because all of the points shown in Figure 2 for the **sNsB** diastereomer lie within 0.09 Å (0.02%) of their average. Thus despite the presence of four diastereomers and great flexibility at the oxidized hydrazine unit for each of them, all produce nearly the same d_{12}(dm) value. It is important that this be the case for a Hush analysis of the optical data to work well.

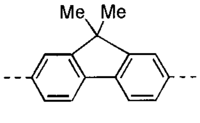


$^{+}$**Hy-PH-Hy (sNsB)**

Similar calculations for other aromatic-bridged bis(hydrazines) in their most stable form are compared with available X-ray data in Table 3. In addition to the compounds discussed above, we include *p*-xylylene (**XY**) and 9,9-dimethyl-2,7-fluorenylene (**FL**), the latter being the central bond twist angle ω = 0 analogue of **BI**. Increasing steric hindrance between the bridge and the hydrazine units by adding methyl groups to the bridge in **XY** and **DU** significantly increases the calculated ϕ values (see Table 3). Diastereomers having the NN bond syn to the methyl-substituted carbon for the **XY** bridge are significantly less stable than those having the NN bond anti (that is, syn to the CH bond, causing less steric hindrance), and only these diastereomers are calculated to be populated, consistent both with the ^{13}C NMR of neutral **Hy−XY−Hy**,[16b] and X-ray data.



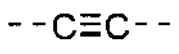
XY



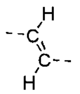
FL

The most stable diastereomer of $^{+}$**Hy−BI−Hy**, **sNsB**, has a central bond twist angle ω = 32.7° in its most stable form. The ω = 0 form (not shown here) is calculated to be 1.1 kcal/mol less stable, and d_{12}(dm) only drops 1% compared to the most stable form. As might be expected because of the similarity in steric interactions, the ϕ values for the **BI**- and **FL**-bridged compounds are calculated to be close to those for the **PH** bridge.

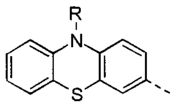
Estimates of d_{12} for IV Arylamines and TTF Derivatives. Similar calculations for IV compounds having arylamine charge-bearing units are summarized in Table 4. Lambert and Nöll recently published an IV-CT band analysis for the acetylene-bridged bis(triarylamine) $^{+}$**An$_2$NPH−C$_2$−PHNAn$_2$** (**An** = *p*-methoxybenzene).[24] They used a *d* of 12.48 Å (the N−N distance) in extracting *H* using eq 2.[24] We get very close to this value for the N−N distance, but obtain a d_{ab}(dm) of 11.4 Å. We also calculated three unsaturated-bridged phenothiazine-2-yl (**PT**) derivatives (R = Me), as models for the R = *n*-Heptyl



C$_2$



(CH)$_2$



PT

TABLE 3: Twist Angles (deg.) and ET Distances (Å) for Aromatic-Bridged Bis(hydrazine) Radical Cations (X-ray Data for Comparison Are Marked with • and Shown in Italics)

bridge	$\theta_+{}^a$	$\phi_+{}^a$	$\phi_0{}^a$	$d_{N,N}$	d_{12}(dm)	$\mu_{12}{}^b$	d_{ab}(dm)^c	d(ESR)^d
PH (**sNsB**)	157.8	55.8	32.8	5.70	4.47	4.30	4.82	[4.6−4.8]
•*(1+)*$[Ph_4B^-]$	142.4	47.6	32.6	5.66				
•$^+$*Hy−PH−H*$[NO_3^-]$	152.8	59.7	—	—				
XY (**aNaB**)	160.1	69.6	58.9	5.71	4.71	3.08	4.88	5.25
•*(2+)*$[Ph_4B^-]_2$	149.7	57.4	—	5.64				
DU (**sNsB**)	164.7	71.6	52.4	5.70	4.58	2.31	4.68	5.66
•*(1+)*$[Ph_4B^-]$	156.7	66.2	50.5^h	5.67^h				
•*Hy−DU−H*$^+[NO_3^-]$	158.3	63.8	—	—				
BI (**sNsB**)^e	157.6	54.3	36.2	9.99	8.41	3.18	8.51	8.0
•*(2+)*$[SbF_6^-]_2{}^f$	144.5	44.0	—	—				
•$^+$*Hy−(PH)*$_2$*H*$[SbF_6^-]^g$	154.8	62.2	—	—				
FL (**sNsB**)	157.2	57.3	35.0	9.72	8.15	3.79	8.30	[7.5]

