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Electron-Transfer Reactions: AM1 and *ab Initio* Studies on Self-Exchange in *p*-Diaminobenzene Systems

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Abstract: AM1 and HF/6-31G* molecular orbital calculations have been used to investigate the electron self-exchange reactions between a series of substituted 1,4-diaminobenzenes and their radical cations. Comparisons with known experimental data and the results of the *ab initio* calculations suggest that AM1 performs well for this problem. The internal reorganization energy, λ_i, has been estimated from the differences between the vertical and adiabatic ionization potentials of the neutral compounds and the corresponding electron affinities of the radical cations and is found to be significantly larger than previous estimates. Direct CI calculations of λ for the radical cation/neutral molecule complex reveal that stabilization of the ground state (complexation) and the corresponding destabilization of the first excited state increase λ further. There is, however, a large zero-point energy contribution that lowers the classical electron-transfer activation energy significantly. The calculated thermodynamics of the classical activation process are in good agreement with experiment.

Electron-transfer reactions are being increasingly recognized as integral components of many organic reaction mechanisms. There are, however, many indications[1] that organic electron transfer differs significantly from its inorganic counterparts. Classical Marcus theory[2–5] has often been applied to inorganic systems with success,[6,7] but many of its basic assumptions may not be valid for closely coupled organic electron-transfer reactions.[1,8–11] It is, for instance, becoming increasingly clear that inner reorganization energy, λ_i, is the major contributor to the activation energy for electron transfer in some organic systems.[12,13] Molecular orbital calculations, which have been used sparingly for inorganic[7,14–16] and organic[8,17–19] systems, are in principle capable of providing reliable values for many of the principal variables necessary to obtain the electron-transfer rate constant from Marcus theory. Most applications of MO theory have concentrated on the electronic matrix coupling element, V_{12} (often called V_{AB}, H_{12}, ...),[7,14–16,17a] or on the inner reorganization energy, λ_i.[12a,20]

The present study has two principal objectives: to assess the reliability of standard AM1 semiempirical MO theory[21] for organic electron-transfer reactions and to investigate a reaction system that is far from the loosely coupled outer sphere systems for which Marcus theory is best suited.

The systems investigated are the ($Ar{:}Ar^{\bullet+} \rightarrow Ar{:}^{\bullet+}{:}Ar]^{\ddagger} \rightarrow Ar^{\bullet+}{:}Ar$) self-exchange reactions, where Ar symbolizes the arenes 1,4-diaminobenzene (**1**), 1-amino-4-(dimethylamino)benzene (**2**), 1,4-bis(dimethylamino)benzene (**3**), and 1,4-diamino-2,3,5,6-tetramethylbenzene (**4**). These systems have been investigated extensively in solution,[12,13,22,23] so that they present many opportunities to compare calculated data with the corresponding values derived from Marcus-theory-based interpretations of experimental data. We have deliberately chosen to investigate the closely coupled reaction occurring within the relatively stable $Ar^{\bullet+}{:}Ar$ complexes in order to identify the major differences between such systems and classical loosely coupled electron transfer. Nelsen *et al.*[12] have previously investigated **3** using AM1, and Goez[20] has used AM1-calculated frequencies to estimate λ_i for **2** and **3**.

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Table I: AM1-Calculated and Experimental Molecular Data for **1–4**

system	ΔH_f^{calc} (kcal/mol)	ΔH_f^{exp} (kcal/mol)	IP_{vert}^{calc} (eV)	IP_{adiab}^{calc}	$IP^{exp\ a}$ (eV)	$\nu_{\pi\to\pi^*}^{calc}$(nm)	$\nu_{\pi\to\pi^*}^{exp}$ (nm)	ZPE (kcal/mol)
1	19.99	25.5	7.64	6.53	7.51	311.8	314.9	86.19
2	30.14		7.64	6.87	7.10	319.4	315.9	121.15
3	40.49		7.63	6.75	6.80	323.9	322.6	156.13
4	−1.01		7.34	6.75	7.00	434.2	454.6	157.52
$1^{+\bullet}$	181.4							
$2^{+\bullet}$	188.5							
$3^{+\bullet}$	196.1							
$4^{+\bullet}$	154.6							

[a] Taken from ref 17.

Table II: HF and MP2 Total Energies (au), Zero-Point Energies (kcal mol^{-1}), and Ionization Potentials (eV)

		energy			IP		
species	PG[a]	HF	MP2	ZPE	HF	MP2	IP^{exp}
1	C_{2h}	−340.754 53	−341.838 12	89.9	5.43	6.23	7.51
	C_{2v}	−340.754 32	−341.837 88	90.0	5.42	6.23	7.51
$1^{+\bullet}$	D_{2h}	−340.555 07	−341.609 27	90.5			

[a] Molecular point group.

Methods

All AM1 calculations used the VAMP program (version 4.4),[24] which is similar to the QCPE programs MOPAC[25] and AMPAC[26] but contains an extended CI section, a modified version of Baker's eigenvector following (EF) geometry optimizer,[27] and has been extensively modified to take advantage of vector computer architecture. The calculations were carried out on a Convex C220/256 and a Cray YMP-432.

All AM1 geometries were optimized until the gradient norm was less than 0.4 kcal Å^{-1}. Gradients were calculated by standard finite difference techniques, where necessary using full SCF calculations at every geometry. Standard AM1 parameters were used throughout. The neutral structures **1–4** were calculated at the RHF level. The half-electron formalism of Dewar *et al.*[28] was used for radical cations **1a–4c**. The reference wave function for the transition states **1c–4c** used three electrons distributed evenly over the highest two MOs (i.e. 1.5 electrons per orbital). Unrestricted Hartree–Fock (UHF) theory proved to be unsuitable for the transition-state calculations because the wave function did not reflect the full symmetry of the molecular structure. UHF was used for the *ab initio* calculations on these transition states, but in this case the wave function was forced to remain symmetrical. This also led to considerable SCF-convergence problems that were less severe in half-electron calculations. Convergence was often obtained using Pulay's DIIS technique.[29] Our present semiempirical program cannot restrict the symmetry of UHF wave functions, but as the half-electron wave function remains symmetrical, the latter method was used.

The energetic difference between the ground state and the first excited state ($2 \times V_{12}$) and the vertical $\pi \to \pi^*$ excitations of the UV spectra were calculated on the RHF-optimized structures using configuration interaction. The CI expansion[30] used includes all possible single and double excitations of seven electrons in eight MOs (CISD = 8, i.e. 338 configurations). This gives reliable vertical excitation energies for many organic systems.[31]

Ab initio calculations used the Convex and Cray versions of Gaussian 90.[32] All calculations used the 6-31G*[33] basis set. Optimizations were carried out using restricted (RHF) and unrestricted Hartree–Fock (UHF) theory for closed- and open-shell systems, respectively. Single-point calculations on the Hartree–Fock geometries included a second-order Møller–Plesset correction (MP2)[34] for electron correlation within the frozen core approximation. Energies quoted are the projected MP2[35] values for open-shell species. All calculations used direct-SCF and post-SCF techniques.

