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Ring Size and Solvent Effects on Sesquibicyclic Hydrazine Self-Electron-Transfer Rates

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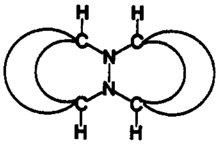
Self-electron-transfer (self-ET) rate constants k_{ex} for sesquibicyclic hydrazines were determined by NMR line broadening at 25 °C in CD_3CN: **6**$^{0/+}$(**21/21**), 18 500 ± 500; **4**$^{0/+}$(**21/u22**), 2290 ± 90; **2**$^{0/+}$(**22/u22**), 12 100 ± 100; **7**$^{0/+}$(**23/u22**), 3370 ± 140; **8**$^{0/+}$(**22/u23**), 3840 ± 110; **3**$^{0/+}$(**22/22**), ~700 (dec); and **9**$^{0/+}$(**23/22**), 580 ± 25 $M^{-1}\,s^{-1}$. Differences in ΔG^*_{ex} for the first five compounds correlate linearly with differences in inner shell vertical relaxation enthalpies calculated by AM1, and it is concluded that changes in Marcus λ_{in} dominate the changes in k_{ex}. The last two compounds show smaller k_{ex} values than predicted by AM1, which incorrectly calculates the twist at the NN bond of the neutral forms. The effects of solvent on k_{ex} are reported for **8**$^{0/+}NO_3^-$ (**22/u23**), solvent polarity range chloroform to methanol, and **4**$^{0/+}PF_6^-$ (**21/u22**) and **8**$^{0/+}PF_6^-$ (**22/u23**), solvent polarity range pyridine to acetonitrile. Plots of the Eyring free-energy barrier ΔG^*_{ex} vs solvent polarity parameters $E_T(30)$ and γ give estimates of the ratio of the inner sphere to total Marcus reorganization barrier, $\lambda_{in}(T)/\lambda(T)$, of 0.78 (vs $E_T(30)$) and 0.75 (vs γ) for **2**$^{0/+}$(**22/u22**) and 0.82 (vs $E_T(30)$) and 0.75 (vs γ) for **4**$^{0/+}$(**21/u22**). The ratios obtained are unreasonably large for the **8**$^{0/+}$(**22/u23**) data (in the range 0.85–0.89), and it is concluded that **22/u23**$^{\cdot+}$ is unstable enough under the experimental conditions to make these ratios inaccurate. It is concluded that self-ET for sesquibicyclic hydrazines is strongly diabatic.

Introduction

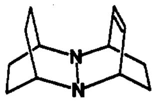
Sesquibicyclic hydrazines are bis(N,N′) bicyclic ones, of general structure **1**. Several examples have been prepared by the "proton driven" Diels–Alder additon of protonated bicyclic azo compounds to cyclic dienes, followed by deprotonation and, for saturated compounds, hydrogenation.[1-4] The bicyclic rings force all four tertiary $C_\alpha H$ bonds to lie near the nodal plane of the NN π system of oxidized forms, minimizing hyperconjugative weakening. As a result, the radical cations of several sesquibicyclic hydrazines are isolable. Examples containing only 5–7-membered rings are forced to have rather small intraring CNNC twist angles, causing them to be cis fused at the nitrogens, with syn lone pairs (twist angle θ near 0°).[5,6] The structural constraints of their tetracyclic systems cause smaller geometry reorganization upon electron loss than for most hydrazines,[7] resulting in the rate constant k_{ex} for self-electron exchange between the neutral and radical cation forms (see eq 1) being fast enough to measure by

$$1^0 + 1^+ \overset{k_{ex}}{\rightleftharpoons} 1^+ + 1^0 \tag{1}$$

NMR line broadening of the neutral form. For convenience, we will designate the process shown in eq 1 as **1**$^{0/+}$. We have previously discussed k_{ex} measurements for **2**$^{0/+}$ and **3**$^{0/+}$,[8] a study of solvent effects for **2**$^{0/+}$,[9] and the rate constant for **4**$^{0/+}$ in CD_3CN.[10] These are the first compounds having a large internal geometry reorganization, that is, a large λ_{in} term in Marcus theory,[11] for which k_{ex} values were measured. In this paper, we report k_{ex}(25 °C) values in CD_3CN for several additional examples of **1**$^{0/+}$ and solvent effects for two of them and discuss the factors which control changes in k_{ex} for these compounds.



1



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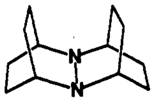

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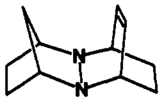

4 (21/u22)

Results

The compounds studied include **5**–**12**. To identify these systems without continually referring to the pictures, a

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[●] Abstract published in *Advance ACS Abstracts*, March 1, 1994.

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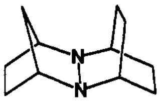
short-hand designation of the rings present, shown in parentheses after the compound number, will be employed. Sesquibicyclic hydrazines have a two-atom bridge containing the nitrogens in each bicyclic ring. Numbers are given showing the other bridge sizes, with unsaturated bridges preceeded by u.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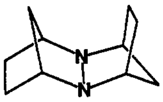
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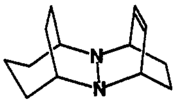
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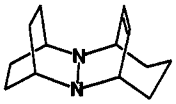
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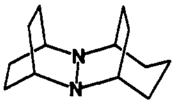
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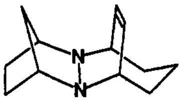
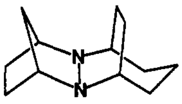
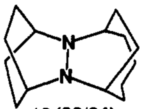

10 (21/u23)


11 (21/23)


12 (22/24)

NMR measurements of k_{ex} were made by mixing the radical cation salt with a ≥ 20-fold excess of neutral hydrazine in deuterated solvent and determining the line broadening caused by electron exchange by how much the line width must be increased for a simulation of the sharper lines in the spectrum of the neutral compound in the absence of radical cation to match that in its presence. Constant k_{ex} values were obtained under these pseudo-first-order conditions as radical cation is added.[8] We have found greatest reproducibility for measurement of k_{ex}(25 °C) by varying the temperature, which allows using several points to interpolate to k_{ex}(25 °C) values in plots of $\ln(k_{ex})$ vs $1/T$. Obviously, making accurate measurements requires that the radical cation is stable in the presence of a large excess of the basic neutral compound. This was shown to be a problem for $3^{0/+}$,[8] where line broadening at room temperature decreases with time as the radical cation decomposes. The protons released upon decomposition cause an increasing downfield shift for the signals of 3 because the signals observed are for 3^0 exchanging rapidly with the protonated compound, $3H^+$. Because of this decomposition problem, only a rather imprecise value of k_{ex}(25 °C) could be estimated by allowing for this decomposition,[8] and because k_{ex} was slow, very little broadening was observed even at room temperature, precluding a variable-temperature study. Some of the compounds studied here also showed decomposition problems, including **5(21/22)**, **10(21/u23)**, and **11(21/23)**. Although 12^+**(22/24)** does not decompose rapidly in the presence of 12^0 at room temperature, no detectable line broadening was observed, and decomposition ensued before significant line broadening resulted at higher temperatures; no rate constant could be estimated. **12** is anti fused at the large ring,[6] making it significantly different structurally from **2–11**, which are syn fused. Other anti-fused bicyclic hydrazines also have k_{ex} values which are too small to measure by NMR line broadening.