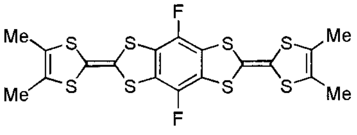
[a] See footnotes for Table 2. θ_0 is insensitive to both compound and conformation, and is not included. [b] Unit: Debye. [c] Calculated from μ_{12} in acetonitrile using eq 5 with d_{12}(dm) as d_{12}. [d] Estimated from dipolar splitting in the ESR spectrum of the triplet bis(cation), and used in our previous work, see refs 16b,c. (Numbers in brackets were estimated from the numbers not in brackets). [e] Twist angle about the central bond, $\omega = 32.7°$. [f] $\omega = 35.4°$. [g] $\omega = 40.9°$. [h] Average over three conformations of the neutral hydrazine unit present, see ref 16b.

TABLE 4: Comparison of $d_{N,N}$, d_{12}(dm), and d_{ab}(dm), Å, for Intervalence Bis(arylamines) and a Dimeric TTF Derivative[a]

compound	$d_{N,N}$	d_{12}(dm)	$\mu_{12}{}^b$	d_{ab}(dm)^c
$^+$**An$_2$N−PHC$_2$PH−NAn$_2$**^{d}	12.46	9.78	11.40	10.87
$^+$**PT−C$_2$−PT**^{e}	12.50	9.09	9.65	9.94
$^+$**PT−(CH)$_2$−PT**^{e}	12.19	8.75	6.89	9.21
$^+$**PT−PH−PT**^{e}	14.26	10.93	5.60	11.18
$^+$**(TTF)$_2$**^{f}	8.61^g	6.84	6.86	7.41

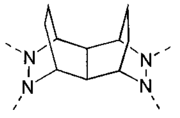
[a] PM3 calculations were used for the sulfur-containing **PT** and **(TTF)$_2$** derivatives. [b] Unit: Debye. Calculated from eq 4 using data from footnotes *d* to *f*. [c] Table 3, footnote *b*. [d] See ref 24. [e] From unpublished work of Daub and Engl. [f] See ref 25. [g] The distance between the centers of the $S_2C{=}CS_2$ bonds that was used in calculating H_{ab} (ref 25) is given.

radical cations that have been studied by Jürgen Daub and Raimund Engl (Regensburg, unpublished). We used PM3-UHF calculations, because AM1 appears to perform poorly for sulfur-containing compounds. These PM3-UHF calculations suffer from massive amounts of spin contamination ($<S^2>$ 1.9−2.3), as do AM1 calculations on these systems. Nevertheless, the d_{ab}(dm) values obtained are contracted relative to the N−N distances by amounts rather similar to those found for the triarylamines (Table 4). The bis(tetrathiofulvalene) derivative **(TTF)$_2$** was included as a representative of the compounds studied by Lahlil and co-workers.[25] The distance between the midpoints of the C═C bonds is 8.6 Å (which we note is a center-to-center instead of an edge-to-edge distance), in contrast to a d_{ab}(dm) value of 7.4 Å for this compound. The calculations discussed provide an internally consistent way to estimate the electron-transfer distance for these compounds.

