

How Far Do Electrons Move? A Semiempirical Investigation of Thermal Electron-Transfer Distances in Cationic Bis(hydrazine) and Bis(hydrazyl) Mixed-Valence Compounds

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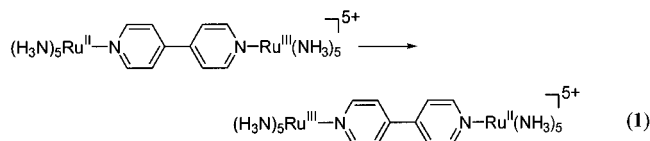
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Abstract: A computational approach for estimating thermal electron-transfer reaction distances in symmetrical mixed-valence compounds is described and applied to a series of bis(hydrazine) and bis(hydrazyl) radical cations and derivatives, some of which have been investigated experimentally by Nelsen and co-workers. Ground-state semiempirical charge distributions are obtained by using optimized reactant geometries. Advantage is then taken of the approximate C_2 symmetry, or the approximate mirror symmetry, of each of the targeted compounds, and the inherent degeneracy of the corresponding electron-transfer reactions, such that the change in dipole moment ($\Delta\mu$) upon charge transfer can be estimated from an appropriately distance-weighted sum of charge differences between approximately symmetry-equivalent atoms found on the donor and acceptor sides of the molecule. $\Delta\mu$ can then be related directly to the effective one-electron-transfer distance. We find that calculated adiabatic electron-transfer distances can differ appreciably from the geometric donor-site/acceptor-site separation distances. Furthermore, for a fixed geometric separation distance, the effective electron-transfer distance can vary considerably, depending on chemical substituent composition and/or isomeric configuration. Further advantage is taken of the approximate donor-site/acceptor-site symmetry, in the context of a Newton–Cave type analysis, to establish the relative importance of electronic delocalization effects versus self-polarization and inductive effects in diminishing or enhancing effective one-electron-transfer distances.

Introduction

In redox processes, the distance over which the electron is transferred plays a central role in modulating the reaction kinetics: reaction rates typically decrease exponentially with increasing transfer distance, both because of exponential decreases in electronic coupling and because of asymptotic increases in solvent or environmental reorganization energy. While it is tempting to identify the effective electron-transfer distance simply with the geometric distance of separation between the nominal electron donor and acceptor sites, experimental studies of several light-induced electron-transfer (ET) reactions have shown that effective one-electron-transfer distances can differ substantially from geometric separation distances.^{1–3} For example, the optical intervalence charge-transfer distance (effective one-electron-transfer distance) measured for eq 1 via electronic Stark effect spectroscopy is ca.



5.5 Å, yet the geometric metal–metal (donor–acceptor) separa-

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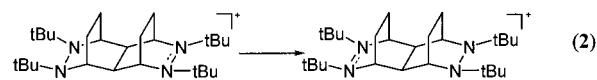
(1) For recent reviews see: (a) Bublitz, G. U.; Boxer, S. G. *Annu. Rev. Phys. Chem.* **1997**, *48*, 213. (b) Vance, F. W.; Williams, R. D.; Hupp, J. T. *Int. Rev. Phys. Chem.* **1998**, *17*, 307.

(2) See also: Brunschwigg, B. S.; Creutz, C.; Sutin, N. *Coord. Chem. Rev.* **1998**, *177*, 61.

(3) Oh, D. H.; Sano, M.; Boxer, S. G. *J. Am. Chem. Soc.* **1991**, *113*, 6880.

tion distance is ca. 11.3 Å.^{3,4} It should be noted that for selected systems, light-induced ET distances can also be assessed via a combination of ground-state dipole moment measurements and transient DC photoconductivity measurements,⁵ where the latter yield values for $\mu_{\text{exc}}^2 - \mu_{\text{gr}}^2$.