For **6–9**, similar line broadening was observed at the same temperature at the beginning and end of the variable temperature run, indicating that radical cation decomposition was not significantly affecting the data. Table 1 shows a sample of the line-broadening data obtained (for **6** in CD_3CN), and Figure 1 shows the Eyring plot of these data, used to obtain k_{ex}(25 °C). The temperature range available for measurement of k_{ex} was limited on the high-temperature end by radical cation decomposition and on the low-temperature end by line broadening becoming too small for accurate estimation. The range of temperatures studied varied from 26 to 62 °C for various data sets. Although we attempted to separate ΔG^{*}_{ex} values at 25 °C into ΔH^* and ΔS^* components, the small temperature range and the statistical uncertainty in the k_{ex} measurements produce errors in the calculated activation parameters which are large enough to preclude useful interpretation in our opinion (see ref 10). The k_{ex}(25 °C) data obtained in acetonitrile are summarized in Table 2.

We examined the solvent effects on k_{ex} for two additional sesquibicyclic hydrazines, $4^{0/+}$**(21/u22)** and $8^{0/+}$**(22/u23)**, to find out whether our previous observation[9] of unusual solvent effects for $2^{0/+}$**(22/u22)** is reproducible with compounds of similar structure or if they are isolated curiosities which might be artifacts. The results are

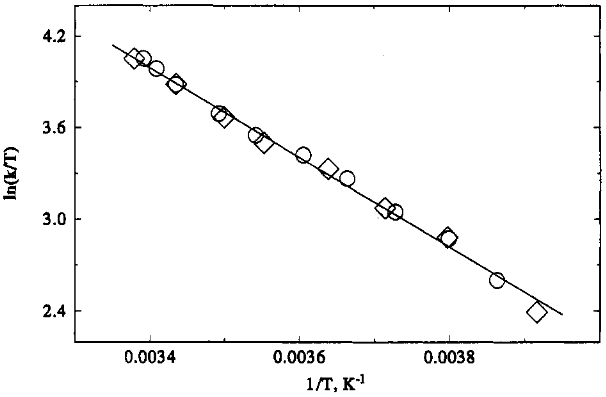


Figure 1. Eyring plot of the rate constant data for $6^{0/+}$**(21/21)** in CD_3CN (data of Table 1; circles, run 1, diamonds, run 2).

Table 1. Line-Broadening Data for 6(21/21)$^{0/+}$ in CD_3CN

run 1: $[6]^0$ = 0.486, 0.0189			run 2: $[6]^0$ = 0.454, 0.0135		
T, °C	$\Delta\nu$, Hz	$10^{-3}k_{ex}$, s^{-1}	T, °C	$\Delta\nu$, Hz	$10^{-3}k_{ex}$, s^{-1}
−14.3	21	3.49	−17.8	12	2.79
−9.9	28	4.65	−9.8	20	4.65
−4.9	34	5.65	−3.9	25	5.82
−0.2	43	7.15	1.7	33	7.68
4.2	51	8.48	8.3	40	9.31
9.2	59	9.10	12.6	48	11.17
13.2	69	11.47	18.8	61	14.20
18.0	85	14.13	22.8	73	16.99
20.2	95	15.79			
21.7	102	16.95			

Table 2. Self-ET Data for Sesquibicyclic Hydrazines in CD_3CN

compound	k_{ex}(25 °C), M^{-1} s^{-1} [a]	T, °C [b]	ΔG^{*}_{ex} [c]
$6^{0/+}$(21/21)	18500 ± 500	−18, 23 (41) [18]	11.63 ± 0.02
$4^{0/+}$(21/u22)	2290 ± 90	−1, 23 (27) [21]	12.87 ± 0.02
$5^{0/+}$(21/22)	slow (dec)		
$2^{0/+}$(22/u22)	12100 ± 100	−10, 30 (49) [26]	11.89 ± 0.05
$3^{0/+}$(22/22)	~700 (dec)		~13.6
$7^{0/+}$(23/u22)	3370 ± 140	−2, 23 (25) [13]	12.64 ± 0.02
$8^{0/+}$(22/u23)	3840 ± 110	−2, 25 (27) [16]	12.57 ± 0.02
$9^{0/+}$(22/23)	580 ± 25	27, 61 (34) [16]	13.69 ± 0.03
$10^{0/+}$(21/u23)	≥400 (dec)		≤13.9
$11^{0/+}$(21/23)	slow (dec)		
$12^{0/+}$(22/42)	slow (dec)		

[a] Ranges quoted are statistical errors (only) at the 95% confidence level from plots of $\ln(k_{ex})$ vs $1/T$. [b] Shown are lowest T, highest T, (range of T), and [number of individual measurements]. [c] Unit: kcal mol^{-1}.

Table 3. Solvent Effects on k_{ex} at 25 °C

cmpd	solvent ($E_T(30)$)	$10^{-3}k_{ex}$, s^{-1} at 25 °C[a]	$k_{ex}/k_{ex}(AN')$	ΔG^*_{ex}(25 °C), kcal/mol
$2^+NO_3^-$ [b] (22/u22)	CD_3OD (55.4)	0.68	0.06	13.6
	C_2D_5OD (51.9)	2.2	0.18	12.9
	$(CD_3)_2CDOD$ (48.4)	3.2	0.26	12.7
	CD_3NO_2 (46.3)	23.4	1.93	11.5
	CD_3CN (45.6)	12.1	1	11.9
	$(CD_3)_2SO$ (45.1)	10.4	0.86	12.0
	$DCON(CD_3)_2$ (43.8)	21.7	1.79	11.5
	CD_2Cl_2 (40.7)	59.0	4.88	10.9
	C_5D_5N (40.5)	65.8	5.44	10.9
	$CDCl_3$ (39.1)	9.5	0.79	12.0
$4^+PF_6^-$ (21/u22)	CD_3NO_2	2.89 ± 0.09	1.26	12.7
	CD_3CN	2.29 ± 0.11	1	12.9
	$DCON(CD_3)_2$	3.71 ± 0.12	1.62	12.6
	CD_2Cl_2	11.5 ± 0.4	5.02	11.9
	C_5D_5N	10.1 ± 0.1	4.41	12.0
$8^+NO_3^-$ (22/u23)	CD_3OD	0.33 ± 0.05	0.10	14.0
	C_2D_5OD	0.86 ± 0.02	0.27	13.4_5
	$(CD_3)_2CDOD$	1.73 ± 0.13	0.54	13.0
	CD_3NO_2	4.97 ± 0.16	1.54	12.4
	CD_3CN	3.23 ± 0.12	1	12.7
	C_5D_5N	8.6 ± 0.5	2.22	12.1
	$CDCl_3$	2.7 ± 0.7	0.82	12.8
$8^+PF_6^-$ (22/u23)	CD_3NO_2	6.1 ± 0.5	1.60	12.3
	CD_3CN	3.84 ± 0.11	1	12.6
	$(CD_3)_2SO$	2.85 ± 0.13	0.74	12.7
	$DCON(CD_3)_2$	4.19 ± 0.17	1.09	12.5
	CD_2Cl_2	13.5 ± 0.6	3.52	11.8
	C_5D_5N	8.5 ± 0.6	2.22	12.1

[a] The ranges quoted for k_{ex} are statistical errors (only) propagated at the 95% confidence level. [b] From ref 6.