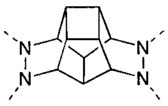


(TTF)$_2$

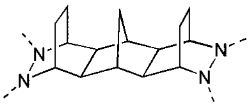
Estimates of d_{12} for Doubly σ-Bridged IV Compounds. The compounds that we consider here with saturated bridges have two links of the same size between the nitrogens, so their NN bonds are nearly exactly perpendicular to the long axis of the molecule. We tabulate the average of the distances between nitrogens linked by the shortest σ chains, $d_{N,N}$, corresponding to the distance between the midpoints of the NN bonds. Because the π system of the charge-bearing unit contains only these two nitrogens, the edge-to-edge and center-to-center distances are the same for these compounds. We studied two sorts of double 4-σ-bond links between the dinitrogen units, the bridges abbreviated here as **4T** (T is for Tetracyclic) and **4H** (H is for Hexacyclic) and one 6-σ-bond linked analogue, **6σ**. Bis-(diazeniums)[8] have one additional substituent on each dinitrogen unit, *tert*-butyl (**B**) for the compounds considered here, and these substituents may be syn or anti (**s** or **a**) relative to each other.



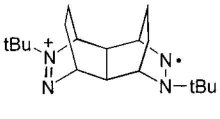
4T



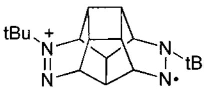
4H



6σ



a$^+$B/4T/B(oB^0)



s$^+$B/4H/B(iB^0)

The oxidized trialkyl diazenium unit of the IV radical cation has a N═N bond and the quaternary carbon of the **B** substituent is coplanar with the C−N═N−C unit. The neutral trialkyldiazenium unit (often called a trialkylhydrazyl) has some twist at the 3e-π NN bond (that is, three electrons in the nitrogen π orbitals perpendicular to the quasiplanar CNNC unit), and the trisubstituted nitrogen is slightly pyramidalized, leading to isomers with the **B** group directed toward the center of the molecule (which we will call **iB^0** for inner) or away from the center of the molecule (**oB^0** for outer), as illustrated for two examples above. The **oB^0** form is calculated to be only slightly more stable than the **iB^0** form for the very rigid **4H** bridge, but the difference is larger for the more twisted **4T**- and **6σ**-bridged compounds (see Table 5). The d_{12}(dm) values are slightly larger (1−2%) for the **iB^0** forms. The syn-**4T** compound has almost the same average $d_{N,N}$ as the anti one, but a slightly larger d_{12}(dm) value. The **4H** compound has a slightly larger $d_{N,N}$ than its **4T** analogue because the four-membered ring tilts the dinitrogen units away from each other, but a smaller d_{12}(dm) value. The **4T**- and **4H**-bridged bis(diazeniums) have k_{ESR} values that are too large to be measured,[8a] but k_{ESR} has been determined for both diastereomers of the **6σ**-bridged compounds.[9]

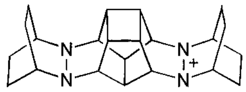
Hydrazines have one additional substituent at each nitrogen. The first bis(hydrazine) radical cation we shall discuss is bis(sesquibicyclic), abbreviated $^+$**22/4H/22**.[8b] AM1 yields no twist at either oxidized or reduced hydrazine units of this sort

TABLE 5: Estimated d Values (Å) for Bis(diazenium) Radical Cations with Saturated Bridges

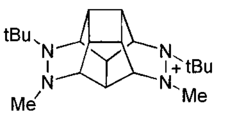
compound	rel. $\Delta H_f{}^a$	ave. $d_{N,N}{}^b$	d_{12}(dm)	$R_\mu{}^c$	$\mu_{12}{}^d$	d_{ab}(dm)
a^+B/4T/B(oB^0)	0	4.82	3.49	.984	2.63	3.60
(iB^0)	0.62	4.84	3.57	.981		
s^+B/4T/B(oB^0)	0	4.83	3.65	.938	3.13	3.66
(iB^0)	0.78	4.84	3.69	.954		
a^+B/4H/B(oB^0)	0	4.94	3.39	.988	3.28	3.65
(iB^0)	0.25	4.95	3.43	.986		
a^+B/6σ/B(oB^0)	0	7.16	5.62	.993	1.07	5.64
(iB^0)	0.67	7.19	5.77	.994		
s^+B/6σ/B(oB^0)	0	7.16	5.62	.974	1.08	5.64
(iB^0)	0.61	7.19	5.77	.976		

[a] Unit: kcal/mol. Relative enthalpies of formation of inner and outer *tert*-butyl at the slightly pyramidalized nitrogen of the reduced unit, in kcal/mol. [b] Here, the long axis essentially bisects the two NN bonds. [c] See Table 2, footnote *e*. [d] Unit: Debye. Calculated using the experimental data of ref 8 with eq 4.

