orbital relative to the cleaved $C_1$–$O_5$ bond found in the simulation is in accord with stereoelectronic requirements.[6,7]

In our proposed Scheme I, a role of the enzyme is to catalyze the reaction by means of orientational (entropic) contributions, instead of the distortional (enthalpic) stabilization assumed in the classic mechanism (Scheme II). In particular, the molecular dynamics simulation indicates that the exocyclic dihedral angle ($O_5$–$C_1$–$O_{4'}$–$C_{4'}$) oscillates in the neighborhood of the value required for optimum stereoelectronic assistance in Scheme I. Further, there is the possibility that interactions with the enzyme aid in maintaining the proper geometry for reclosing the ring in site D and are involved in the retention of configuration at $C_1$. The role of the catalytic residues Glu 35 and Asp 52 in the enzymatic reaction is analogous in the two pathways.

Although the molecular dynamics results are only suggestive (e.g., it is possible that hydrogen bonding of Glu 35 to the substrate $O_4$ is a rare event not sampled by the simulation), it is hoped that the formulation of an alternative mechanism will lead to renewed interest in the catalysis of polyglycoside hydrolysis and transglycosylation by lysozyme; nothing in the present analysis would require that the same mechanism is found in all $\beta$-glycosidases. Experiments that aim to establish whether the hydrolytic pathway proceeds according to Scheme I or II in lysozyme are in progress.[26]

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## Stereoelectronic Effects in Intramolecular Long-Distance Electron Transfer in Radical Anions as Predicted by ab Initio MO Calculations

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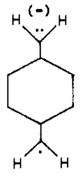
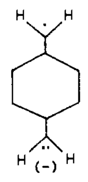
Recent experimental work has been directed toward the study of intramolecular electron transfer (ET) rates in radical anions of the type

$$A_1^-\text{–Sp–}A_2 \rightarrow A_1\text{–Sp–}A_2^-$$

where $A_1$ and $A_2$ are electron acceptors and Sp is a rigid hydrocarbon spacer with no electron affinity of its own.[1] Specifically, for the case of $A_1$ = 4-biphenylyl, $A_2$ = 2-naphthyl, and Sp = 1,4-cyclohexadiyl it was found that the cis isomer reacts slower than the trans although the distance between acceptors is shorter for the cis isomer.[2] With other spacers, such as decalins, it also appears that distance between acceptors is not the only factor in determining the rate.[2] It is most probable that electronic coupling between donor and acceptor is influenced by the $\sigma$-orbitals of the spacer, making it a function of the position as well as the geometry of attachment. While the problem of through-bond coupling has been addressed before,[3] here we want to pay attention to stereoelectronic effects.[4] To test this hypothesis we have carried out ab initio calculations for the simplified model **1** with trans-equatorial-equatorial (*t*-(e,e)-**1**), trans-axial-axial (*t*-(a,a)-**1**), and cis-equatorial-axial (*c*-(e,a)-**1**) geometries.


**1a**


**1b**

The calculations consist of finding the UHF broken-symmetry solutions as diabatic wavefunctions[5] and their energies corresponding to the localized electronic structures **1a** and **1b** as function of the torsional angles of the $CH_2$-groups which were restricted to be planar. The interaction matrix element between nonorthogonal UHF wavefunctions

$$V_{a,b} = (1 - S_{\mathrm{a,b}}{}^2)^{-1}|\langle a|H|b\rangle - S_{a,b}(\langle a|H|a\rangle + \langle b|H|b\rangle)/2|$$

was evaluated along with the seam of their crossing, with $|a\rangle$ and $|b\rangle$ being the diabatic wavefunctions for **1a** and **1b**, $S_{a,b}$ the overlap integral, and $H$ the electronic Hamiltonian.[6] Since in the isolated molecule model the ET promoting mode is restricted to the torsional motion of the $CH_2$ groups, the seam of the energy surface where **1a** and **1b** are isoenergetic is considered to describe the conformations where ET can take place.[7] In the trans isomer symmetry determines the seam for both *t*-(e,e)-**1** and *t*-(a,a)-**1** conformations. The rotational conformations are defined by the dihedral angle $\theta$ between the tertiary cyclohexane hydrogens and one of the $CH_2$ hydrogens (Figure 1 insert).