Here we consider a closely related problem: the effective distance for *thermally* activated electron transfer. We find for symmetrical electron-transfer reactions (i.e., thermoneutral, exchange-type reactions) that distances can be derived in a straightforward fashion from appropriately defined ground-state dipole moment calculations. We consider specifically a family of organic mixed-valence ions: bis(hydrazine) and bis(hydrazyl) radical cations consisting of two fused 2,3-diazabicyclo[2.2.2]-octyl units. These intriguing assemblies have been extensively investigated by Nelsen and co-workers.⁶ They have noted that the compounds generally exhibit intervalence charge-transfer absorption bands corresponding to light-induced reactions analogous to eq 2.⁷ They have also observed that the assemblies



engage in degenerate thermal electron transfer, and that in some

(4) Hupp, J. T.; Dong, Y.; Blackburn, R. L. *J. Phys. Chem.* **1993**, *97*, 3278.

(5) See, for example: Smirnov, S. N.; Braun, C. L. *Rev. Sci. Instrum.* **1998**, *69*, 2875 and references therein.

(6) (a) Nelsen, S. F.; Adamus, J.; Wolff, J. J. *J. Am. Chem. Soc.* **1994**, *116*, 6, 1589. (b) Nelsen, S. F.; Chang, H.; Wolff, J. J.; Adamus, J. *J. Am. Chem. Soc.* **1993**, *115*, 12276. (c) Nelsen, S. F. *J. Am. Chem. Soc.* **1996**, *118*, 2047. (d) Nelsen, S. F.; Ramm, M. T.; Wolff, J. J.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 6863. (e) Nelsen, S. F.; Trieber, D. A., II; Wolff, J. J.; Powell, D. R.; Rogers-Crowley, S. *J. Am. Chem. Soc.* **1997**, *119*, 6873.

instances the temperature-dependent rate of charge exchange or transfer is amenable to experimental evaluation via line broadening methods.^{6d} Because very few other examples of intramolecular electron exchange rate assessment have been described experimentally,⁸ the diaza assemblies are of considerable fundamental interest.

From the modeling studies outlined below we find that effective distances for intramolecular electron transfer within the diaza assemblies can differ substantially from simple geometric donor–acceptor separation distances. Furthermore, we find that when the geometric separation distance is intentionally fixed, the effective electron-transfer distance can vary significantly with substituent chemical composition and isomeric configuration. Potential physical interpretations for the effective distance variations are examined within the context of a Newton–Cave treatment.⁹

Methods and Approach

Cave and Newton have emphasized the simple but important connection between the distance of electron transfer, R , and the ET-induced change in dipole moment, $\Delta\mu$, for the reacting system.⁹ For adiabatic states, the relationship is:

$$\Delta\mu_{12} = e \cdot R_{12} \quad (3)$$

where e is the unit electronic charge.

For symmetric thermal electron-exchange reactions, such as eq 1, the initial and final redox states have nearly identical geometries; in terms of charge, the states are related as mirror images. Furthermore, the reactant (or product) itself is characterized by an approximate mirror plane (see Figure 1a). The existence of the approximate mirror plane makes the assessment of the adiabatic change in dipole moment and, therefore, the adiabatic charge transfer distance particularly straightforward. As illustrated in eq 1 and Figure 1, for every atom on the left side of the symmetry plane, another symmetry-equivalent atom can be found on the right side of the plane. When intramolecular electron transfer occurs, each atom on the left side acquires the charge previously associated with the corresponding atom on the right side, and vice versa. Subtracting the calculated point charge of a right-side atom from the point charge of the corresponding left-side atom yields the total charge change occurring at those atoms upon thermal electron transfer. (Atoms lying within the plane suffer no change in charge and, therefore, are ignored.) Multiplying the charge change by the separation distance between the atoms yields the contribution of these two atoms to the change in molecular dipole moment, $\Delta\mu_{12}$. Summing the contributions from all atoms yields the overall change in dipole moment, and from eq 3, the adiabatic electron-transfer distance.