(lone pair, lone pair dihedral angle $\theta = 0°$), but there is still conformational complexity because the alkyl groups may be directed outer or inner in both oxidation states, leading to four stereoisomers, of which the **o^{0}o$^+$** form is shown. The relative energies and d_{12}(dm) values are shown in Table 6. Smaller d_{12}(est) is obtained when the alkyl groups on the oxidized hydrazine are directed **i** than when they are directed **o**, and when alkyl groups on the neutral hydrazine are directed **o** than **i**. The range in d_{12}(dm) is 9%.



$^+$22/4H/22(o$^+$o^0)



s$^+$BM/4H/BM(oB^{0}iM^0,iB$^+$iM$^+$)

Because of their relatively high point group symmetry (C_s for minimum energy equilibrium configuration and C_{2v} for symmetric transition state structure), the **oo** and **ii** diastereomers of **$^+$22/4H/22** offer a clear understanding of the roles played by the different dipole moment components. For C_s or C_{2v} symmetry, the component of $\vec{\mu}_1$ parallel to the NN bonds is zero, and we denote the remaining two components as $\mu_{||}$ (parallel to the long axis) and $\mu_\perp$ (perpendicular to the N_4 plane). Table 7 reports the results of three sets of calculations. For the equilibrium structures, the dominant $\vec{\mu}_1$ component is $\mu_{||}$, which yields the d_{12}(dm) values cited in Table 6 (i.e., $2\mu_{||}/4.8032$). The value of $\mu_\perp$ is, however, seen to be appreciable. Similar $\vec{\mu}_1$ components and d_{12}(dm) values are found for the minimum energy C_{2v} structure (the d_{12}(dm) values are ~90% of those for the C_s structures). Due to symmetry-breaking (with respect to C_{2v}) the calculations yield charge densities corresponding to the lower C_s symmetry. Despite the artifactual nature of this symmetry breaking, such symmetry broken wave functions have nevertheless been shown to be useful in modeling ET processes,[26] and in fact, the calculated relative ΔH_f values provide rough estimates (actually, diabatic upper limits) of activation energies. Finally, it is possible using the C_{2v} structures to obtain a higher energy SCF solution by constraining the charge density to C_{2v} symmetry.[27] These latter charge densities yield $\mu_{||} = 0$ (as required for symmetrically delocalized states), but with the $\mu_\perp$ component little changed relative to the C_s result. This roughly constant $\mu_\perp$ (for all entries in Table 7) is not relevant to the ET process of interest and thus should not be included in the implementations of eqs 1, 3, 5, and 7.[28,29]

When nitrogen substituents external to the bridge are not linked, the neutral hydrazine unit has these substituents directed on opposite sides of the nearly planar $C_{br}NNC_{br}$ unit ($\theta_0 \approx 130°$ and insensitive to diastereomer present), but the oxidized hydrazine unit for these saturated compounds is almost always more stable with its substituents on the same sides of the $C_{br}NNC_{br}$ unit (θ near 0°), in contrast to the aromatic-bridged bis(**Hy**) compounds, which are calculated to have large θ for oxidized as well as neutral hydrazine units. Several forms of some *tert*-butyl, isopropyl, and methyl substituents have been studied experimentally,[8] and calculations on the *t*-Butyl, Methyl (**BM**) compounds studied appear in Table 6. We abbreviate the conformation of **s$^+$BM/4H/BM** having the disposition of substituents indicated above as **iB$^+$iM$^+$,oB^{0}iM^0**. We found only large θ alkyl group minima for **a$^+$BM/4T/BM**. Rather little difference in d_{12}(dm) is predicted between small and large θ forms when the same substituents are present, and we only show d_{ab}(dm) values for the most stable diastereomer in Table 6. Only optical analyses are available for **4T-** and **4H**-bridged **BM**-substituted compounds because k_{ESR} is too small to measure.