Results

Ground-State Monomers. The AM1-calculated energetic and electron data for **1–4** are shown in Table I, and the *ab initio* data, in Table II. As expected for C,H,N-containing molecules, the calculated AM1 structures (shown in Chart I) are in good agreement with experimental (X-ray) data.[36] The most significant differences between the neutral structure and the corresponding radical cation are the decrease in the C–N bond length and the change of the nitrogen atom from an sp^3 to an sp^2 geometry, both of which are expected from a quinonoid deformation on oxidation (Chart II). The RHF/6-31G*-optimized structures for C_{2h} (*anti*) and C_{2v} (*syn*) **1** have identical heavy-atom bond lengths. The agreement with the apparently *anti* structure found in the X-ray analysis of the crystal structure is excellent.

Table II shows the calculated HF and MP2 energies for **1** and $\mathbf{1}^{\bullet+}$. The latter shows far stronger quinonoid deformations at 6-31G* than with AM1. The two alternative structures for **1** have essentially the same energies. The C_{2h} isomer is preferred by 0.13 kcal mol^{-1} at RHF/6-31G* and 0.15 kcal mol^{-1} at RMP2/6-31G*.

The experimental heat of formation of **1** has been determined for the crystalline phase, but the heat of sublimation has not been determined. Bondi's incremental method[37] gives a heat of sublimation of 22.4 kcal mol^{-1}, yielding a gas-phase heat of formation of 25.5 kcal mol^{-1}, in fair agreement with the AM1-calculated value (19.99 kcal mol^{-1}). Table I also shows the calculated and experimental ionization potentials of **1–4**. The differences between the two values are small (0.13 and 0.33 eV) for the compounds without *N*-methyl groups, but increase by about 0.2 eV per NCH_3 for compounds **2** and **3**. These results

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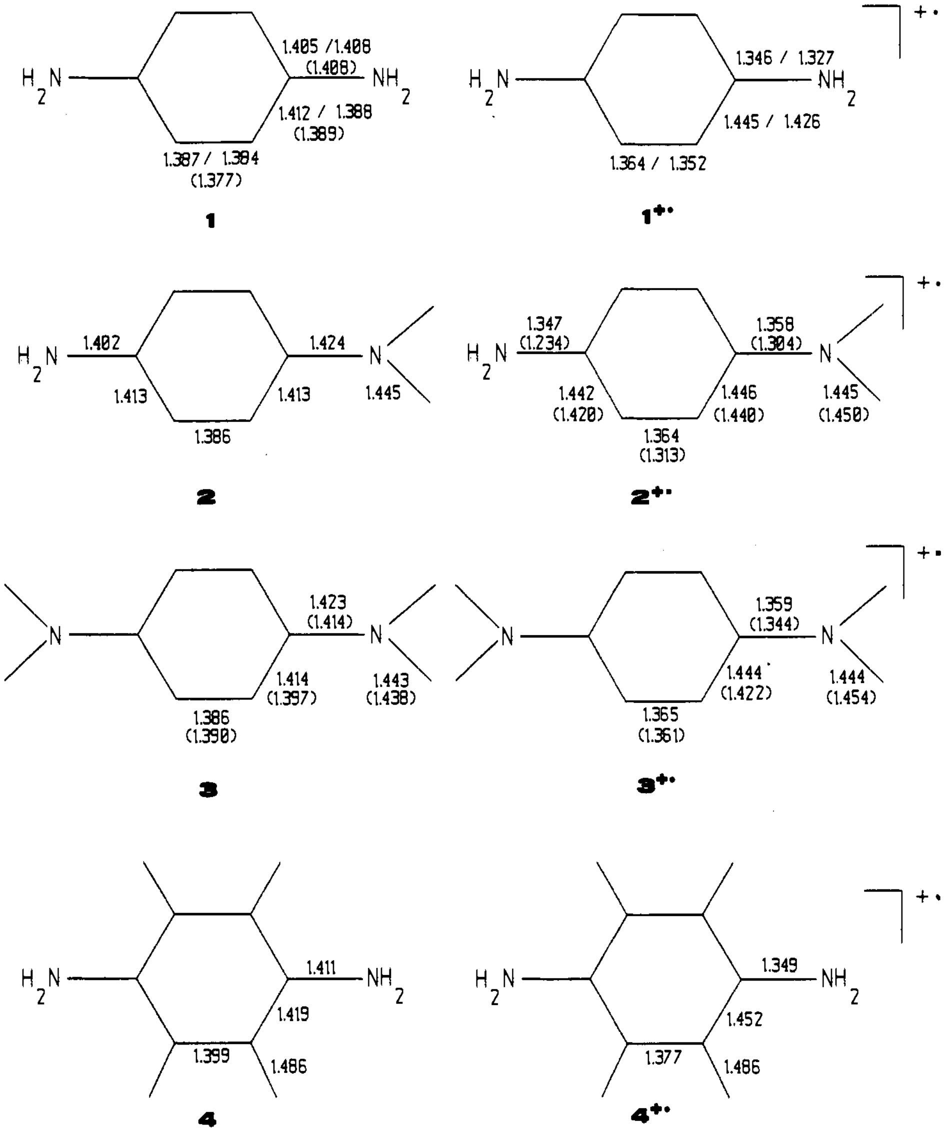
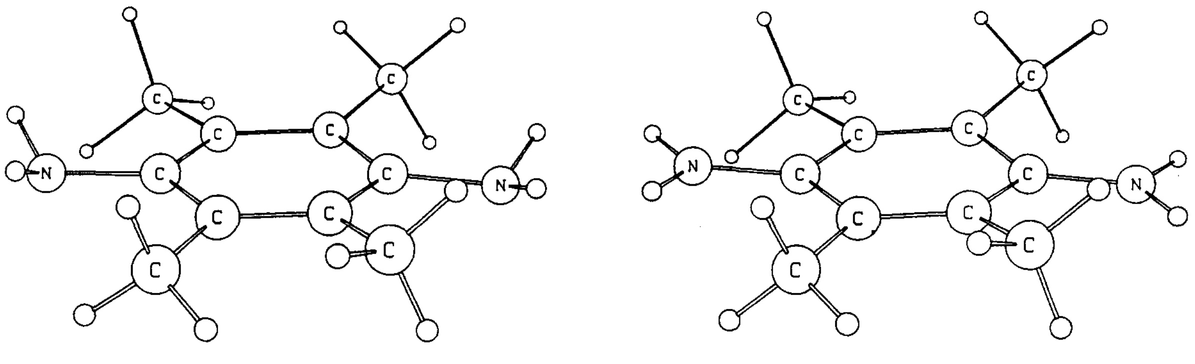
Chart I: Structures of **1**–**4**$^{•+a}$



1 **1**$^{+•}$ **2** **2**$^{+•}$ **3** **3**$^{+•}$ **4** **4**$^{+•}$

[a] Calculated (left, AM1; right, 6-31G*) and experimental (X-ray in parentheses)[29] bond lengths in angstroms.