In all, six rotational conformations were tested in each of the *t*-(e,e)-**1** and *t*-(a,a)-**1** geometries by using a STO-3G basis set. The results are shown in Figure 1. It is found that the energy along the seam of crossing in *t*-(e,e)-**1** has a minimum for the 0,0-conformation in which the $CH_2$ planes bisect the cyclohexane ring. This is also the conformation with the largest $V_{a,b}$. The energetically least favored 90,90-conformation has an interaction element 12 times smaller corresponding to a rate difference of 144. In contrast, *t*-(a,a)-**1** shows an energy maximum for the 0,0-conformation and a maximum for $V_{a,b}$. Since the energies of the rotamers are largely determined by nonbonded interactions, $CH_2$ groups may be considered poor models for the 2-naphthyl

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[6] If the UHF broken space symmetry solutions, $|a\rangle$ and $|b\rangle$, are strongly, charge-localized, they are appropriate for use as the zero-order initialand final electronic states in the time-dependent perturbation theory treatment. By the symmetric orthogonalization, they become $|a_0\rangle = C_1|a\rangle - C_2|b\rangle$ and $|b_0\rangle = -C_2|a\rangle + C_1|b\rangle$, where $C_1 = [(1 - S_{a,b})^{-1/2} + (1 + S_{a,b})^{-1/2}]/2$ and $C_2 = [(1 - S_{a,b})^{-1/2} - (1 + S_{a,b})^{-1/2}]/2$. Here we assume the existence of the zero-order Hamiltonian, of which $|a_0\rangle$ and $|b_0\rangle$ are eigenfunctions: $H^0|a_0\rangle = E_a{}^0|a_0\rangle$; $H^0|b_0\rangle = E_b{}^0|b_0\rangle$. Then the perturbation $H'$ which causes the electron transfer is defined as the difference of the total electronic Hamiltonian $H$ and this zero-order Hamiltonian $H^0$ as $H' = H - H^0$. The matrix element for the electron transfer between $|a_0\rangle$ and $|b_0\rangle$ defined as $V_{a,b} = |\langle a_0|H'|b_0\rangle|$ is calculated to be the expression given in the text. The crossing seam between $|a_0\rangle$ and $|b_0\rangle$ is exactly the same as the seam between $|a\rangle$ and $|b\rangle$ in the high-symmetry conformation. Even in the low-symmetry case, this is a reasonable approximation for small overlap $S_{a,b}$.

[7] Under the conditions of the experiment of the seam covers a much larger area of the surface because of the effect of solvation. However, here we are only interested in the electronic part contributing to the rate and we neglect the relative Franck–Condon factors including other vibrational modes.

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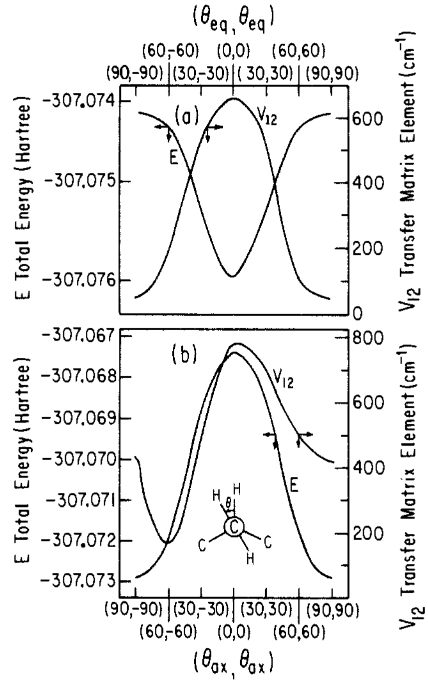

**Figure 1.** Total energy $E$ (hartree) and transfer matrix element $V_{12}$ (cm$^{-1}$) along the seam of crossing between diabatic energy surfaces for $t$-(e,e)-**1** (a) and $t$-(a,a)-**1** (b) as a function of dihedral angle $\theta$ (deg). The insert defines $\theta$ with Newman projections along the methylene–cyclohexane C–C bond.

and 4-biphenylyl groups of the compounds used in the experiments. Therefore, MM2 force field calculations[8] were carried out for the corresponding 1,4-diphenylcyclohexanes **2**. It was found that $t$-(e,e)-**2** does indeed prefer a 0,0-conformation while the minimum for $t$-(a,a)-**2** lies close to 55,55. Comparing the matrix elements of the two conformers of $t$-**1** at rotation angles corresponding to the MM2 energy minima for $t$-**2**, it is predicted that molecules with the $t$-(e,e) geometry will react considerably faster than those with a $t$-(a,a) structure. It is noteworthy that very large rate differences are predicted for the different rotamers without any change in distance.

