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Supplementary Material Available: Tables of crystallographic details, including thermal parameters and torsion angles for **1**β and **2**β (4 pages); listing of observed and calculated structure factors for **1**β and **2**β (31 pages). Ordering information is given on any current masthead page.

Molecular Bridge Effects on Distant Charge Tunneling[†]

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Abstract: The question arises as to whether different hydrocarbon bridges should give different electron-transfer rates. We answer this question on the basis of energetic and topological (interference) effects that can be gleaned from one-electron models. A discussion of model compound electron-transfer rates based on this interpretation is given. The approximations implicit in the periodic models used here (and in previous work) are carefully justified.

I. Introduction

In previous studies, we presented predictions for the tunneling matrix element dependence on donor, acceptor, and bridge energetics and topology for several linkers.[1] We also distinguished the nature and importance of through-bond vs. through-space pathways for some model potentials.[2] Here, we simplify and unify the results for tunneling through organic linkers. We begin by discussing considerable simplifications that arise when charge mediation by either the bonding (valence) or the antibonding (conduction) states dominates the donor–acceptor interaction. We discuss the validity of the periodic, weak coupling, and small backscattering approximations. Next, we compare tunneling matrix elements for several linkers and show, analytically, how topological effects in cyclic bridges can enhance or decrease the matrix element. Both constructive- and destructive-interference effects are found to be important. An understanding of how these effects influence the distance decay of the matrix element for different organic donor–acceptor bridges of current experimental interest is the main goal of this paper. (Recall that the rate is proportional to the square of the matrix element in the nonadiabatic limit.[3]) We also discuss the predictions of Hush[4] and Schipper[5] that electron-transfer matrix elements decay in a polynomial rather than in an exponential fashion with distance.

The goal of this work is to show why different hydrocarbon bridges are expected to give different electron-transfer rates even for the same donors, acceptors, and transfer distance. A consistent method is given to predict the efficiency of different bridges for mediating the donor–acceptor interaction. This method is given in a simple enough form so that it can be directly applied by experimentalists when considering target bridging molecules, and it is also of use for understanding electron-transfer rates in existing model compounds. It may also be useful for designing new molecules with novel applications to microelectronics.[6]

II. One-Band Model for Bond-Mediated Electron Tunneling

In the first part of this section we show how the electron-transfer rate dependence on distance for a linear alkane bridge can be described with a one orbital per bond model. This description permits a clearer understanding of the terms electron and hole transfer. It also identifies the contributions of different "tunneling pathways" to the tunneling matrix element.

Let us represent an alkane chain by a set of sp^3 orbitals. Orbitals on the same carbon atom have an interaction γ, and orbitals in the same bond have an interaction β. For simplicity we neglect the C–H bonds in this section. For realistic parameters, $|\beta| \gg |\gamma|$. Thus, if the donor is coupled to an n-alkane with N carbon atoms ($2N$ sp^3 carbon orbitals participating in the C–C bonds), the Hamiltonian is given in (2.1). The zero of the energy scale is chosen so that $\alpha_{\mathrm{sp}^3} = 0$. Also, β and γ are defined as negative quantities in the usual Hückel convention, which follows from the assumption that the basis functions all have the same phase.[7]

$$H_D = \Delta_D a_D^\dagger a_D + \beta_D(a_D^\dagger a_1 + a_1^\dagger a_D) + \sum_{i=1}^{N}\gamma(a_{2i-1}^\dagger a_{2i} + a_{2i}^\dagger a_{2i-1}) + \sum_{i=1}^{N-1}\beta(a_{2i}^\dagger a_{2i+1} + a_{2i+1}^\dagger a_{2i}) \quad (2.1)$$

This Hamiltonian describes N carbon atoms, each with two sp^3 orbitals participating in the backbone bonds. The hybrid orbitals participating in the C–H bonds, considered in section III, are not included at this stage for reasons of simplicity. The parameter γ couples hybrid orbitals on the same carbon atom, and β couples hybrid orbitals participating in a bond. Only nearest-neighbor interactions are included. Notice that the Hamiltonian, written here in operator notation, is just the common one-electron extended Hückel representation of the problem using a basis set of hybrid orbitals.