Chart II: Structures of **4** and **4**$^{•+}$



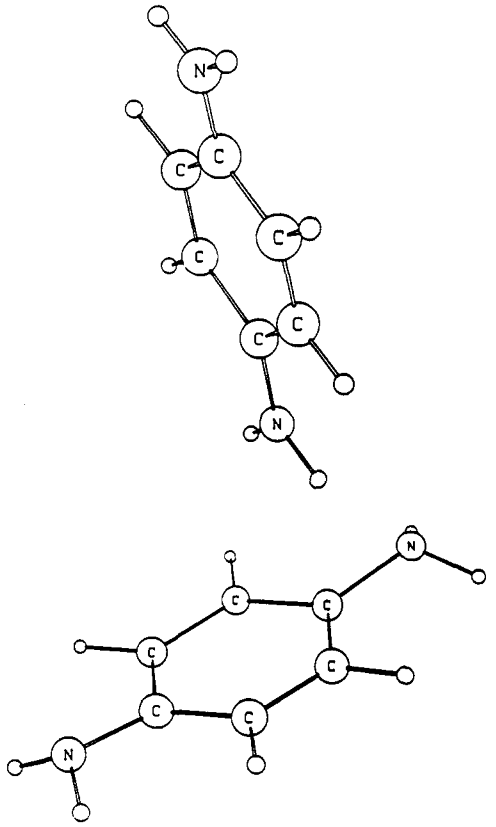
4 **4**$^{+•}$

reflect the known weakness of AM1 in reproducing alkyl group stabilization of cationic centers. The MP2/6-31G*-calculated ionization potential for **1** (Table II) shows a far larger error than the AM1 value (Table I).

The AM1-calculated vertical $\pi \rightarrow \pi^*$ excitation energies show excellent agreement with experiment for **1**–**3**, confirming the good performance of the CI expansion used. The above results led us to conclude that AM1 is capable of describing the basic electronic characteristics of these *p*-diaminobenzene systems well. The only major weakness lies in the treatment of NCH_3 groups, but this has no effect on system **1**, which will be discussed in most detail.

Ground-State Complexes. Two types of structures for the complexes between the neutral molecules and their radical cations were found. The T-shaped structures **1a**–**2a** (Chart III) are actually the most stable dimeric radical cation isomers found for **1** and **2**. Although the reorganization energy calculated (AM1/

Chart III: T-Shaped Ground State of **1a**



1a

CI) for these complexes is similar to those for **1b**–**4b** (see below), electron transfer in these species involves very extensive molecular movement (the neutral molecule and the cation swap positions). We have therefore restricted our studies to the layered complexes **1b**–**4b**, which have symmetrically equivalent diaminobenzene moieties in the electron-transfer transition states (Chart IV).

Complexes **1b**–**4b**, which lie *ca.* 2.5 kcal mol^{-1} higher in energy than **1a**–**4a** in the gas phase, are well suited for degenerate electron self-exchange. Their energies are summarized in Table III; their geometries, in Table IV. The distances between ring centers vary between 3.67 and 4.19 Å, but there is little apparent correlation between the substitution pattern and the inter-ring distances, which are in any case very soft parameters. Fritz *et al.*[38] found an inter-ring distance of 3.2 Å in the hexafluorophosphate of the bis(naphthalene) radical anion. This distance is significantly shorter than those found here, although we expect the amino groups to lengthen the inter-ring distance in our systems.

The two molecules in the complexes **1b**–**4b** show the typical geometrical characteristics of discrete neutral and radical cation fragments, as shown in Table IV. The Coulson charge distributions (shown in Table VI) also reflect the neutral/cation nature of these complexes.

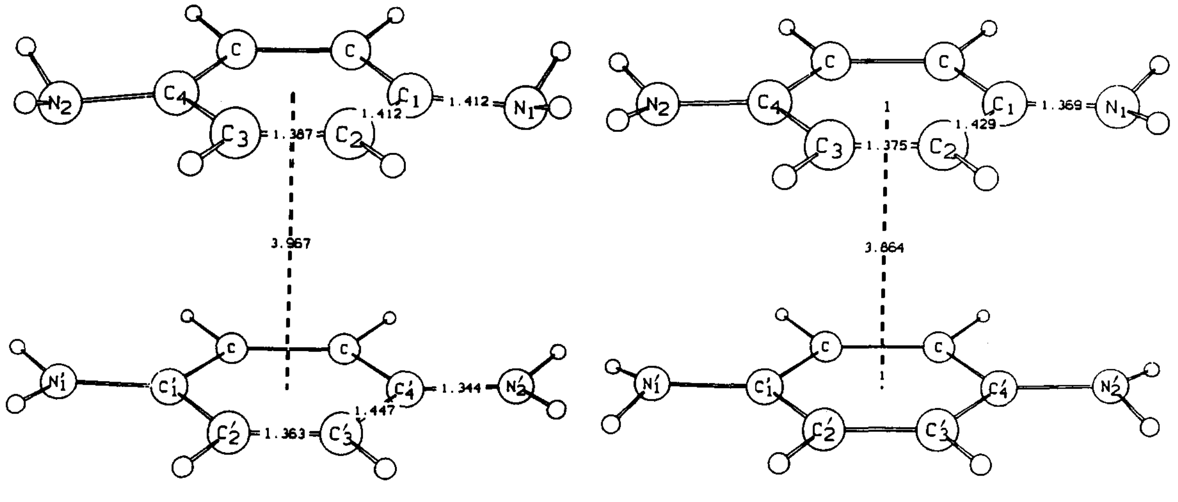
The complexation energies decrease monotonically with higher substitution of the amino groups. Remarkable is the high complexation energy of **4b** (Chart V), which can be explained by the boat conformation of this structure. In contrast to **1b**–**3b**, in this structure the positive charge of the complex is centered at the exposed amino groups. The majority of the binding energy seems to involve N–N odd-electron bonding, which is most effective for unsubstituted amino groups. The boat-like deformations of **4** and $\mathbf{4}^{\bullet+}$ favor this type of interaction. Such distortions have been noted by Siegel *et al.*[39] and Nelsen and Wolff[40] for 1,3,5-tris(dialkylamino)-2,4,6-trinitrobenzenes. Such deformations, which Siegel has attributed to the effect of a combination of steric repulsions and strong push–pull conjugation, allow close approach (3.1 Å) of the nitrogens at longer (3.7 Å) ring–ring distances (Chart V).

We have also optimized **1b** at UHF/6-31G* and find the structure given in Table V. The geometries of the individual molecules resemble those of the monomers closely. The ring–ring distance at 3.89 Å, in excellent agreement with the AM1-calculated value of 3.97 Å. The UHF/6-31G* complexation energy is calculated to be −8.6 kcal mol^{-1}, compared with the AM1 value of −7.1 kcal mol^{-1}. Once again, these results suggest that AM1 is well suited for this problem.