Table 4. Comparison of Rates and Barriers for Sesquibiyclic Hydrazine Self-ET (25 °C in CD_3CN) with Calculated Inner Sphere Barriers

	observed		calculated by AM1				
compound	k_{rel}	$\Delta\Delta G^*$ [a]	$\Delta\Delta H'_{in}$[a]	$\Delta H'_{in}$[a]	$\Delta\alpha_{av}$	r_x, Å[b]	rel $(2r_x)^{-1}$
$6^{0/+}$(21/21)	100	[0]	[0]	8.81	5.9	3.73	[1]
$4^{0/+}$(21/u22)	$12._4$	1.2_4	0.92	9.72	6.7	3.80	0.99
$5^{0/+}$(21/22)	dec		0.51	9.32	6.1	3.83	0.98
$2^{0/+}$(22/u22)	$65._4$	0.2_6	0.33	9.14	5.7	3.93	0.96
$3^{0/+}$(22/22)	~4	~2.0	−0.51[c]	8.30	4.6	3.95	0.95
$7^{0/+}$(23/u22)	$17._7$	1.0_7	0.76	9.57	5.8	4.02[d]	0.94
$8^{0/+}$(22/u23)	$20._8$	0.9_4	0.75	9.56	5.8	4.02[d]	0.94
$9^{0/+}$(22/23)	~3	~2.1	−0.16[c]	8.66	4.8	4.05[d]	0.93
$10^{0/+}$(21/u23)	>2	<2.3	1.22	10.34	6.7	3.92[d]	0.96
$11^{0/+}$(21/23)	dec		0.98	9.79	6.3	3.96	0.95

[a] Unit: kcal/mol. [b] r_x is the radius of a sphere occupying the same volume a molecule occupies in the crystal.[6a] [c] AM1 estimate is certainly too low; see text. [d] Estimated from AM1 calculations.[6b]

summarized in Table 3. The PF_6^- salts of both 4^+ and 8^+ proved to be too insoluble in both chloroform and alcohols to allow rate constant measurements, and the nitrate salt of 8^+ was also studied. The effect of switching from the PF_6^- to NO_3^- counterion on k_{ex} for $8^{0/+}$ is rather small; $k_{ex}(NO_3^-$ salt$)/k_{ex}(PF_6^-$ salt) values of 0.81, 0.84, and 1.01 are observed in nitromethane, acetonitrile, and pyridine, respectively. The k_{ex} values obtained are not of the same quality for all solvents, and the poorest data are clearly for CD_3OD, where the lowest k_{ex} values and therefore the least line broadening occur, as indicated by the larger statistical error found for the CD_3OD data set.

Discussion

Effect of Ring Size on k_{ex}(25 °C). Compounds 2–11 are a closely related series, and we hoped to be able to understand the variation in the k_{ex} values measured, about a factor of 50 (see Table 4), by consideration of the parameters employed in Marcus' development of ET theory.[11] In Marcus theory, the thermal barrier for a self-ET is estimated from λ, the barrier for vertical ET between the neutral and radical cation in the precursor complex. The crossing point between the precursor and successor complex free-energy curves for thermal ET is λ/4, which is designated ΔG^*, and the exchange rate k_{ex} may be given by eq 2. λ is assumed to consist of additive terms for the

$$k_{ex} = \text{PRE} \exp(-\Delta G^*/RT) = \text{PRE} \exp(-\lambda/4RT) \quad (2)$$

solvent reorganization barrier λ_{out} and the internal geometry reorganization barrier λ_{in} (eq 3). λ_{out} is believed

$$\lambda = \lambda_{out} + \lambda_{in} \quad (3)$$

to be affected principally by molecular size and shape and to be calculable using eq 4. γ is a solvent parameter,

$$\lambda_{out} = e^2 g(r,d)\gamma \quad (4)$$

obtained from the refractive index and dielectric constant. The distance parameter $g(r,d)$ is frequently approximated as $(1/r - 1/d)$ for spheres of radius r at a center distance d in the ET transition state. Touching spheres would have $g(r,d) = 1/2r$, which is sometimes used as an approximation to calculate λ_{out} using eq 4. These molecules are not spheres and also have charge distributed in a nonuniform manner, so that neither r nor d seem very well defined. Nevertheless, the structural similarity of the series studied is great enough that we would expect λ_{out} to be rather insensitive to compound. Table 4 includes, as an estimate of the molecular radius, values for r_x, the radius of a sphere of the same volume an average molecule occupies in the crystal (obtained from the molecular weight and calculated density of the crystal).[6] As shown in the last column of Table 3, $1/2r_x$ would predict λ_{out} for the largest compound studied, 23/22, to be 94% that for the smallest, 21/21. We conclude that λ_{out} changes should be both small and regular enough as structure is changed in this series that we probably should not be able to detect changes.

λ_{in} obviously varies for this series. We shall consider how the quantitative predictions of λ_{in} changes from semiempirical AM1 calculations, which we have argued work well for sesquibicyclic hydrazines,[4,8b] compare with the observed $\Delta\Delta G^*_{ex}$ values for the compounds studied. The precursor pair for an intermolecular neutral, radical cation self-ET reaction may be represented as $[n^0,c^+]$, where n and c refer to the geometry-relaxed neutral and radical cation oxidation states, respectively, including both internal geometry and the solvent shell around them, and the superscripts represent the charges present. The vertical ET pair is then $[n^+,c^0]$, where neither internal geometry nor solvent shell have relaxed when charge was transferred, and the Marcus λ value is the free-energy difference between them. The enthalpy contribution to λ_{in} is the difference in heats of formation for n^+ and c^0 plus that for n^0 and c^+, which we call λ'_{in}. λ'_{in} may be written as the sum of the relaxation energies of the cation radicals and the neutral compounds, ΔH_r(cat) and ΔH_r(neu) (eq 5). The results of AM1 calculations using geometry-

$$\lambda'_{in} = [\Delta H_f(n^+) - \Delta H_f(c^+)] + [\Delta H_f(c^0) - \Delta H_f(n^0)] = \Delta H_r(\text{cat}) + \Delta H_r(\text{neu}) \quad (5)$$