A mirror plane exists for *syn*-symmetry reactants such as the compound shown in eq 1, and for *syn*-substituted reactants such as the compound shown in Figure 1a. For *anti*-substituted compounds, rotation rather than reflection renders the reactant and product forms equivalent. The adiabatic change in dipole moment upon electron transfer again can be found by subtracting the charge of an atom from the charge of the approximately symmetry-equivalent atom elsewhere in the molecule, multiplying the charge difference by the separation distance, and summing the contributions from all pairs of atoms. Because the vectors defining the atom–atom pair contributions to the overall change in molecular dipole moment are no longer strictly parallel, but instead are rotated to varying extents around the symmetry axis, it is important here to perform the summation in a vector, rather than scalar, fashion

(7) For a review of molecular mixed-valence compounds and properties, see: Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(8) (a) Elliott, C. M.; Derr, D. L.; Matyashou, D. V.; Newton, M. D. *J. Am. Chem. Soc.* **1998**, *120*, 11714. (b) Ito, T.; Hamaguchi, T.; Nagino, H.; Yamaguchi, T.; Washington, J.; Kubiak, C. P. *Science* **1997**, *277*, 660. (c) Kroon, J.; Overing, H.; Verhoeven, J. W.; Warman, J. M.; Oliver, A. M. *J. Phys. Chem.* **1993**, *97*, 5065. (d) Ryu, C. K.; Wang, R.; Schmehl, R. H.; Ferrere, S.; Ludwikow, M.; Merkert, J. W.; Headford, C. E. L.; Elliott, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 430.

(9) Cave, R. J.; Newton, M. D. *Chem. Phys. Lett.* **1996**, *249*, 15.

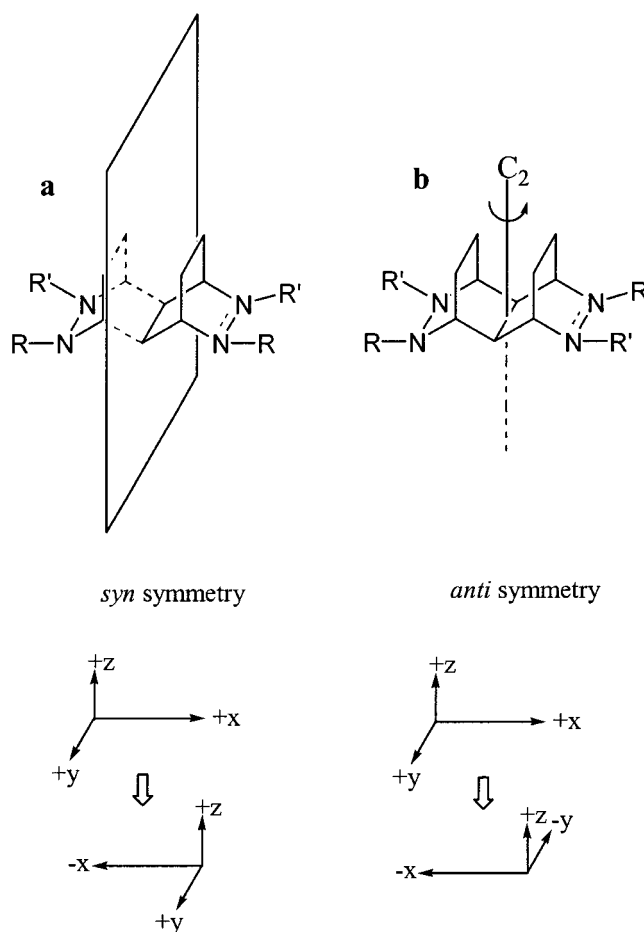


Figure 1. Illustration of symmetry elements for the bis(hydrazine) and bis(hydrazyl) cations studied here. Beneath each illustration is the effect of operating that symmetry element on the components of the dipole moment vector. Only the components that are inverted by the operation are included when calculating $\Delta\mu$.

(see Figure 1b). (Simple scalar summation will overestimate the dipole-moment change and electron-transfer distance.)

We note that the donor and acceptor site geometries in our optimized structures are in fact not identical. Indeed, finite changes in bond lengths—and, therefore, nuclear coordinates—must accompany charge redistribution. As a result, since our simplification for determining dipole moment differences does not account for these structural changes, it does not yield *precise* values for $\Delta\mu_{12}$. However, the electron transfer-induced structural changes are minor for these rigid systems (e.g., bond length differences generally of a few hundredths of an angstrom or less¹⁰). Consequently, we believe our symmetry approximation yields usefully accurate estimates of $\Delta\mu_{12}$ in these cases.