Transition States and Classical Activation Energies. For all systems except **4** the ring–ring distance decreases by *ca.* 0.1 Å between the ground-state complex and the transition state. Although these trends are consistent, they have little energetic significance because the potential energy hypersurface is so flat. The ring-methylated compound **4** behaves completely differently, probably because of the unusual bonding in **4b** (see above). The calculated inter-ring distances (measured between the ring centers) for the transition states are all smaller than those derived from experimental data by Grampp *et al.* These experimentally derived values rely, however, on a number of approximations and should not be considered to be more than estimated values.

Table IV shows the most important geometrical parameters for the aromatic moieties in the complexes and the transition states. The changes in charge distribution are shown as selected

Chart IV: Ground State **1b** and Transition States **1c** of the Electron-Transfer Complex



1b **1c**

Table III: Calculated Energies (kcal mol^{-1}) and Ring–Ring Distances (Å) for Complexes **1b–4c**

system	NIMAG[a]	PG[b]	ΔH_f	R_{calc}[c]	R_{exp}[c,d]	ΔH_{pix}[e]	$\Delta H^{\ddagger}_{calc}$	$\Delta H^{\ddagger}_{exp}$	V_{12}
1b	0	C_{2v}	194.28	3.97		−7.14			
1c	1	D_{2h}	204.99	3.87	4.6		10.71	3.13	1.65
2b	0	C_1	212.85	4.19		−5.78			
2c	1	C_2	223.23	4.12	5.1		10.38	2.94	0.44
3b	0	C_2	231.70	4.13		−4.84			
3c	?[f]	D_2	241.53	4.07	6.8		9.83	2.77	0.50
4b	0	C_2	145.32	3.67		−8.27			
4c	1	D_2	158.36	4.10	5.1		13.04	2.63	1.05

[a] Number of imaginary normal vibrations. [b] Molecular point group. [c] Ring-center to ring-center distance. [d] G. Grampp, private communication. [e] Heat of complexation. [f] The numerical second-derivative calculation actually gives two negative eigenvalues for this structure. This is, however, caused by state-switching during the finite step calculations. We assume that **3c** is the correct transition state by analogy with the other systems.

Table IV: Selected Geometrical Parameters (AM1) of **1b–4c** (Å and deg)

parameter	**1b**	**1c**	**2b**	**2c**	**3b**	**3c**	**4b**	**4c**
				Bond Lengths				
C_1N_1	1.412	1.369	1.420	1.378	1.420	1.379	1.415	1.373
$C_1'N_1'$	1.344	1.369	1.357	1.378	1.358	1.379	1.348	1.373
C_4N_2	1.412	1.369	1.411	1.374	1.420	1.379	1.415	1.373
$C_4'N_2'$	1.344	1.369	1.347	1.374	1.358	1.379	1.348	1.373
C_1C_2	1.412	1.429	1.413	1.431	1.413	1.429	1.418	1.435
$C_1'C_2'$	1.447	1.429	1.446	1.431	1.444	1.429	1.453	1.435
C_4C_4	1.412	1.429	1.410	1.426	1.413	1.429	1.420	1.435
$C_3'C_4'$	1.447	1.429	1.442	1.426	1.444	1.429	1.453	1.435
C_2C_3	1.389	1.376	1.388	1.376	1.389	1.377	1.401	1.389
$C_2'C_3'$	1.363	1.376	1.364	1.376	1.364	1.377	1.375	1.389
				Bond Angles				
$N_1C_1R_p$[a,b]	6.219	1.339	5.090	0.126	5.140	0.402	7.677	3.175
$N_1'C_1'R_p'$	−2.174	−1.339	−0.798	−0.120	−0.336	−0.402	−17.433	−3.175
$N_2C_4R_p$	6.219	1.339	4.837	1.835	5.140	0.402	7.677	3.175
$N_2'C_4'R_p'$	−2.174	−1.339	−0.594	−1.835	−0.336	−0.402	−17.433	−3.175
				Dihedral Angles				
S[b,c]$N_1C_1C_2$	150.34	167.25	156.90	176.95	158.36	176.96	142.29	169.73
$S'N_1'C_1'C_2'$	−175.18	−167.25	−175.46	−176.95	−176.94	−176.96	−171.21	−169.72
$SN_2C_4C_3$	150.34	167.25	150.46	163.41	158.36	176.96	158.12	162.53
$S'N_2'C_4'C_3'$	−175.18	−167.25	−176.10	−163.41	−176.94	−176.96	−171.68	−162.53

[a] R_p symbolizes the ring plane. [b] The sign of the angle indicates the direction relative to the ring plane. [c] S symbolizes the atom next to the nitrogen atom, H for **1b,c**, **2b,c**, and **4b,c** and C for **2b,c** and **3b,c** (Chart I).

Table V: Selected Geometrical Parameters (6-31G*) of **1b** and **1c** (Å and deg)

parameter	**1b**	**1c**	parameter	**1b**	**1c**
Bond Lengths			Bond Angles		
C_1N_1	1.411	1.360	$N_1C_1R_p$[a,b]	2.995	0.298
$C_1'N_1'$	1.328	1.360	$N_1'C_1'R_p'$	−1.586	−0.298
C_4N_2	1.411	1.360	$N_2C_4R_p$	2.995	0.298
$C_4'N_2'$	1.328	1.360	$N_2'C_4'R_p'$	−1.586	−0.298
C_1C_2	1.390	1.409			
$C_1'C_2'$	1.425	1.409	Dihedral Angles		
C_3C_4	1.390	1.409	H[b]$N_1C_1C_2$	151.40	163.96
$C_3'C_4'$	1.425	1.409	$H'N_1'C_1'C_2'$	188.04	−163.96
C_2C_3	1.384	1.367	$HN_2C_4C_3$	151.40	163.96
$C_2'C_3'$	1.350	1.367	$H'N_2'C_4'C_{3'}$	188.04	−163.96
			ring–ring	3.890	3.577

[a] R_p symbolizes the ring plane. [b] The sign of the angle indicates the direction relative to the ring plane.

net atomic charges in Table VI. The trends in the calculated classical activation energies of the electron-transfer reactions of the unsymmetrical $Ar:Ar^{\bullet +}$ complexes **1b–3b** agree well with experiment (Table III), although the calculated values are all much larger than the experimental enthalpies of activation.

The UHF/6-31G* structure for the transition state **1c**, shown in Table V, has a ring–ring distance of 3.58 Å, 0.31 Å shorter than in the complex **1b**. The *ab initio* results therefore confirm the shortening of this distance between the minimum and the transition state. The UHF/6-31G* activation energy, 15.1 kcal mol^{-1}, is even higher than that (10.7 kcal mol^{-1}) given by AM1. Note that UMP2 cannot be applied to **1c** because the UHF wave function is not stable toward symmetry lowering.

We note here that we also located AM1 electron-transfer transition states with C_{2h} symmetry for **1** and **2**. In these structures, the two rings are translated by about 2.4 Å relative to each other. These structures are, however, less stable than the transition states **1c** and **2c** and represent extremely shallow saddle points that are probably an artifact of the AM1/half-electron method. We have not considered them further.