optimized structures and UHF energies for the open-shell

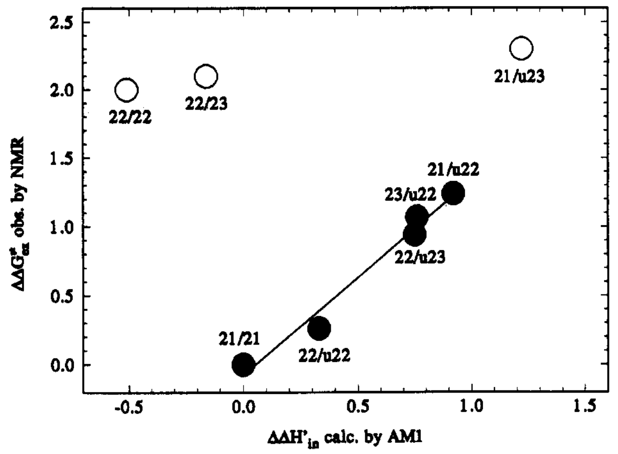


Figure 2. Plot of experimental change in free-energy barrier for self-electron exchange vs AM1-calculated enthalpy of inner sphere relaxation, relative to 6(21/21).

radical cations are summarized in Table 4 as $\Delta H'_{in} = \lambda'_{in}/4$ values. Figure 2 shows a plot of observed $\Delta\Delta G^{\ddagger}_{ex}$ vs $\Delta\Delta H'_{in}$ (relative to **21/21**) obtained by AM1. The points for the five compounds shown as filled circles give a linear correlation, $\Delta G^{\ddagger}_{ex} = 1.40\Delta H'_{in} - 0.77$, with $r^2 = 0.97_8$, and an average deviation of $\Delta G^{\ddagger}_{ex}$ from the line of 0.06 kcal/mol. This is not much larger than the statistical error in $\Delta G^{\ddagger}_{ex}$ and is likely to be no larger than the true experimental error in determining $\Delta G^{\ddagger}_{ex}$. The points which deviate from the line of Figure 2 are especially instructive. **21/u23**$^{0/+}$ has a higher $\Delta\Delta G^{\ddagger}_{ex}$ than predicted. This radical cation noticeably decomposed during the rate measurement, and the rate constant measured for **21/u23**$^{0/+}$ is only a minimum value; an increase in k_{ex} by a factor of 3 (corresponding to a change in $\Delta G^{\ddagger}_{ex}$ of 0.65 kcal/mol) would put the point on the line. The **22/22**$^{\cdot+}$ point also shows a large positive deviation in Figure 2. It also decomposes, but more slowly, and a correction to the line width was applied;[8] we do not believe that the $\Delta\Delta G^{\ddagger}_{ex}$ value employed is likely to be in serious error. Furthermore, **22/23**$^{\cdot+}$ does not decompose detectably on the time scale of the NMR measurement, and its point deviates about as much as does the **22/22**$^{0/+}$ point. We suggest that the deviations for the **22/22**$^{0/+}$ and **22/23**$^{0/+}$ points can be clearly attributed to poor calculated λ'_{in} values. These compounds are the only ones considered that are significantly twisted about the NN bond in the neutral form; this twisting is important in determining the size of λ'_{in}, and AM1 incorrectly obtains untwisted structures. As the quantitative measure of twisting, we shall use the lone pair,lone pair dihedral angle θ. Assuming that the lone pair axis at N' bisects the CNC angle in a projection down the NN' bond, θ is the average of the intra-ring CN,N'C dihedral angles. θ is 15.0° and 16.7°, respectively, for **22/22** and **22/23** from X-ray crystal structures; the other compounds are essentially untwisted, the maximum twist found being that for **21/u22**, for which θ is 2.7°.[6] AM1 calculations optimize all the structures nearly untwisted (the maximum values are θ = 0.5° and 1.7°, respectively, for **22/22** and **22/23**).[6] Because twisting in the vertical electron-transfer cation n^+ is especially costly in energy, the incorrect AM1 geometry ought to lower the calculated λ'_{in} values for these compounds from their true values. The correlation of Figure 2 suggests that the deviation in predicted $\Delta\Delta G^{\ddagger}_{ex}$ that results from using the bad λ'_{in} estimation for these twisted compounds is on the order of 2 kcal/mol.

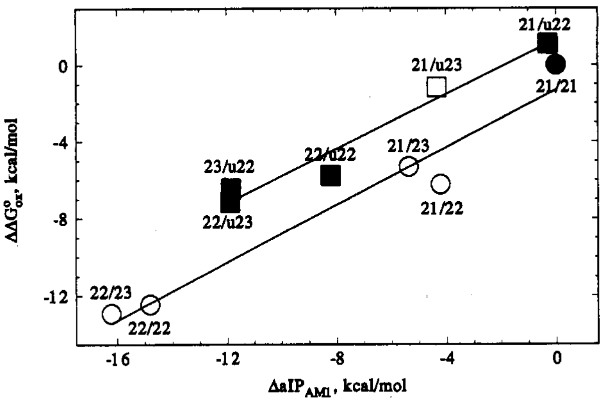


Figure 3. Plot of experimental change in free energy for oxidation vs AM1-calculated enthalpy of adiabatic ionization, relative to 6(21/21).

We do not think it is likely that the correlation for the five untwisted compounds shown in Figure 2 is simply an accident, but obtaining a linear correlation of $\Delta\Delta G^{\ddagger}_{ex}$ with calculated $\Delta\Delta H'_{in}$ certainly surprised us.[12] This correlation appears to us to imply that two conditions are fulfilled, (i) that AM1 properly calculates the change in $\Delta H'_{in}$ in this series and (ii) that any other changes in parameters that affect $\Delta G^{\ddagger}_{ex}$ in this series change regularly with λ_{in}. We believe that condition (i) is the most controversial one and shall consider it first. There is no way that AM1 would have been predicted in advance to calculate $\Delta H'_{in}$ very accurately; this could only happen if a fortuitous cancellation of errors occurred. Equation 5 shows that $\Delta\Delta H'_{in}$ calculations involve differences for different bicyclic ring sizes of differences of ΔH_f values for geometry-relaxed neutrals and cations and their vertical ET products of each compound. The ΔH_f values obtained by AM1 for these species are not very accurate, but it is not the ΔH_f values themselves but their differences are what is used. The errors in the individual ΔH_f values could either tend to build up, which would make the calculations useless for understanding experimental data, or tend to cancel. One can find out how well AM1 does at handling the effect of bicyclic ring size on ΔH_f calculations for these compounds by examining the changes in the thermodynamics for electron transfer in the series.[4] The difference in formal potentials for oxidation ($E^{\circ\prime}$) is the difference in thermodynamic ease of electron removal, which we will call $\Delta\Delta G^{\circ}_{ox}$, and has been experimentally measured to be about 0.2 kcal/mol at 25 °C in acetonitrile for the compounds under consideration by cyclic voltammetric measurements.[4,10] The AM1 calculation of the enthalpy contribution to oxidation potential is given by the differences between the enthalpies of oxidation $\Delta\Delta H_{ox} = \Delta H_f(c^+) - \Delta H_f(n^0)$ for different compounds, i.e., the calculated adiabatic ionization potential, which we shall call aIP_{AM1}. Figure 3 shows a plot of $\Delta\Delta G^{\circ}_{ox}$ vs ΔaIP_{AM1}, and the data plotted appear in Table 5. The five compounds which give the linear plot in Figure 2 are those shown with filled symbols in Figure 3; only these compounds go into making the line shown in Figure 2. The regression line through