In principle, the needed atomic charges could be computed in any of several ways. We chose an approach that corresponds to an intermediate level of computational sophistication and neglects the charge-stabilizing role of a polar solvent environment. Presumably, more accurate results could be obtained by performing higher level calculations and by taking into account environmental interactions. In any case, ground-state dipole moments were obtained by first optimizing the geometry of each molecule via a UHF/AM1 calculation using PC Spartan Plus 1.5.2.¹¹ The counterion was ignored in the geometry optimizations because its location with respect to the cation is not relevant to the intervalence charge transfer (unless ion pairing occurs¹²). The optimization was performed without symmetry constraints. The optimized geometries of the bis(hydrazine) compounds featured *trans*-

(10) The largest calculated bond length changes are those for the nitrogen–nitrogen bonds. Because these bonds are geometrically orthogonal to the electron-transfer axis, the differences do not affect $\Delta\mu$.

(11) Wavefunction, Inc.: 18401 Von Karman Ave., Suite 370, Irvine, CA 92612.

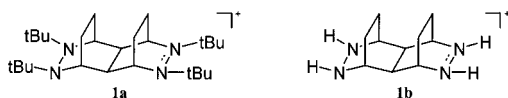
substituted hydrazine units, in agreement with several experimentally determined structures of similar compounds.^{6b,d} In several cases multiple minima were found during the optimization process—in these cases, only the lowest energy conformation was used. The optimized coordinates were then translated and rotated to define the origin and coordinate axes consistently, as described below. Partial charges at each nucleus were subsequently obtained from the electrostatic potential generated by the AM1 calculation.

The analysis can also be performed by imagining a hypothetical dipole moment for the charged reactant molecule.¹³ If we ignore the counterion, the dipole moment of the charged molecule becomes origin dependent. For our purposes, an acceptable origin is one that yields identical absolute dipole moments for the reactant and product forms of the molecule. For unsubstituted compounds, uniformly substituted compounds, and *syn*-substituted compounds, this condition is satisfied by designating as the origin any point within the mirror plane (see Figure 1a). Regardless of which point is chosen, the *x* axis is defined as an axis parallel to a line connecting the center of the electron donor (diaz group) to the center of the electron of the electron acceptor (diaz cation). The *y* and *z* axes then define the mirror plane. Note that reflection inverts the *x* coordinate, but leaves the *y* and *z* coordinates unchanged. It follows that upon electron transfer, charge is redistributed only in the *x* direction, i.e., only $\Delta\mu_x$ is used in eq 3. The relevant dipole moment of the reactant is then calculated by determining the charge on each atom, multiplying the charge by the *x* component of the vector connecting the atom to the origin, and summing the charge-distance products for all the atoms. Note that when defined in this way, μ_x for the reactant is equal, but opposite in sign to μ_x for the product. (The values for $\mu_{y(\text{reactant})}$ and $\mu_{y(\text{product})}$, on the other hand, are equal in magnitude and identically signed, as are $\mu_{z(\text{reactant})}$ and $\mu_{z(\text{product})}$.) The magnitude of the change in dipole moment following thermal electron transfer is then given by twice the *x* component of the dipole moment for the reactant: $|\Delta\mu| = |\mu_{x,y,z(\text{reactant})} - \mu_{x,y,z(\text{product})}| = |\mu_{x(\text{reactant})} - \mu_{x(\text{product})}| = |\mu_{x(\text{reactant})} - (-\mu_{x(\text{reactant})})| = 2|\mu_{x(\text{reactant})}|$.

A similar protocol can be used for *anti*-substituted compounds, except that (a) the choice of origin is now constrained to points along the *z* axis (the approximate C_2 symmetry axis) and (b) contributions to $\Delta\mu$ from charge redistribution along the *y* axis must be considered (see Figure 1b). The relevant quantity for eq 3 is then $|\Delta\mu| = 2(|\Delta\mu_{x(\text{reactant})}|^2 + |\Delta\mu_{y(\text{reactant})}|^2)^{1/2}$.