The Nature of the Hypersurface. Both complexes **1b–4b** and the transition states **1c–4c** have very flat potential energy hypersurfaces for the degrees of freedom governing the relative positions of the two molecules. This is demonstrated for **1c** in the contour diagram shown in Figure 1. If we assume an arbitrary energy limit of 0.5 kcal mol^{-1} for energetically accessible structures (RT = 0.58 kcal mol^{-1} at 293 K), the limits for the inter-ring distances are 3.55 and 4.95 Å in the parallel (Θ = 180°) orientation and 4.0 and 4.38 Å in the less favorable perpendicular (Θ = 90°) orientation. Calculated zero-point energies (ZPEs) also remain constant within these ranges. Grampp *et al.*'s experimentally derived value lies at the high end of this range. It is, however, clear that electron transfer can occur at a very large range of intermolecular structures.

Discussion

The Internal Reorganization Energy, λ_i. The reorganization energy, λ, is split into inner (λ_i) and outer (λ_o) components for *weakly coupled systems* in Marcus theory.[5] Weakly coupled in this context refers to the interaction between the reactants. Our system therefore corresponds to the Marcus "inner" reorganization

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Table VI: Selected AM1 Coulson Net Atomic Charges of **1b**–**4c**

atom	1b	1c	2b	2c	3b	3c	4b	4c
N_1	–0.315	–0.322	–0.241	–0.222	–0.249	–0.233	–0.324	–0.325
N_1'	–0.251	–0.322	–0.138	–0.222	–0.159	–0.233	–0.250	–0.325
N_2	–0.315	–0.322	–0.314	–0.322	–0.249	–0.233	–0.324	–0.325
N_2'	–0.251	–0.322	–0.265	–0.322	–0.159	–0.233	–0.250	–0.325
C_1	–0.008	0.092	0.017	0.087	0.007	0.086	–0.008	0.100
C_1'	0.144	0.092	0.105	0.087	0.104	0.086	0.150	0.100
C_4	–0.008	0.092	–0.008	0.083	0.007	0.086	–0.008	0.100
C_4'	0.144	0.092	0.149	0.083	0.104	0.086	0.150	0.100
C_2	–0.151	–0.146	–0.150	–0.141	–0.154	–0.144	–0.085	–0.086
C_2'	–0.130	–0.146	–0.115	–0.141	–0.133	–0.146	–0.074	–0.084
C_3	–0.151	–0.146	–0.155	–0.150	–0.153	–0.144	–0.087	–0.086
C_3'	–0.130	–0.146	–0.143	–0.150	–0.136	–0.146	–0.080	–0.084

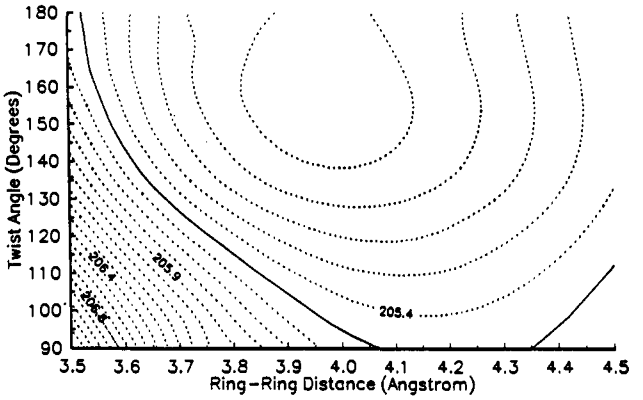
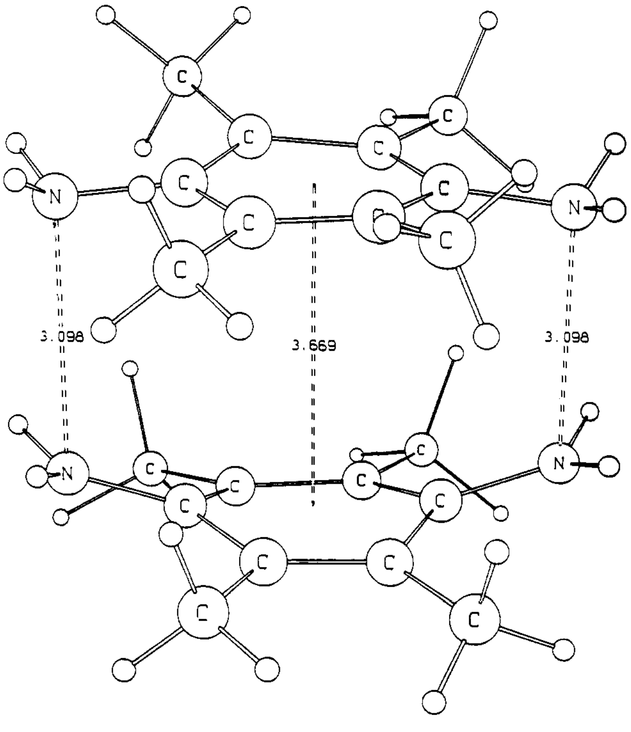


Figure 1. Heat of formation contour map of the D_2 hypersurface of **1**.

Chart V: AM1-Optimized Structure of **4b**



4b

model. The complexes calculated here are clearly strongly coupled, so that the traditional definitions of λ_i and λ_o do not apply. Nevertheless, the differences between the behavior predicted for a loosely coupled system and our relatively tight complexes are important, and so we will first consider the magnitude of λ_i, the internal reorganization energy for noncoupled systems.

Both Nelsen *et al.*[12] and Grampp *et al.*[13] have suggested consistently that λ_i is significantly larger for organic electron-transfer reactions than has commonly been assumed. Unfortunately, direct AM1 calculations of λ_i for 1,4-bis(dimethylamino)benzene (**3**) and its radical cation contained an error,[12] so that the published values are far too low. Goez[20] estimated λ_i for **2** and **3** to be 3.8 and 4.4 kcal mol^{-1}, respectively. We find these values to be far too low. Our calculated λ_i values are extremely large, but cannot be grossly in error because all the calculational methods used yield similar results. It is extremely unlikely that AM1, UHF/6-31G*, and UMP2/6-31G* all give an order of magnitude error.

Table VII: Calculated ΔH_i and ΔE_i Values According to Eqs 1 and 2 (kcal mol^{-1})

system	ΔH_i AM1	ΔE_i UHF/6-31G*	UMP2/6-31G*
1	22.7	31.3	26.9
2	25.6		
3	27.7		
4	22.5		

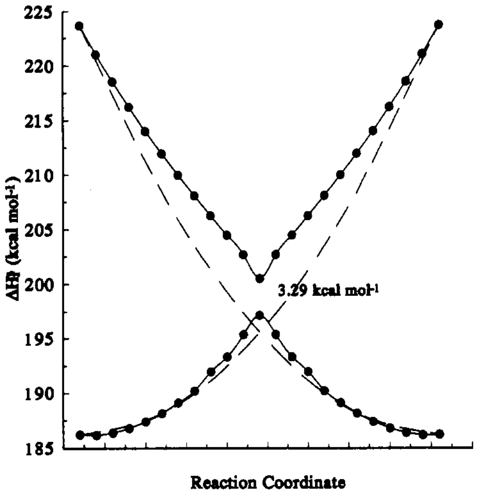


Figure 2. State energy level diagram for **1b** and **1c**. The values have been determined via a linear synchronous transit calculation.