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(12) There is no possibility of our unconsciously adjusting the k_{ex} values to produce a better correlation. We did not realize why the twisted compounds deviated and, hence, did not know there was a good correlation between λ'_{in} and $\Delta G^{\ddagger}_{ex}$ for the other compounds until well after all the data were in hand.

Table 5. Comparison of Observed and Calculated Thermodynamics for Oxidation[a]

compound	E° [b]	$\Delta\Delta G^{\circ}_{ox}$ [c,d]	ΔaIP_{AM1} [c,d]	aIP_{AM1} [c,e]
6(21/21)*	0.01	0	0	166.56
5(21/22)	−0.26	-6.2_3	−4.22	162.34
11(21/23)	−0.22	-5.3_0	−5.38	161.17
3(22/22)	−0.53	-12.4_5	−14.81	151.75
9(22/23)	−0.55	-12.9_1	−16.22	149.94
4(21/u22)*	0.05_8[f]	1.1_1	−0.29	166.27
10(21/u23)	−0.04	-1.1_5	−4.34	162.22
2(22/u22)*	-0.24_1[f]	-5.7_7	−8.22	158.34
7(23/u22)*	−0.27	-6.4_6	−11.86	154.70
8(22/u23)*	−0.30	-7.4_5	−11.89	154.67

[a] An asterisk designates a compound for which $\Delta\Delta G^{\ddagger}_{ex}$ correlates with $\Delta\Delta H'_{in}$. [b] In V, for CH_3CN solutions containing 0.1 M tetrabutylammonium perchlorate, vs SCE. From ref 4 except where indicated. [c] Unit: kcal/mol. [d] Relative to the entry for **21/21**. [e] Calculated using $aIP_{AM1} = \Delta H_f(c^+) - \Delta H_f(n^0)$ from AM1 calculations. [f] Calculated using $aIP_{AM1} = \Delta H_f(c^+) - \Delta H_f(n^0)$ from AM1 calculations. [f] From ref 10.

these five compounds (not drawn) has r^2 0.96, slope 0.64, and an average $\Delta\Delta G^{\circ}_{ox}$ deviation of 0.59 kcal/mol. We note that the only saturated compound, **21/21**, lies near the filled-symbol regression line but relatively far from the line for the other saturated compounds. The point of examining the oxidation thermodynamics has been to document the fact that AM1 calculation of the ΔH contribution (only) rather successfully correlates the experimental $\Delta\Delta G^{\circ}_{ox}$ free-energy values for these five compounds. The range of $\Delta\Delta G^{\circ}_{ox}$ values is 8.3 kcal/mol, and the average deviation is 0.6 kcal/mol (7% of the range); the greatest deviation is found for **22/u22**, 1.0 kcal/mol, or 12% of the range. The AM1 (gas phase) enthalpy calculations therefore estimate the effect of these ring-size changes to this level of accuracy on experimental free energies measured in solution. As has been pointed out,[4] this type of result is not a general one and occurs here because of the special constraints of sesquibicyclic stuctures. The solvation energies of hydrazine radical cations correlate linearly with molecular size and gas-phase ionization potentials.[4] This fact, which might not have been anticipated, is presumably important in obtaining the linear correlations of Figures 2 and 3. The regression observed for $\Delta\Delta G^{\ddagger}_{ex}$ vs $\Delta\Delta H'_{in}$ (Figure 2) has an average deviation of 0.06 kcal/mol, which is 5% of the range of $\Delta\Delta G^{\ddagger}_{ex}$ values, and the maximum deviation is shown by **22/u22**, which corresponds to 10% of the range. The largest deviator in both Figure 2 and 3 is **22/u22**. We doubt that this is caused by poor experimental data and suggest that a deviation in calculation of its oxidation potential might be expected to be accompanied by deviation in its calculated λ_{in}. We conclude that because AM1 calculations of the enthalpy for oxidation of these five specially constrained compounds have been shown to estimate the differences in their free energies for solution oxidation to an average of 7% of their range, they might be able to calculate their enthalpies of vertical ET to a comparable accuracy; it does not prove they have. Nevertheless, it appears plausible to us that condition (i), above, is met for this series.

Concerning condition (ii), even if $\Delta\Delta H'_{in}$ does accurately represent changes in λ_{in}, observing a good correlation with $\Delta\Delta G^{\ddagger}_{ex}$ implies that only λ_{in} may be changing detectably in this series. Significant changes in λ_{out}, the precursor complex formation constant K_p, the effective barrier crossing frequency $h\nu_{in}$, or the electronic coupling matrix element V would also change $\Delta\Delta G^{\ddagger}_{ex}$. However, both K_p and λ_{out} are thought to be determined by molecular size and shape,[11] and only undetectably small effects should be present for these parameters. We do not know how V and $h\nu_{in}$ might change in this series, but all these molecules have strongly convex, largely alkane or alkene surfaces and are structurally similar enough that it may be that both V and $h\nu_{in}$ either are relatively constant or (perhaps more likely) vary regularly enough with λ_{in} to maintain a linear correlation. The slope of the $\Delta G^{\ddagger}_{ex}$ vs $\Delta H'_{in}$ correlation is 1.4, so either AM1 underestimates the spread in λ_{in} changes or other factors which scale with $\Delta H'_{in}$ contribute to $\Delta G^{\ddagger}_{ex}$. Nevertheless, there is no experimental evidence for any factor affecting k_{ex} in this series other than changes in λ_{in}, which appear to be calculated well by AM1. In particular, a hypothesis that better electronic coupling between the partners at the transition state (i.e., higher V, leading to higher electronic transmission coefficient κ_{el}) is responsible for the larger k_{ex} values of the unsaturated compounds, which was once a favorite hypothesis of ours, lacks any evidence.

The approximately linear correlation of Figure 2 requires that $\Delta G^{\ddagger}_{ex} - \Delta H'_{in}$ is relatively constant. If the calculated $\Delta H'_{in}$ values were close to ΔG^{*}_{in}, their difference would be close to ΔG^{*}_{out} *if* PRE in eq 2 were close to 6×10^{12} s^{-1}. For the five compounds showing the correlation in Figure 1, $\Delta G^{\ddagger}_{ex} - \Delta H'_{in}$ is 2.96 ± 0.21 kcal/mol. If PRE were smaller than k_BT/h, this number would be larger than ΔG^{*}_{out}.