Results and Discussion

Preliminary Observations, State-Mixing Effects, and Molecular Length Effects. Analysis of ET within the cationic tetracyclic, tetra-*tert*-butyl compound, **1a**, shown in eq 2 yields



a $\Delta\mu_{12}$ value of 16.3 D, corresponding to an adiabatic transfer distance of 3.38 Å. For the analogous compound, **1b**, featuring hydrogen atoms in place of *tert*-butyl groups, $\Delta\mu_{12}$ is 13.6 D, corresponding to a transfer distance of 2.84 Å. The nominal geometric charge-transfer distance, R_{geom} , corresponding to the distance from the center of the electron donor (diaz group) to the center of the electron acceptor (diaz cation) is significantly greater—ca. 4.8 to 4.9 Å in both cases (see Table 1). Briefly, R_{12} and R_{geom} would be exactly equal if (a) no delocalization

(12) See, for example: (a) Staley, S. W.; Grimm, R. A.; Boman, P.; Eliasson, B. *J. Am. Chem. Soc.* **1999**, *121*, 7182. (b) Blackburn, R. L.; Hupp, J. T. *Chem. Phys. Lett.* **1988**, *150*, 399. (c) Blackburn, R. L.; Dong, Y.; Lyon, L. A.; Hupp, J. T. *Inorg. Chem.* **1994**, *33*, 4446.

(13) Shortly after this article was submitted, a paper describing a close variant of this approach and illustrating its application to organic mixed-valence ions appeared (Nelsen, S. F.; Newton, M. D. *J. Phys. Chem. A* **2000**, *104*, 10023). For a very preliminary description of the ground-state dipole moment doubling approach, see: Williams, R. D.; Hupp, J. T.; Ramm, M. T.; Nelsen, S. F. *J. Phys. Chem. A* **1999**, *103*, 11172.

Table 1. Calculated ET Distances and Amount of Charge Transferred for **1–6**

	$R_{\text{geom}}/\text{Å}$	$R_{12}/\text{Å}$	$R_{\text{ab}}/\text{Å}$	Δq
1a	4.89	3.38	4.84	0.70
1b	4.81	2.84	3.89	0.73
2a	7.16	4.74	6.75	0.70
2b	9.23	7.30	8.88	0.82
2c	11.22	9.28	11.35	0.82
3	4.86	3.02	4.31	0.70
4	4.87	3.26	4.53	0.72
5	4.86	3.58	4.94	0.73
6	4.88	3.94	5.56	0.71

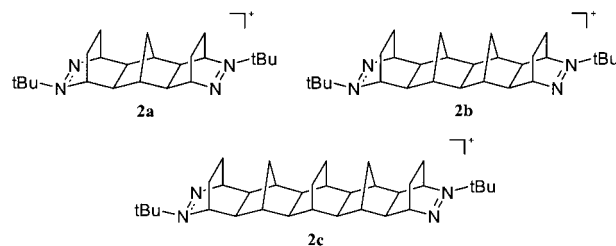
of charge between the donor and acceptor fragments occurred and (b) the redistribution or transfer of charge involved only the four nitrogen atoms comprising the nominal donor and acceptor sites. In a two-state picture, condition (a) corresponds to the hypothetical case of diabatic initial and final states (noninteracting zeroth-order states).

The role of state mixing in diminishing the effective electron-transfer distance can be gauged by comparing R_{12} with the nonadiabatic (diabatic) electron-transfer distance, R_{ab} . Assuming negligible differences in atomic coordinates for adiabatic and diabatic structures, the two are related by:⁹

$$R_{\text{ab}} = R_{12}(\epsilon/\Delta q) \quad (4)$$

where Δq is the actual amount of charge transferred—generally less than the unit electronic charge. The deficit can be viewed as a measure of initial-state/final-state electronic mixing.¹⁴ For **1a** and **1b**, the values for R_{ab} are 4.84 and 3.89 Å—greater than the adiabatic ET distances but equal to and less than the geometric distances, respectively. Small effective transfer distances as observed here for **1b** have been encountered experimentally for a number of optical electron-transfer reactions involving transition-metal-based compounds.¹⁵

The remaining differences here presumably arise from self-polarization effects and/or more general inductive effects.^{2,16} For example, the cationic electron acceptor site should display an electrostatic attraction for electrons located on the donor portion of the molecule. The attraction or self-polarization could result in a net displacement of electrons (and, therefore, charge) toward the acceptor site and an effective decrease in $\Delta\mu$ and R . To distinguish, at least qualitatively, between self-polarization, as described above, and more general inductive effects, upon R , we note that the effects of self-polarization should diminish if the geometric donor/acceptor separation distance is intentionally increased. To test this idea, distances for nonadiabatic electron transfer within compounds **2a–c** were examined. (We



note that compound **2a** and its *syn*-substituted counterpart have

(14) For symmetrical electron-transfer reactions, Δq can be obtained by subtracting the sum of the atomic charges found on the donor side of the molecule from the sum obtained on the acceptor side.