The enthalpic component of λ_i, ΔH_i, can be calculated using the nomenclature introduced by Nelsen[12] as

$$\Delta H_i = [\Delta H_f^\circ(c^\circ) - \Delta H_f^\circ(n^\circ)] + [\Delta H_f^\circ(n^+) - \Delta H_f^\circ(c^+)] \quad (1)$$

for the AM1 results or, using total energies for the *ab initio* methods,

$$\Delta E_i = [E(c^\circ) - E(n^\circ)] + [E(n^+) - E(c^+)] \quad (2)$$

where (c) and (n) indicate the geometry (that of the cation or neutral species, respectively) and the superscripts (°) and (+) indicate the charge on the species calculated.[12] Table VII shows the results obtained. The "least reliable" calculational method (AM1) yields the lowest ΔH_i value for **1**, but the agreement between AM1 and MP2/6-31G* is good, so that we conclude that ΔH_i (or ΔE_i) for **1**/**1**$^{\bullet+}$ is about 23–27 kcal mol^{-1}. If λ_i is

Table VIII Correlation between the Normal Vibrations of **1b** and **1c**

Irreducible Representations

1b (C_{2v})		**1c** (D_{2h})	**1b** (C_{2v})		**1c** (D_{2h})
a_1	→	a_g, b_{2u}	b_1	→	b_{3g}, b_{1u}
a_2	→	a_u, b_{2g}	b_2	→	b_{3u}, b_{1g}

Normal Vibrations

1b (C_{2v})	cm^{-1}	**1c** (D_{2h})	cm^{-1}	shift (cm^{-1})[a]	**1b** (C_{2v})	cm^{-1}	**1c** (D_{2h})	cm^{-1}	shift (cm^{-1})[a]
1 b_2	30.3	1 b_{3u}	26.9	−3.4	9 b_1	1093.4	5 b_{3g}	1109.0	+15.6
2 b_2	35.1	1 b_{1g}	29.0	−6.1	12 a_2	1133.7	7 a_u	1153.2	+19.5
1 a_1	42.3	1 a_g	33.5	−8.8	14 b_2	1141.0	7 b_{1g}	1117.1	−23.9
1 a_2	50.7	1 a_u	22.8	−27.9	10 b_1	1145.2	5 b_{1u}	1109.0	−36.2
1 b_1	54.2	1 b_{3g}	29.9	−24.3	13 a_2	1222.6	6 b_{2g}	1154.0	−68.6
2 b_1	68.8	1 b_{1u}	60.3	−8.5	11 b_1	1232.6	6 b_{3g}	1232.7	+0.1
2 a_1	104.4	2 b_{2u}	113.5	+9.1	12 b_1	1251.2	6 b_{1u}	1233.0	−18.2
3 a_1	139.3	2 a_g	120.6	−18.7	14 a_1	1272.8	7 b_{2u}	1219.7	−53.1
3 b_2	278.7	2 b_{1g}	257.8	−20.9	15 a_1	1277.4	8 a_g	1273.1	−4.3
2 a_2	287.2	2 a_u	348.9	+61.7	14 a_2	1354.4	8 a_u	1355.8	+1.4
3 b_1	291.8	2 b_{3g}	381.7	+89.9	15 a_2	1364.3	7 b_{2g}	1356.7	−8.1
4 b_2	344.4	2 b_{3u}	309.7	−34.7	13 b_1	1385.4	7 b_{3g}	1476.5	+91.1
3 a_2	348.5	1 b_{2g}	355.7	+7.2	15 b_2	1392.6	8 b_{1g}	1410.1	+17.5
4 a_2	376.9	3 a_u	421.3	+44.4	16 b_2	1404.7	8 b_{1g}	1410.2	+5.5
4 b_1	380.6	2 b_{1u}	382.0	+1.4	14 b_1	1504.0	7 b_{1u}	1473.6	−30.4
5 b_1	387.7	3 b_{3g}	404.4	+16.7	16 a_2	1589.6	8 b_{2g}	1657.9	+68.3
4 a_1	491.4	3 a_g	481.1	−10.3	15 b_1	1592.8	8 b_{1u}	1614.1	+21.3
6 b_1	495.9	2 b_{1u}	420.5	−75.4	16 a_1	1634.3	8 b_{2u}	1293.5	−340.8*
5 a_2	498.9	2 b_{2g}	430.9	−68.0	16 b_1	1679.4	8 b_{1u}	1614.5	−64.9
6 a_2	503.6	4 a_u	499.0	−4.6	17 a_1	1680.8	9 a_g	1660.9	−19.9
5 a_1	515.4	3 b_{2u}	491.3	−24.1	17 b_2	1682.3	8 b_{3u}	1687.7	+5.4
7 a_2	516.7	4 a_g	499.2	−17.5	18 b_2	1684.4	9 b_{1g}	1683.4	−1.0
6 a_1	543.8	4 a_g	508.2	−35.6	19 b_2	1741.1	9 b_{3u}	1661.1	−80.0
7 a_1	557.4	4 b_{2u}	518.4	−39.0	17 a_2	1745.0	9 a_u	1659.6	−85.4
5 b_2	607.7	3 b_{1g}	323.7	−284.0*	18 a_1	1773.4	9 b_{2u}	1669.1	−104.3
8 a_1	628.3	1 b_{2u}	−1052.0	−628.3**	20 b_2	1780.5	10 b_{1g}	1738.3	−42.2
8 a_2	667.2	5 a_u	674.9	+7.7	19 a_1	1822.1	11 a_g	1809.8	−12.3
6 b_2	676.5	3 b_{3u}	465.9	−210.6*	20 a_1	1862.9	10 b_{2u}	1736.1	−126.8*
9 a_2	684.0	4 b_{2g}	675.2	−8.8	21 a_1	1885.4	10 a_g	1736.6	−148.8*
7 b_2	710.8	4 b_{3u}	688.7	−22.1	18 a_2	3144.5	10 a_u	3161.7	+17.2
8 b_2	839.9	4 b_{1g}	689.6	−150.3*	21 b_2	3149.8	11 b_{1g}	3164.9	+15.1
7 b_1	856.3	4 b_{3g}	858.5	+2.2	17 b_1	3152.1	9 b_{3g}	3171.7	+19.6
9 b_2	868.0	5 b_{3u}	873.6	+5.6	19 a_2	3173.8	9 b_{3g}	3162.0	−11.8
8 b_1	883.1	4 b_{1u}	865.4	−17.7	22 b_2	3175.4	11 b_{3u}	3165.1	−10.3
9 a_1	894.6	5 b_{2u}	851.9	−42.7	22 a_1	3176.5	11 b_{2u}	3058.8	−117.7
10 a_1	909.4	5 a_g	542.9	−366.5*	18 b_1	3181.5	9 b_{1u}	3172.1	−9.4
10 b_2	921.4	5 b_{1g}	873.7	−47.7	23 a_1	3221.3	12 a_g	3177.7	−43.6
11 b_2	979.7	6 b_{3u}	974.1	−5.6	20 a_2	3416.4	11 a_u	3486.9	+70.5
10 a_2	980.1	6 a_u	972.9	−7.2	19 b_1	3416.5	10 b_{3g}	3486.1	+69.6
11 a_2	983.2	5 b_{2g}	975.0	−8.2	20 b_1	3438.3	10 b_{1u}	3487.1	+48.8
11 a_1	988.3	6 a_g	886.4	−101.9	21 a_2	3449.3	10 b_{2g}	3488.1	+38.8
12 b_2	993.2	6 b_{1g}	971.4	−21.8	23 b_2	3459.1	12 b_{1g}	3500.2	+41.1
12 a_1	1024.4	6 b_{2u}	995.5	−28.9	24 b_2	3459.9	12 b_{3u}	3501.8	+41.9
13 a_1	1063.5	7 a_g	1043.0	−20.5	24 a_1	3485.5	12 b_{2u}	3428.2	−57.3
13 b_2	1090.4	7 b_{3u}	1116.8	+26.4	25 a_1	3488.0	13 a_g	3508.5	+20.5
						total (hydrogen stretches)			+133.0