Estimation of λ_{in}/λ from Solvent Effects on k_{ex}. We suggest that the clearest comparison of the assumptions that $\Delta G^{\ddagger}_{ex}$ (or $\ln(k_{ex})$ or λ) varies linearly with the Marcus solvent parameter γ (see eq 4) and with another solvent parameter such as $E_T(30)$[13] may be made by comparing the differences in $\Delta G^{\ddagger}_{ex}$ predicted in various solvents from those in acetonitrile (eq 6). Acetonitrile is not only a

$$\Delta\Delta G^{\ddagger}_{ex}[\text{solv}] = \Delta G^{\ddagger}_{ex}[\text{solv}] - \Delta G^{\ddagger}_{ex}[\text{AN}] \qquad (6)$$

convenient polar aprotic solvent in which most ET reactions have been studied but also has one of the lower viscosities and faster tumbling rates of usefully polar solvents, so that solvent friction effects[14] in it are minimized,[15] which allows more meaningful comparison of exchange rate constants in acetonitrile for different systems than do most solvents. Making the usual assumption that $\Delta G^{\ddagger}_{in}$ is independent of solvent, $\Delta\Delta G^{\ddagger}_{ex}$[solv] measures only changes in the outer sphere term, eq 7, where R is the ratio $\Delta G^{\ddagger}_{out}[\text{solv}]/\Delta G^{\ddagger}_{out}[\text{AN}]$. If the

$$\Delta\Delta G^{\ddagger}_{ex}[\text{solv}] = \Delta G^{\ddagger}_{out}[\text{solv}] - \Delta G^{\ddagger}_{out}[\text{AN}] = (R-1)\Delta G^{\ddagger}_{out}[\text{AN}] \qquad (7)$$

Marcus solvent effect (eq 4) is assumed to hold, R is given by eq 8. Making the equivalent assumption that $\Delta G^{\ddagger}_{out}$ disappears in a hydrocarbon solvent, assuming linearity of $\ln(k_{ex})$ with $E_T(30)$ leads to eq 9 for evaluation of R. A

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(13) (a) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlman, F. *Justus Liebigs Ann. Chem.* **1963**, *661*, 1. (b) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1988.

(14) For a recent review, see: Weaver, M. J.; McManis, G. E. *Acc. Chem. Res.* **1990**, *23*, 294.

(15) (a) For example, from the rate data reported by Weaver and coworkers,[16b,c] ferrocene in acetonitrile has solvent friction effects which are undetectably small, which is certainly not true for most of the solvents they studied. (b) Nielson, R. M.; McManis, G. E.; Safford, L. K.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 2152. (c) McManis, G. E.; Nielson, R. M.; Gochev, A.; Weaver, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5533.

$\ln(k_{ex})$ linear with γ:

$$R = \gamma[\text{solv}]/\gamma[\text{AN}] \qquad (8)$$

$\ln(k_{ex})$ linear with $E_T(30)$:

$$R = (E_T(30)[\text{solv}] - 31.0)/(E_T(30)[\text{AN}] - 31.0) \qquad (9)$$

comparison of R values for the solvents used here appears in Table 6. Use of $E_T(30)$ as the solvent parameter allows use of data in alcohol solvents, in which ΔG^{*}_{ex} values do not follow γ, presumably because of a combination of very non-Debye behavior and hydrogen-bonding effects. Use of $E_T(30)$ as the solvent polarity parameter for our data more than doubles the range of solvent polarity available for extrapolation of ΔG^{*}_{ex} to its value in a hydrocarbon solvent, where λ_{out} is assumed to disappear.

The solvent effect data of Table 3 are compared graphically as ΔG^{*}_{ex} vs $E_T(30)$ plots in Figure 4. The three hydrazines show very similar behavior as solvent is changed. Both $2^{0/+}$ and $8^{0/+}$ show anomalously slow exchange in chloroform, and the size of the effect is similar (1.3 and 1.0 kcal/mol higher than the regression line, respectively). This anomaly also occurs in plots vs γ (note the similar R values for chloroform in Table 6). We suggest that an ion-pairing effect is likely to be slowing the electron exchange in chloroform. Self-ET reactions should become slower in nonpolar enough solvents than a ΔG^{*}_{ex} vs solvent parameter plot for polar solvents predicts. Eventually, tight ion pairing will become strong enough that the counterion for the cation must be transferred at the same time as the electron, presumably significantly changing the ET transition-state geometry by forcing the molecules apart, which should decrease the rate constant. An alternate way of considering the smaller k_{ex} expected is that if ion pairing stabilizes the radical cation, ΔG° for an ET which does not transfer the counterion is no longer zero, principally because the cation in the successor pair will not enjoy ion-pairing stabilization and the ET barrier will increase.

The comparison in Figure 4 demonstrates that the deviations from linearity of the ΔG^{*}_{ex} vs $E_T(30)$ plots for sesquibicyclic hydrazines are unlikely to arise simply from experimental error (although our data are obviously not free from experimental scatter); the same is true for plots vs γ. Neither γ nor $E_T(30)$ as a polarity parameter perfectly predict the changes which occur in ET barrier for sesquibicyclic hydrazines. Use of $E_T(30)$ gives better correlation than does use of γ, principally because $E_T(30)$ allows use of alcohols in the correlation, extending the polarity range available. Nevertheless, there is an approximately linear trend toward decreasing ΔG^{*}_{ex} as both measures of solvent polarity decrease, and we shall examine both γ and $E_T(30)$ as solvent parameters for partitioning of the inner and outer shell barriers for these compounds.

It has been traditional to use eq 4 to estimate λ_{out} from the assumed distance at the transition state and the size of the molecules involved.[1] As has been pointed out in the context of mixed-valence transition-metal compounds, this equation is difficult to apply because real molecules are not spheres and their charge is not homogeneously distributed. Schemes of varying complexity have been used in attempts to evaluate $g(r,d)$ more accurately.[17]

Table 6. Comparison of γ with $E_T(30)$ as Solvent Polarity Parameters

solvent	R^a if $\ln(k)$ linear with γ^b	$E_T(30)^c$
AN(CH_3CN)	[1]	[1]
$MeNO_2$	0.95	1.05
DMSO	0.83	0.97
DMF	0.88	0.88
MC(CH_2Cl_2)	0.73	0.66
pyr	0.69	0.65
chl($CHCl_3$)	0.51	0.55
MeOH	0.90^d	1.67
EtOH	0.95^d	1.43
*i*PrOH	1.02^d	1.19

[a] $\Delta G^{*}_{out}[\text{solv}]/\Delta G_{out}[\text{AN}]$. [b] Using eqs 6 and 7. [c] Using eqs 6 and 8. [d] No one assumes that γ values of alcohols actually measure their polarity in a useful way; these numbers are only included for comparison with the $E_T(30)$ scale.