Discussion

Because of their relative structural simplicity (dominated by the quasirectangular N_4 grouping), we commence the discussion by considering the IV compounds with saturated bridges. The separation of the charge-bearing N_2 units is essentially the same, whether viewed as edge-to-edge or center-to-center, corresponding to $d_{N,N}$. By default, we previously used $d_{N,N}$ values in determining H_{ab} values from optical spectra.[8,9] The pattern of relative energies calculated for different nitrogen invertomers is complex, depending upon both bridge and alkyl substituents. The sensitivity of d_{12}(dm) for these compounds is largest for the saturated-bridged bis-hydrazines (especially the **4T** bridged systems of Table 6, with total ranges 19 and 24% for **s** and **a** diastereomers), but the calculated enthalpy differences between invertomers are rather large, and if the calculations were accurate, only the more stable conformations would contribute much to the optical measurements. It should be noted that the d_{ab}(dm) values are always smaller than the $d_{N,N}$ values. The range of d_{ab}(dm)/$d_{N,N}$ ratios is 0.74 to 0.79 for the bis(diazenium) compounds of Table 5 and 0.72 to 0.85 for the bis(hydrazine) compounds of Table 6. Using d_{ab}(dm) values instead of $d_{N,N}$ values would accordingly increase the H_{ab} values obtained from the optical data. The sizes of the changes are not very large, and incorporation of a refractive index correction to the ϵ_{max} used in calculating H_{ab} (which was not employed previously)[8,9,16,17] would tend to cancel changes caused by decreasing the ET distance used.

Because the NN bonds are at approximately 120° angles to the long axis of the aromatic-bridged molecules, the center-to-center (of the NN bond) distance is significantly larger than the edge-to-edge distances quoted as $d_{N,N}$ in Table 3, with ratios of 1.13−1.15 for the 5-bond-bridged compounds having **PH**, **XY**, and **DU** bridges, and 1.08−1.09 for the 9-bond-bridged compounds having **BI** and **FL** bridges. The range of d_{ab}(dm)/$d_{N,N}$ ratios is 0.82−0.85 for the bis(hydrazines) of Table 3 and 0.76 to 0.87 for the bis(arylamines) of Table 4. We used d_{ab} estimates that were obtained from ESR measurements on the dication oxidation states (the d_{12}(ESR) values in Table 3) to estimate H_{ab} values for the bis(hydrazines) previously.[16,17] The d_{ab}(dm) values depend, of course, on the quality of the calculated charge distributions. The AM1 calculations give a reasonable overall account of variation of ET distance with system size but there appear to be problems in accounting for the differential effects of increased twisting caused by introduction of methyl groups in the series **PH→XY→DU**. As shown in Figure 3,

TABLE 6: Estimated Twist Angles (deg.) and *d* Values (Å) for Bis(hydrazine) Radical Cations Having Saturated Bridges