(15) Vance, F. W.; Karki, L.; Reigle, J. K.; Hupp, J. T.; Ratner, M. A. *J. Phys. Chem. A* **1998**, *102*, 8320.

(16) Reimers, J. R.; Hush, N. S. *J. Phys. Chem.* **1991**, *95*, 9773.

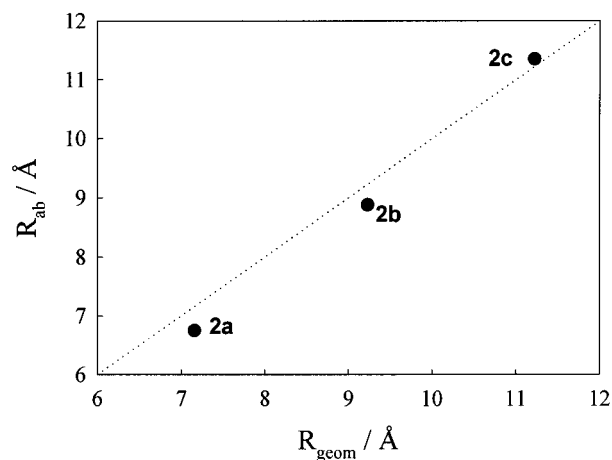
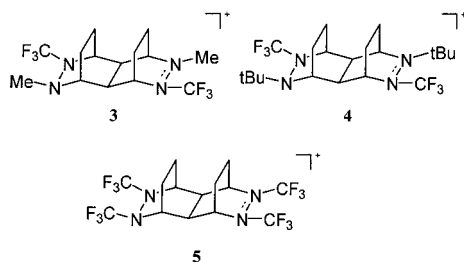


Figure 2. Effective nonadiabatic charge-transfer distance (R_{ab}) vs geometric donor–acceptor separation distance (R_{geom}) for the series **2a–c** (see text). The dotted line represents $R_{ab} = R_{geom}$.

previously been synthesized and studied,^{6c} while **2b** and **2c** have not been prepared.) The results are presented in Figure 2 in the form of a plot of R_{ab} versus R_{geom} . Even at geometric distances as great as 9.2 Å, differences persist— R_{ab} being smaller. The magnitude of the disparity decreases to essentially zero as the molecule is lengthened, as expected if self-polarization is primarily responsible for the disparity.¹⁷

Chemical Substituent Effects. We reasoned that the effective charge transfer distance might also prove susceptible to systematic manipulation via changes in the electronic character of substituents, even if the geometric transfer distance were held approximately constant. A comparison of calculated nonadiabatic ET distances for **1a**, **1b**, **3**, **4**, and **5** shows that modest



substituent effects exist. From Table 1, electron-withdrawing groups slightly lengthen the transfer distance, while electron-releasing groups slightly decrease the distance.¹⁸ Again, there is an experimental precedent in the Stark-effect literature on inorganic compounds.¹⁹ Returning to ET in the diaza compounds, the calculations show that substituent identity also has

(17) Again, in separating out electronic effects upon R by using the Cave–Newton analysis as embodied in eq 4, we have neglected any secondary effects due to atomic coordinated differences for adiabatic versus diabatic structures. Given that the calculated structural differences (for example, bond length differences) between neutral and cationic halves of the mixed-valence compounds amount, typically, to only hundredths of angstroms, we believe that the likely smaller differences between adiabatic and diabatic structures will have little effect upon calculated charge transfer distances. Clearly, in the limit of long donor/acceptor geometric separation, where electronic coupling becomes negligible, the distinction between adiabatic and diabatic structures will all but vanish. We feel confident in concluding, from Figure 2, that effects beyond state mixing and self-polarization contribute to differences between calculated charge-transfer distances and geometric donor/acceptor separation distances.