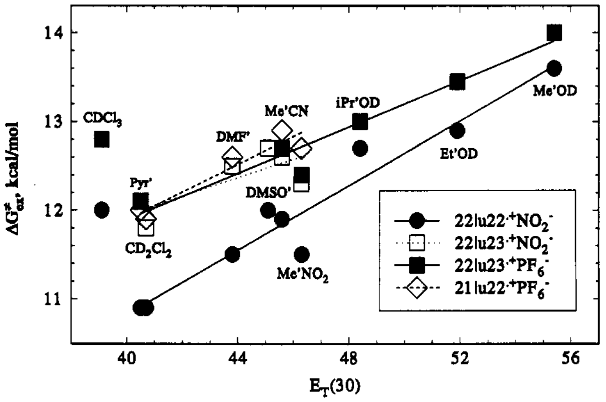

Figure 4. ΔG^{*}_{ex}, 25 °C, vs $E_T(30)$ plot for self-ET of sesquibicyclic hydrazines $2^{0/+}$, $4^{0/+}$, and $8^{\cdot+}$.

Intermolecular ET reactions are expected to occur from many relative orientations of the molecules, making evaluation of $g(r,d)$ from the structure of the components difficult. We suggest that the information really available from solvent studies on intermolecular self-ET reactions is not separation of λ_{out} from λ_{in}, but the ratio of λ_{in}/λ for a given solvent. We note that the λ_{in}/λ ratio does not depend upon the preexponential factor assumed (so is the same as $\Delta G^{*}_{in}/\Delta G^{*}$) nor does it use $g(r,d)$ of eq 4. It does assume that k_{ex} changes with solvent polarity because λ_{out} changes, that λ_{in} is independent of solvent, and that λ_{out} will disappear in a nonpolar solvent.

Analysis of the k_{ex} variation with solvent results is summarized in Table 7. Although only a narrow range of R is available for the $4^{0/+}$ ET, the $\Delta\Delta G^{*}$ values observed are rather similar to those for $2^{0/+}$, indicating that ΔG^{*}_{out} is about the size of that for $2^{\cdot+}$, as would be expected from their structures. For $8^{0/+}$, where the same solvent range is available as for $2^{0/+}$, the smaller range of $\Delta\Delta G^{*}$ values implies a smaller $\Delta G^{*}_{out}[\text{AN}]$ and a correspondingly larger λ_{in}/λ value. However, a ca. 30% smaller $\Delta G^{*}_{out}[\text{AN}]$ for $8^{0/+}$ than for $2^{0/+}$ and $4^{0/+}$ is not very reasonable. 8 is only slightly larger than either 2 or 4 (Table 4, last column) and would be expected to have only a slightly smaller ΔG^{*}_{out} value, using eq 4. It seems likely to us that ΔG^{*}_{out} values should be closer for these compounds, which do not differ very much in size. It is difficult to estimate the true errors in our measurements of k_{ex}. $8^{\cdot+}$ is noticeably less stable than $2^{\cdot+}$, and its k_{ex} values are smaller; errors might be larger. It is not obvious from our data, but we believe that ΔG^{*}_{out} (and hence λ_{in}/λ) values are likely to be closer for

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[16] Phelps, D. K.; Ramm, M. T.; Wang, Y.; Nelsen, S. F.; Weaver, M. J. *J. Phys. Chem.* **1993**, *97*, 181.

[17] Braunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3659.

Table 7. λ_{in}/λ and $\Delta G^{\ddagger}_{out}$[AN] from Solvent Effect Data[a]

	from $\Delta G^{\ddagger}_{ex}$ vs $E_T(30)$ plot				from $\Delta G^{\ddagger}_{ex}$ vs γ plot			
compound	R range[b]	pts (r^2)	λ_{in}/λ[c]	$\Delta G^{\ddagger}_{out}$[d]	R range	pts (r^2)	λ_{in}/λ[c]	$\Delta G^{\ddagger}_{out}$[d]
$\mathbf{2}^+NO_3^-$ (**22/u22**)	0.65–1.67	9 (.94)	0.78	2.7	0.69–1.0	6 (.58)	0.75	3.0
$\mathbf{4}^+PF_6^-$ (**21/u22**)	0.65–1.67	5 (.91)	0.82	2.3	0.69–1.0	5 (.96)	0.75	3.2
$\mathbf{8}^+NO_3^-$ (**22/u23**)	0.65–1.67	6 (.94)	0.85	1.9	0.69–1.0	3 (.88)	0.87	1.7
$\mathbf{8}^+PF_6^-$ (**22/u23**)	0.65–1.05	6 (.60)	0.89	1.4	0.69–1.0	6 (.45)	0.85	1.9

[a] Energy unit: kcal/mol. [b] See Table 2 for R values. [c] $\lambda_{in}/\lambda(CD_3CN)$. [d] In CD_3CN.

Table 8. Estimation of ET Parameters using the Solvent Dependence of k_{ex} Data

compound	k_{ex},[a] $M^{-1}\,s^{-1}$	λ_{rat}[b]	λ_{in}, kcal/mol	λ_{out}, kcal/mol	$h\nu_{in}$, cm^{-1}	J, if K_p 0.3 (0.7 M^{-1}),[c] kcal/mol
$\mathbf{2}^{0/(}$**22/u22**)	12100	0.78 (i)	34.6	9.8	900–1200	0.06–0.02 (0.04–0.01)
			36.6	10.3	900–1200	0.09–0.03 (0.06–0.02)
			38.6	10.9	900–1200	0.14–0.05 (0.09–0.03)
		0.75 (ii)	34.6	11.5	900–1200	0.09–0.03 (0.06–0.02)
			36.6	12.2	900–1200	0.14–0.05 (0.09–0.03)
			38.6	12.9	900–1200	0.21–0.08 (0.14–0.05)
$\mathbf{4}^{0/(}$**21/u22**)	2290	0.82 (i)	40.5	8.9	900–1200	0.05–0.02 (0.03–0.01)
		0.75 (ii)	40.5	13.5	900–1200	0.15–0.05 (0.10–0.03)
$\mathbf{8}^{0/+}$(**22/u32**)	3230	0.85 (ii)	39.3	6.9	900–1200	0.03–0.01 (0.02–0.01)

[a] In CD_3CN, 25 °C (Table 2). [b] $\lambda_{rat} = \lambda_{in}(T)/\lambda(T)$ (Table 7), assuming (i) linearity of λ_{out} with $E_T(30)$ or (ii) linearity with γ. [c] Calculated using eqs 10 and 11.

these compounds than the numbers we measured produce, and we suggest that the values quoted for $\mathbf{2}^{0/+}$ and $\mathbf{4}^{0/+}$ are likely to be better than those quoted for $\mathbf{8}^{0/+}$ in Table 7, despite our best efforts in measuring the k_{ex} values.