cmpnd. form	rel. ΔH_f[a]	ϕ_0	ϕ_+	ave. $d_{N,N}$[b]	d_{12}(dm)	R_μ[c]	μ_{12}[d]	d_{ab}(dm)[e]
				$^+$22/4H/22				
$\mathbf{i^+o^0}$	0	0.0	0.0	4.93	3.59	.998	1.95	3.68
$\mathbf{o^+,o^0}$	0.42	0.0	0.0	4.91	3.98	.978		4.06[f]
$\mathbf{o^+,i^0}$	1.81	0.0	0.0	4.99	4.20	1.000		
$\mathbf{i^+,i^0}$	1.92	0.0	0.0	5.00	3.80	.966		
				***a*$^+$BM/4T/BM**				
$\mathbf{iB^+iM^+,iB^0oM^0}$	0	129.4	3.0	4.88	3.42	.999	1.66	3.48
$\mathbf{oB^+iM^+,iB^0oM^0}$	0.23	130.0	8.6	4.87	3.96	.996		
$\mathbf{iB^+iM^+,oB^0iM^0}$	0.43	130.5	6.5	4.87	3.82	.987		
$\mathbf{iB^+oM^+,oB^0iM^0}$	0.90	130.2	164.9	4.86	4.07		.977	
				***s*$^+$BM/4T/BM**				
$\mathbf{iB^+iM^+,iB^0oM^0}$	0	129.6	7.0	4.88	3.48	1.000	1.63	3.54
$\mathbf{oB^+oM^+,iB^0oM^0}$	0.65	129.7	0.8	4.87	3.96	.990		
$\mathbf{iB^+iM^+,oB^0iM^0}$	0.40	130.3	0.8	4.87	3.87	.988		
$\mathbf{oB^+oM^+,oB^0iM^0}$	0.91	130.2	7.9	4.86	4.33	.996		
				***a*$^+$BM/4H/BM**				
$\mathbf{oB^0iM^0,oB^+iM^+}$	0	130.3	2.2	4.98	4.18	.999	1.55	4.23
$\mathbf{oB^0iM^0,iB^+iM^+}$	0.48	133.7	2.8	4.99	3.92	.984		
$\mathbf{iB^0oM^0,iB^+iM^+}$	0.43	129.8	0.5	5.00	3.78	.997		
$\mathbf{iB^0oM^0,oB^+oM^+}$	0.08	129.8	4.4	4.99	4.00	.992		

[a] Unit: kcal/mol. [b] The average of the shorter $N-N$ distances across the 4- or 6-σ-bond bridges is used as $d_{N,N}$. [c] See Table 2, footnote *e*. [d] Unit: Debye. Same as Table 4, footnote *b*, using the optical data from refs 8b and 8c. [e] Calculated for the conformation of lowest calculated enthalpy only, using eq 5. [f] Calculated using d_{12}(dm) for $\mathbf{o^+,o^0}$, despite the fact that a symmetrical invertomer is unlikely, given the anomalous temperature dependence of k_{ESR} (ref 27).

TABLE 7: Dipole Moment Components Calculated for 22/4H/22 Cations

diastereomer	sym.	charge distribution[a]	relative ΔH_f (kcal/mol)	$\mu_\parallel$ (Debye)[b]	$\mu_\perp$ (Debye)[c]	relative d_{12}(dm)
o^+,o^0	C_s	uns	0	9.55	2.03	1
$(oo)^+$	C_{2v}	uns	7.89	9.27	2.52	0.97
		sym	20.14	0.00	2.65	
i^+,i^0	C_s	uns	0	9.13	2.46	1
$(ii)^+$	C_{2v}	uns	7.00	8.17	2.65	0.89
		sym	13.48	0.00	2.63	

[a] Symmetry of the charge density (*uns*ymmetrical or *sym*metrical) is defined relative to the point group symmetry. [b] $\mu_\parallel$ is the component of μ_1 along the long axis. [c] $\mu_\perp$ is the component of μ_1 perpendicular to the N_4 plane.

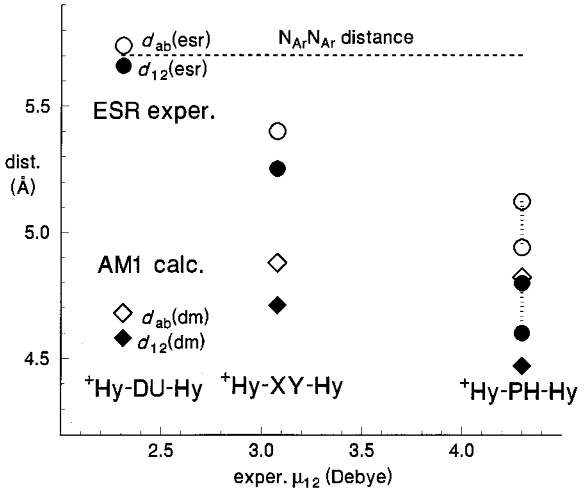


Figure 3. Plot of various distances versus the experimental IV charge-transfer transition dipole moment (μ_{12}). The circles represent quantities obtained from the ESR dipolar splitting, and the diamonds ones from AM1 dipole moments. The filled symbols represent d_{12}(dm) values and the open ones d_{ab}(dm) values obtained using the μ_{12} values with eq 5. The paired symbols connected by dots for the $^+$**Hy**$-$**PH**$-$**Hy** entries reflect uncertainty in the d_{12}(ESR) estimate.