(18) There is some ambiguity in the results for **3–5** due to pyramidalization of the CF_3 -functionalized nitrogen atoms.

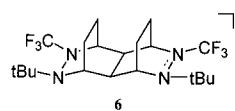
(19) (a) Vance, F. W.; Slone, R. V.; Stern, C. S.; Hupp, J. T. *Chem. Phys.* **2000**, 253, 313. (b) Shin, Y. K.; Brunschwig, B. S.; Creutz, C.; Sutin, N. *J. Phys. Chem.* **1996**, 100, 8157.

Table 2. Calculated ET Distances and Amount of Charge Transferred for **7–12**

	$R_{geom}/\text{Å}$	$R_{12}/\text{Å}$	Δq
7	4.99	3.37	0.52
8	4.99	3.36	0.52
9	4.82	3.57	0.66
10	4.84	3.20	0.64
11	4.95	3.10	0.42
12	4.95	3.05	0.42

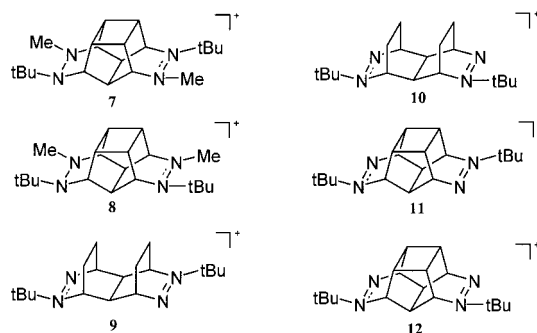
a slight effect upon the amount of charge transferred; the values range from 0.82 to 0.70, with no obvious pattern to the variations.

In nearly all cases examined, the calculated ET distance is less than the geometric donor–acceptor separation distance. In principle, however, the adiabatic transfer distance could exceed the geometric distance. Compound **6** is one such hypothetical example: R_{geom} is 4.88 Å, while R_{ab} is 5.56 Å.



Isomer Behavior. Bis(hydrazine) compounds bearing mixed pairs of substituents can exist in three isomeric forms, two of which preserve the energetic equivalence of the reactant and product states (cf. eq 2). Calculations show that isomers **4** and **6**, featuring virtually identical R_{geom} values, are characterized by different effective electron-transfer distances: $R_{12}(\mathbf{4}) = 3.26$ Å; $R_{12}(\mathbf{6}) = 3.94$ Å. In addition, a consideration of the vector nature of $\Delta\mu_{12}$ shows that electron transfer within **4** occurs at an angle that is slightly displaced from a line connecting the diaza donor center (N–N midpoint) to the diaza acceptor center. The magnitude of the displacement is 7.2° and the direction is toward the electron-withdrawing substituents.

Other Structures. Closely related to tetracyclic bis(hydrazine) compounds are hexacyclic bis(hydrazine) compounds^{6b} such as **7** and **8**, tetracyclic bis(hydrazyl) compounds^{6c} such as **9** and **10**, and hexacyclic bis(hydrazyl) compounds^{6b} such as **11** and **12**. Table 2 summarizes the ET distances calculated for these six compounds. Also listed are values calculated for Δq . In each case, the effective electron-transfer distance is less than the geometric donor/acceptor separation distance. As a rule, however, the effective distances for ET within hexacyclic compounds are greater than those calculated for analogous tetracyclic compounds. Examination of charge-difference maps (not shown) reveals that the longer effective transfer distances and the smaller Δq values for the hexacyclic species compared to the tetracyclic species are associated primarily with differences in the amount of charge redistribution occurring on the nominal donor and acceptor atoms and substituent groups—the



extent of charge redistribution occurring on atoms comprising the bridging framework being fairly similar for the various reactions.

In contrast to the tetracyclic bis(hydrazine) compounds discussed above, each of the three new sets of compounds displays only very slight isomer-structure-dependent electron-transfer distances. Additional calculations (not included in Table 2) show, however, that the effective ET distances do vary as a function of substituent identity. Given the comparatively small Δq values for ET reactions involving hexacyclic reactants, we hesitate to interpret the results further. Recall that small Δq values imply extensive electronic coupling—a condition that may strain the reliability of AM1 calculations.