Diabaticity of Hydrazine Self-ET. The large $\lambda_{in}/\lambda(CD_3CN)$ ratios obtained from the solvent effects on k_{ex} require large λ_{in} values to produce reasonable $\lambda_{out}(CD_3CN)$ values. For $\mathbf{2}^{0/+}$(**22/u22**), the experimental ratios of 0.78 (vs E_T30) and 0.75 (vs γ) require λ_{in} of ≥ 34.6 for $\lambda_{out}(CD_3CN)$ of ≥ 9.8 and 11.5 kcal/mol, respectively (see Table 7). We do not believe that $\lambda_{out}(CD_3CN)$ is likely to be much smaller than these values. Use of eq 4 with the r_x value of 3.93 Å produces effective distances at the transition state, d_{eff} of ≤ 5.03 Å for $\lambda_{out}(CD_3CN)$ of ≤ 9.8 kcal/mol. Calculations suggest that serious steric interactions develop when the distance between the NN units drops below about 5 Å in most orientations. We conclude that λ_{in} is indeed likely to be at least 34.6 kcal/mol and that the AM1-calculated λ'_{in} of 36.6 is probably not very far from λ_{in}.

A λ_{in} of ≤ 38.6 kcal/mol makes self-ET for **22/u22**$^{0/+}$ strongly diabatic using modern ET theory.[11] ET reactions were originally assumed to be adiabatic and to proceed whenever the reactants achieved enough energy, but it was later realized that sufficient separation of the ground-state and excited-state surfaces at the ET transition state, measured by the size of the electronic coupling matrix element V, might not be present to allow the ET rate to be limited by the activation barrier.[11] Although hydrazines clearly have larger self-ET barriers than previously studied compounds, whether or not their ET is adiabatic also affects the rate constant. Tunneling is clearly important for organic compounds, and we employ eq 10 for diabatic

$$k_{ex}(\text{diabatic}) = K_p\, g(V^2/\lambda^{1/2})\, \Gamma_n \exp(-\lambda/4RT) \quad (10)$$

$$\Gamma_n = 2F\cos(2F)\exp[(\lambda_{in}/h\nu_{in})(\tanh(F) - F)] \quad (11)$$

ET, using Hush's evaluation of the tunneling factor, Γ_n, shown in eq 11.[18] We have written eq 11 employing $F = h\nu_{in}/4kT$ for brevity.[19] We employ precursor complex formation constants K_p (which have not been satisfactorily measured experimentally) in the range 0.3–0.7, accepting the discussion in Grampp and Jaenicke's extensive tetramethyl-p-phenylenediamine self-ET work.[20] We employ $h\nu_{in}$ values in the range of 900–1200 cm^{-1}. This is lower than usually used for organic compounds,[20] but the hydrazine self-ET barrier is dominated by low-frequency vibrations which change nitrogen pyramidality,[21] and we believe that this is the proper range to consider for the compounds under discussion. It may be noted from Table 8 that V for **22/u22**$^{0/+}$ only approaches 0.2 kcal/mol for the highest λ_{in},λ_{out} pair, the smallest K_p, and the smallest $h\nu_{in}$ considered. This entry corresponds to an electronic transmission coefficient κ_{el} of 0.04; these self-ET reactions are strongly diabatic (if it is accepted that our $h\nu_{in}$ and K_p ranges are valid). The use of higher $h\nu_{in}$ values would make the reactions calculated as being more diabatic.

The entries for $\mathbf{4}^{0/+}$ and $\mathbf{8}^{0/+}$ use as λ_{in} the AM1-calculated λ'_{in} for $\mathbf{2}^{0/+}$ increased by 4 times the difference in $\Delta\Delta G^{\ddagger}$ (Table 4), that is, assuming the only reason for a decrease in rate constant was an increase in λ_{in}. It may be seen that the high $\lambda_{in}/\lambda(CD_3CN)$ value observed for **22/u23**$^{0/+}$ produces low $\lambda_{out}(CD_3CN)$ values, probably indicating systematic error in the rate measurements, as discussed above.

Conclusions

The k_{ex} values for sesquibicyclic hydrazines are near the lower limit for NMR measurements and were too small to even allow estimation of k_{ex} for 3 of the 11 compounds studied. For the five untwisted compounds for which accurate k_{ex} values could be determined, the observed $\Delta G^{\ddagger}_{ex}$ values correlate linearly with $\Delta H^{\ddagger}_{in}$ values calculated by AM1. AM1 calculations give $\Delta H'_{in}$ values for **22/22** and **22/23** which are too low, rather clearly because they

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(18) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135. Use of the somewhat smaller tunneling correction introduced by Holstein (see ref 11b,c), which lacks the $2F$ cosh$(2F)$ terms of eq 11, makes these reactions even more diabatic than the values shown in Table 8.

(19) It is more common to use a "temperature-dependent λ_{in}", absorbing the effect of Γ_n into the exponential term and making the ET barrier lower because of tunneling.[20] We prefer to use eqs 10 and 11, which are numerically equivalent to using a $\lambda_{in}(T)$ formulation.

(20) (a) Grampp, G.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 325. (b) *Ibid.* **1984**, *88*, 335. (c) *Ibid.* **1991**, *95*, 904.

(21) Such low values of $h\nu_{in}$ are consistent with calculations by AM1 (mentioned in ref 16) and also with unpublished optical data on intermolecular ET in bis-hydrazine radical cations. We will defer discussion of this point until more data are available.

incorrectly calculate untwisted structures for these compounds. The effect of solvent polarity on k_{ex} is consistent with λ_{in} comprising 75% or more of the total barrier λ, far higher than for previously studied systems, but large λ_{in} values are expected for hydrazines because of the large geometry change upon electron transfer. The observed rate constants are consistent either with k_{ex} only varying because λ_{in} changes or with all other parameters which affect k_{ex} changing linearly with λ_{in} for the series of compounds studied. Despite the large electron-transfer barriers λ which are present for sesquibicyclic hydrazines because of their large λ_{in} values, the k_{ex} values observed are small enough to be consistent with the rate constant being significantly limited by poor electronic overlap at the transition state; the electron transfers are estimated to be significantly diabatic. The large alkyl substituents of sesquibicyclic hydrazines appear to us to prevent close approach of the two-atom π systems of these molecules at the transition state, and it does not seem surprising to us that V is rather small. Grampp and Jaenicke have argued that V is even smaller for tetramethyl-*p*-phenylenediamine, where π overlap at the transition state should be much better,[20] but their estimate was based on a λ_{in} value for this system which appears to be significantly too small, based upon recent calculations,[22] and V is probably significantly higher than their estimates.

Experimental Section

Compound preparation,[4,6] NMR measurement of k_{ex} values,[9,10,16] and the computational methods employed[6,8] have all been described previously.

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[22] Rauhut, M.; Clark, T. *J. Am. Chem. Soc.* **1993**, *115*, 9127.