the experimental d_{12} estimate, d(ESR), clearly increases significantly in this series (ca. 4.7→5.25→5.66, relative sizes 0.90, 1, and 1.08), but the AM1-calculated d_{12}(dm) values do not (4.47→4.71→4.58, relative sizes 0.95, 1, and 0.97). Although d_{ab} might have been expected to be constant, the d_{ab}(ESR) obtained from eq 5 using d_{12}(ESR) and experimental μ_{12} values clearly is not. The AM1 calculated d_{ab}(dm) values are much more nearly constant (4.82→4.88→4.68), but have the **DU**-bridged compound out of order. It is conceivable that this occurs principally because the **DU**-bridged compound has more minima (the nitrogens are significantly flatter and twisting is greater), and we might not have yet found suitable conformations. However, the sensitivity of d_{12}(dm) to diastereomer for $^+$**Hy**$-$**PH**$-$**Hy** (Table 2) is quite small, with a total range under 0.25%, and the minima found thus far for the **DU**-bridged compound have quite similar d_{12}(dm) that are anomalously small relative to those for the **XY**-bridged compound. Rate constants obtained from the optical spectra using eq 2 to calculate H_{ab} show slightly better agreement with the experimental values when the d_{12} estimate (d(ESR)) is used[16] instead of d_{ab}(dm), but the difference between using d_{ab} and d_{12} only becomes important as H_{ab}/E_{op} becomes large, and we do not have a very accurate experimental rate constant for the largest H_{ab} compound, $^+$**Hy**$-$**PH**$-$**Hy**, because its k_{12} value is inconveniently large for our ESR method. It appears that despite having the same charge-bearing units and the structural similarity of the bridges in the series **PH**→**XY**→**DU**, the effective diabatic surfaces are not the same for these compounds, a result that would rationalize the dependence of ET distance upon the introduction of methyl groups on the bridge, as shown in Figure

3. Nevertheless, the two state model suffices for predicting k_{ESR} from the optical spectrum for these compounds.[16c,17]

Conclusions

The calculations reported here provide an internally consistent way of evaluating d_{ab} for organic compounds in which the excess charge on the charge-bearing units is appreciably delocalized, and allow treating systems having π systems perpendicular, parallel, or canted with respect to the electron-transfer direction in a unified manner, which has not been done previously. The use of AM1 calculations with the simple estimate of d_{12} from the long-axis component of μ_1 (eq 7) seems to be appropriate for estimating the electron-transfer distance. The calculations indicate that d_{ab} is not very sensitive to the diastereoisomeric mixture expected to be present for most of the compounds studied. It appears to us to be quite reasonable to employ d_{ab}(dm) values for extracting H_{ab} from optical data, and to use the smaller refractive index correction $f(n)$,[7c] which for most of the compounds we studied, will give rather similar values to those obtained by employing d_{12}(dm) values and omitting a refractive index correction. There appears to be a problem with the d_{12}(dm) and hence d_{ab}(dm) values obtained for the most twisted compound, $^+$**Hy**−**DU**−**Hy**; the former are smaller than those for $^+$**Hy**−**XY**−**Hy**, and thus not consistent with either experiment or expectation.

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(29) Table 7 displays only $\vec{\mu}_1$ values, but very similar results in the symmetric charge density C_{2v} case are expected for $\vec{\mu}_2$ (i.e. $\mu_{\|} = 0$ and $\mu_{\perp}$ essentially the same as for $\vec{\mu}_1$), yielding the result $\Delta\vec{\mu} \cong 0$, an expectation borne out by the supplementary INDO/CI results noted above. (See ref 22.)

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