[a] (*)Vibrations with large shifts (shown in Figure 3). **The imaginary vibration in **1c**.

similar in magnitude, these results are inconsistent with the observed low activation energies in acetonitrile if the harmonic approximation is valid.[13] Note that the trends observed above in the complexation energies are reversed for ΔH_i (i.e. ΔH_i increases monotonically with higher substitution of the amino groups).

Reorganization Energies in Precursor Complexes, λ_{ic}. Because of the tight coupling in our calculated complexes, we define a quantity, λ_{ic}, that represents the reorganization energy (without any solvent contribution) within the precursor complexes. As shown below, this quantity differs considerably from λ_i in a manner that depends directly on the complexation energy. Figure 2 shows the AM1 CI-calculated state energy level diagram for a linear synchronous reaction path (LST)[41] for the self-exchange process in $\mathbf{1}/\mathbf{1}^{\bullet+}$. This curve reveals a further component of λ_{ic}. If we consider the complexation energy as a resonance energy between two hypothetical "no bond resonance" states, as appears reasonable from the behavior of odd-electron bonds[42],

$$\mathbf{1}\ \mathbf{1}^{\bullet+} \leftrightarrow \mathbf{1}^{\bullet+}\ \mathbf{1}$$

the ground state is stabilized by the complexation energy and *the first excited state is destabilized by about the same amount.* The resulting expression for the reorganization enthalpy in the complex, ΔH_{ic}, is

$$\Delta H_{ic} = [\Delta H_f^\circ(c^\circ) - \Delta H_f^\circ(n^\circ)] + [\Delta H_f^\circ(n^+) - \Delta H_f^\circ(c^+)] - 2\Delta H_{cplx} \quad (3)$$

where ΔH_{cplx} is the enthalpy of complexation:

$$\Delta H_{cplx} = \Delta H_f^\circ(\mathbf{1}{:}\mathbf{1}^{\bullet+}) - \Delta H_f^\circ(\mathbf{1}) - \Delta H_f^\circ(\mathbf{1}^{\bullet+}) \quad (4)$$

Equation 3 gives a calculated value of 36.7 kcal mol^{-1} for ΔH_{ic}, compared with the value of 42.7 kcal mol^{-1} given by the state-

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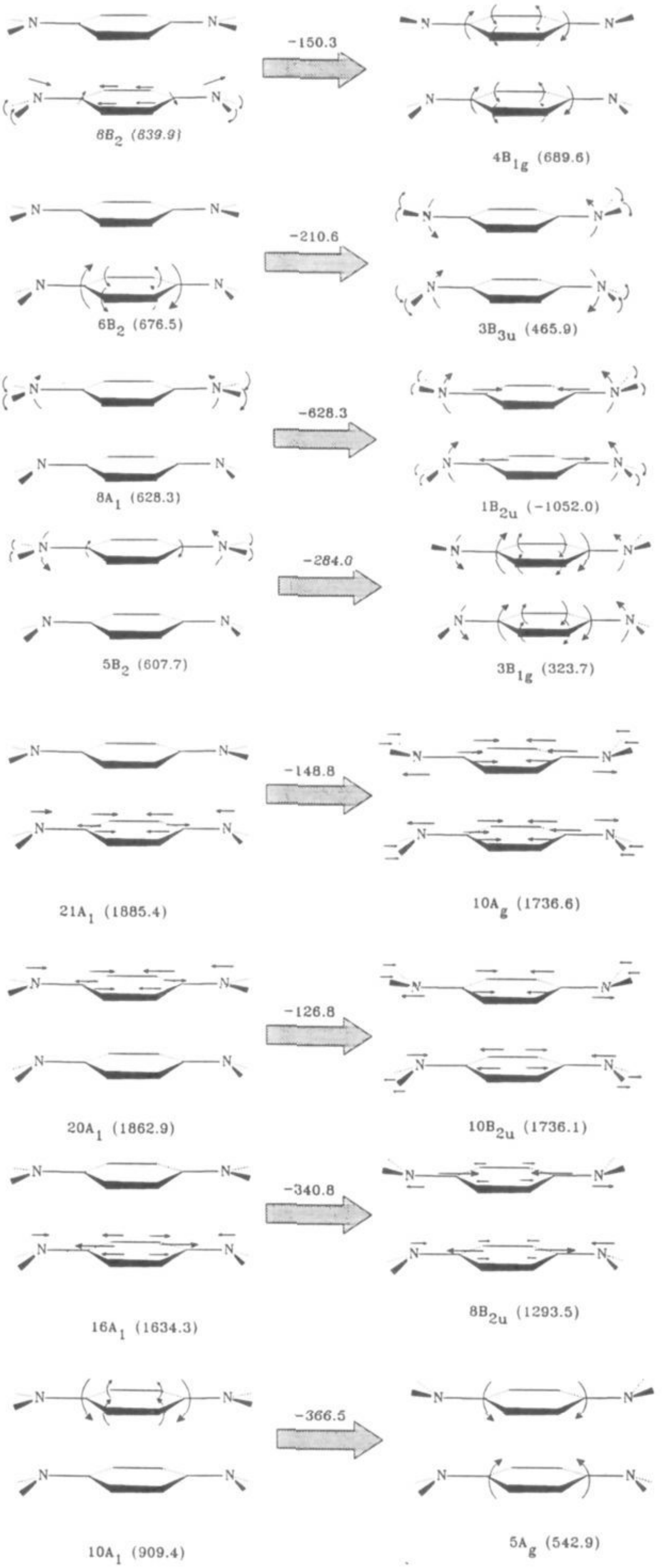

Figure 3. Correlated vibrations of **1b** and **1c** that are largely responsible for the change in the ZPE.