Other Effects. The calculated existence of thermal ET distances that are significantly shorter than geometric separation distances has implications in terms of solvent reorganization. Shorter ET distances translate into smaller reorganization energies, λ_s . For example, for compound **2a** in acetonitrile a simple ellipsoidal-cavity/dipole-switch model for solvent reorganization²⁰ yields a λ_s value of 62 kJ mol⁻¹ based on a dipole length of 7.16 eÅ, but only 37 kJ mol⁻¹ based on a dipole length of 5.01 eÅ (see Table 2).²¹

The observation of differences between R_{12} and R_{geom} also has implications for the experimental evaluation of initial-state/final-state electronic coupling energies, H_{ab} , from oscillator strengths for the corresponding optical electron-transfer reactions. The coupling energy is usually obtained by dividing the oscillator strength (plus constants) by the adiabatic electron-transfer distance and the unit electronic charge.^{9,22} Clearly, if the geometric separation distance is mistakenly used in place of R_{12} , the coupling energy will be underestimated.

Finally, since experimental measures of R_{12} typically involve Stark spectroscopy and optical electron transfer, some mention should be made of possible differences between optical and thermal electron-transfer distances. First, because the optical product state is necessarily prepared as a vertical state, it is energetically closer to higher lying excited states than is either the initial state or the product state of the thermal ET reaction (see Figure 3). Given the energetic proximity, enhanced mixing with the higher lying excited states might be expected for the optical product state. To the extent that the higher lying states are not charge-transfer states, mixing would decrease the charge-transfer character of the optical product state and decrease the electron-transfer distance in comparison to the transfer distance associated with thermal reaction. Second, because the optical product state is prepared as a vertical state, i.e., a state with nuclear coordinates identical with those of the initial state, reactions that ultimately entail significant structural changes—for example, redox-driven changes in nitrogen pyramidalization—might yield different thermal ET versus instantaneous optical

(20) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657.

(21) Ellipsoidal cavity dimensions: long axis = 17 Å, short axes = 9 Å.

(22) (a) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135. (b) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.

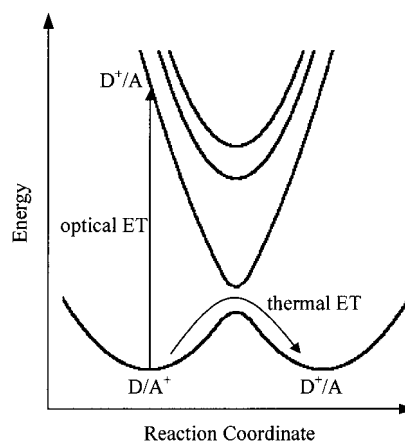


Figure 3. Mixing of the optical product state with higher excited states may decrease the effective electron-transfer distance relative to that associated with the thermal electron-transfer reaction ($D/A^+ \rightarrow D^+/A$); see text.

ET distances. It will be interesting to extend the studies here to optical electron-transfer processes.

Conclusions

The approximate C_2 symmetry, or the approximate mirror symmetry, of each of several reactants can be exploited to obtain values for $\Delta\mu$ for thermal electron transfer, from ground-state electronic structure calculations. The $\Delta\mu$ values, in turn, can be directly related to effective one-electron-transfer distances via a simple Cave–Newton analysis (Mulliken–Hush analysis). For cationic bis(hydrazine) and bis(hydrazyl) mixed-valence compounds, calculated adiabatic electron-transfer distances can differ appreciably from geometric donor-site/acceptor-site separation distances. Furthermore, for a fixed geometric separation distance, the effective ET distance can vary significantly, depending on chemical substituent identity and/or isomeric configuration. A comparative evaluation of nonadiabatic ET distances reveals that electronic delocalization effects, as well as self-polarization and more general inductive effects, can cause effective one-electron-transfer distances to differ from simple geometric separation distances.

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Supporting Information Available: AM1-optimized geometries of **1–12**. This material is available free of charge via the Internet at <http://pubs.acs.org> as set of Cartesian coordinates and minimized total energies (PDF).

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