The lack of symmetry in $c$-(e,a)-**1** required a search on a two-dimensional grid to locate a possible seam. The regions near 60,60 and 60,−60 are close to isoenergetic and give interaction energies of 100 and 170 cm$^{-1}$, respectively. At no point was $V_{a,b}$ found to exceed one-third of the maximum value found for the trans isomers. the MM-2 minimum energy for $c$-(e,a)-**2** is found for 0-e and 55-a which is not a crossing point in *cis*-**1**. The $V_{a,b}$ at this geometry for $c$-(e,a)-**1** is about 8 times smaller than that of $t$-(e,e)-**1** at its minimum energy. This finding is in qualitative agreement with the experimental data.

To improve the reliability of these predictions the two extreme rotamers of $t$-(e,e)-**1** were calculated with a split-valance 4-31G basis set. Qualitatively, the same results were obtained, with the 0,0-rotamer giving the largest interaction (1790 cm$^{-1}$) and the lowest energy. To check the magnitude of this element against the experimental rate constant ($2 \times 10^9$ s$^{-1}$) one has to consider the reduced electron densities at the attachment positions of 4-biphenylyl and 2-naphthyl negative ions, $\rho_b$ and $\rho_n$, compared to the essentially unit densities in our model. From densities determined by ESR[9] of the respective negative ions, an interaction energy of 215 cm$^{-1}$ is obtained (1790 $(\rho_b\rho_n)^{1/2}$) fairly close to that estimated from the experimental rate (150 cm$^{-1}$) using theory essentially due to Jortner.[10]

Finally, to give an estimate of the magnitude of the through-space interaction, calculations with 4-31G and 6-311G** basis sets were carried out on the interaction of a methyl radical with a planar methyl anion at the same distance and geometry as in $t$-(e,e)-**1**, the latter basis set having a better tail behavior essential in the through-space interaction.[11] The calculated through-space interaction, 2.7 and 19.8 cm$^{-1}$, respectively, is fairly small.

In summary, as far as the aromatic anions in solution are described well within the flexible valence basis set, these calculations together with the experimental results show clearly that intramolecular long-distance ET proceeds mostly by through-bond interaction involving the spacer and does so in a very stereospecific manner. Similar mechanisms may be at work in intermolecular ET where molecules are held apart by rigid matrices[12] or by proteins.[13] In these cases the solvent molecules or the protein fragment will provide the MO's for interaction, although the coupling should be weaker.

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(8) The molecular mechanics (MM2) program was written by N. Allinger and Y. H. Yuh, University of Georgia (1980), and was obtained from the Quantum Chemistry Program Exchange, University of Indiana.

(9) Densities used are for an unsubstituted naphthalene negative ion at position **2** (0.072) and a biphenyl negative ion at position **4** (0.202): Atherton, N. M.; Weissman, S. I. *J. Am. Chem. Soc.* **1961**, *83*, 1330. Snyder, L. C.; Amos, T. *J. Chem. Phys.* **1965**, *42*, 3670.

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(11) If a diffuse anion function is included in this model calculation, the through-space interaction becomes much larger, e.g., 721 cm$^{-1}$ with 6-311G** + anion sp ($\alpha$ = 0.0438). However, this basis function is not very appropriate for a real system which is composed of delocalized aromatic anions measured in solution.

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# Electron-Transfer Pathways in the Hydride Abstraction by $Ph_3C^+$ from Exo-Substituted Cyclohexadiene Fe(0) Complexes: A Key Step in the Synthesis of Heterobifunctional Cyclohexadienes from Benzene

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Double nucleophilic attack at a transition-metal benzene complex[1-6] is an attractive way to make heterobifunctional cyclo-

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