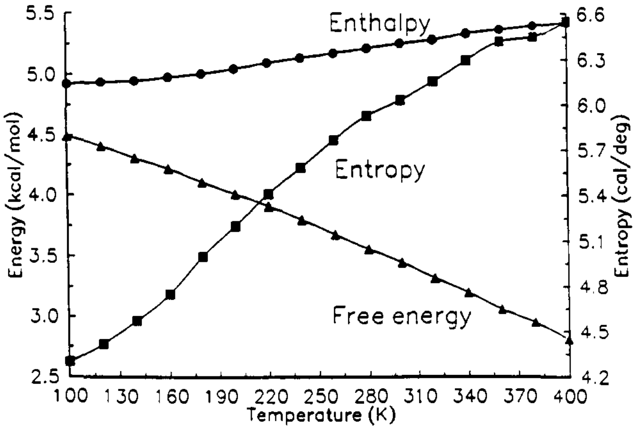

Figure 4. Thermodynamic activation parameters of **1c** as a function of temperature.

splitting using AM1/CI. Equation 3 therefore gives a realistic estimate of ΔH_{ic} as we have defined it. Note that traditional Marcus theory for bimolecular processes involves a work term to bring the molecules together to form the precursor complex.[43] This work term is clearly related to the complexation energy contribution to λ_{ic}. The above discussion (and eqs 3 and 4) assumes that ΔH_i remains constant in the complex. This assumption seems realistic when the very small geometrical changes between isolated reactants and the individual components of the complex are considered. Note that eq 3 predicts an increase in ΔH_{ic} with increasing complexation energy. If the harmonic approximation ($\Delta H^{\ddagger} = \Delta H_{ic}/4$) applies, this results in an increase in the classical activation energy of $\Delta H_{cplx}/2$ for the activation energy relative to the separated reactants. Note that these trends are opposite to what one might expect because the coupling in the complex is much stronger than that in the transition state.

The Classical Activation Energy. The parabolas assumed by Marcus theory (dotted curves) superimposed on Figure 2 deviate moderately from the calculated linear synchronous transit energies. The calculated activation energy (10.7 kcal mol^{-1}) is significantly larger than $\lambda_{ic}/4$ (9.4 kcal mol^{-1}), especially considering the large V_{12} value (1.7 kcal mol^{-1}). As discussed above, however, this value is too high to be reconciled with the experimental data. In an attempt to resolve this difference, we have calculated the zero-point vibration energies (ZPEs) for the minimum **1b** and the transistion state **1c**. Note that, although AM1-calculated energies are usually described as heats of formation (which contain the ZPE), they are based on total energy calculations on the hypothetical motionless state. It is therefore legitimate to correct the relative energies of isomers because the assumption of equal ZPEs for isomers is inherent in the parametrization.

The calculated (AM1) ZPEs for the minimum and transition state are 174.5 and 168.7 kcal mol^{-1}, respectively, so that the ZPE-corrected activation energy is only 4.91 kcal mol^{-1}, in far better agreement with experiment than the motionless value. A ZPE correction of this magnitude is unprecedented in our experience (it corresponds to the loss of a 4050-cm^{-1} vibration), and so we have correlated and analyzed the normal vibrations of **1b** and **1c**. The results are shown in Table VIII for all 90 vibrations and in Figure 3 for the eight vibrations (marked with asterisks in Table VIII) that are largely responsible for the change in ZPE. These vibrations are related to the quinonoid deformation of the ring, the pyramidalization of the nitrogens, and out-of-plane deformations of the ring. There is strong coupling between the latter two types of vibration, so that these vibrations all relate directly to the geometric variation associated with internal reorganization. Marcus theory assumes that the internal reorganization vibrational frequency, ν_n, is constant throughout the reaction. In our closely coupled system this is clearly not the case, so that we must correct the activation energy in the complex correspondingly:

$$\Delta H^{\ddagger}_{ic} = \frac{\lambda_{ic}}{4} - \sum_{n=1}^{3N-6} \frac{h\delta\nu_n}{2} - V_{12} \qquad (5)$$

where $\Delta\nu_n$ is the difference between the frequency of the n^{th} vibration in the precursor complex and the transition state.

Thermodynamics of the Classical Activation Process. The enthalpy and free energy of activation for the classical activation process for self-exchange in **1** can be calculated from the AM1 energies, geometries, and vibrational frequencies. The results are shown in Figure 4. Note that these data do not include any correction for heavy-atom tunneling or solvent effects. The enthalpy of activation increases slightly (from 4,92 and 5.53 kcal mol^{-1}) between 100 and 400 K. In this range, $\Delta S^{\ddagger}$ increases from 4.3 to 6.6 cal K^{-1}, so that $\Delta G^{\ddagger}$ decreases from 4.49 to 2.81 kcal mol^{-1}. The calculated values for $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$, and $\Delta S^{\ddagger}$ at 300 K are 5.26 and 3.45 kcal mol^{-1} and 6.0 cal K^{-1}, respectively. The thermodynamics calculated here apply to the activation process between the complex and the transistion state. They do not take the softness of both species into account, but should nevertheless provide an indication of the reliability of the calculations.

The Electronic Coupling Matrix Element. Within a two-state model, the splitting between the two electronic states at the transition state is equal to twice the matrix element coupling these two states, V_{12} (Table III). Rather than calculate V_{12} directly, we have calculated the state-splitting at the transistion state using AM1/CI. The magnitude of V_{12} determines whether the reaction proceeds adiabatically ($V_{12} \geq RT$) or nonadiabatically ($V_{12} \ll RT$).[5] The calculated values for V_{12} at the optimized transistion states (Table III) are smaller than RT (0.58 kcal mol^{-1}) for **2c** and **4c**, but larger for **1c** and **3c**. These values agree rather well with those of Grampp *et al.*, recalculated from experimental data. Grampp determined V_{12} for **1c**–**4c** as 0,10, 0.14, 0.11, and 0.14 kcal mol^{-1}. However, at longer distances V_{12} is considerably smaller. The experimentally determined V_{12} values and inter-ring distances are mutually compatible for an electron-transfer process occurring at larger distances than given by our model.

Conclusions

The present study underlines the usefulness of semiempirical calculations for studying electron-transfer reactions. The performance of AM1 for this problem shows no significant deviations from the known experimental data.

The calculated (AM1 and MP2/6-31G*) values for λ_i are larger than have been previously assumed, and the vertical excitation energy calculated for the precursor complexes is even higher. These values would be incompatible with the harmonic ($\lambda/4$) approximation of Marcus theory were it not for a very large (5.8 kcal mol^{-1}) lowering of the calculated barrier by the zero-point energy correction.

The calculated activation thermodynamics and magnitude of the electronic matrix coupling element V_{12} are in good agreement with values derived from experiment in solution.

Our calculations therefore suggest strongly that the inner reorganization energy is the major contributor to the activation energy in *p*-diaminobenzene electron-transfer reactions and that the close coupling found for the gas-phase reaction *increases* the barrier height from the precursor complex but *decreases* it from the separated reactants. Further studies are needed to confirm the major role played by changes in vibrational frequencies along the reaction path.

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