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This Hamiltonian employs a one-electron model. Discussions of the reasons that this approximation works for the electron-transfer problem have been given by several authors.[8,9] Because we are working in the weak-coupling limit (donor–bridge and bridge–bridge orbital interactions are "small"), many electron effects are expected to be unimportant. Assuming that orbitals in the bridge can be represented well in the tight-binding limit,[2] the one-electron wave function is a good approximation for the donor and acceptor states far from the nuclei. This is because the electrons of the bridge are closed-shell "core" electrons.[8] Electron correlation strongly affects the orbital energies, but the hopping matrix element between bridge sites is basically a one-electron matrix element. A similar argument has been given for the electron-exchange process in aqueous Fe^{2+}–Fe^{3+}.[9]

Real systems have an acceptor bound to the Nth atom of the bridge. In a Franck–Condon approach, the electronic energy, which determines the tunneling matrix element for the "activated complex", is identical for the donor and acceptor. If the coupling matrix element between atom N of the bridge and the acceptor is, in this extended Hückel framework, β_A, the tunneling matrix element is exactly β_A times the amplitude of the donor wave function on the terminal bridge atom. Therefore, *all* of the distance dependence of the tunneling matrix element, and hence of the electron-transfer rate, is contained in the donor wave function calculated at the appropriate energy. A more complete discussion of this result is given in ref 1, 2, and 8. The validity of the Franck–Condon approximation is discussed in ref 8.

If the alkane chain were infinite, we could use Bloch conditions and write the donor wave function at bonding orbital k as in (2.2).

$$\Phi_k{}^{D} = \epsilon^k(a\phi_{2k} + b\phi_{2k+1}) \tag{2.2}$$

Here ϕ_k is the orbital wave function of the kth sp^3 orbital. These two orbitals participate in a single C–C bond between two adjacent atoms. The total number of hybrid orbitals in the chain is $2N$. The ϵ^k term arises from the translational symmetry.

We now calculate the donor-localized state of the Hamiltonian in (2.1) for $N \rightarrow \infty$. The system of equations to solve is then given in (2.3), where E is the energy of the donor state. If the donor

$$\begin{pmatrix} 0 & \beta + \gamma/\epsilon \\ \beta + \gamma\epsilon & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E \begin{pmatrix} a \\ b \end{pmatrix} \tag{2.3}$$

interacts weakly with the chain, then $E \approx \Delta_D$ for the localized state. This approximation is reasonable, and its validity is discussed later in this section. Equation 2.3 gives eq 2.4. In the case of

$$\epsilon + 1/\epsilon = (E^2 - \gamma^2 - \beta^2)/\gamma\beta \tag{2.4}$$

an alkane chain, $|\beta| \gg |\gamma|$. If we had an infinite chain of alkane (without the donor), the solution of eq 2.4 would lead to two bands: one with energy states between $\beta + \gamma$ and $\beta - \gamma$, and the other, between $-(\beta - \gamma)$ and $-(\beta + \gamma)$. The first band is composed of the bonding states of the chain and is called the valence band, and the second one is composed of the antibonding states and is called the conduction band. The donor state interacts mainly with the band that is energetically closer to it. From eq 2.4, we see that any state in the band gap ($|E| < |\beta|$) has a negative value for ϵ. Because the gap between the two bands is large (about 10 eV), one band generally dominates the interaction. In most of the systems discussed in the next section, the energy level of the transfer electron is near that of the valence band. Now we show how to formally neglect the effect of the energetically distant band and include only the donor interaction with the closest one.

Assume that the donor-state energy E is close to that of the valence band. Then, E is negative and $|E - \beta|,|\gamma| \ll |\beta|$. Because the donor state is in the band gap (localized), $|E - \beta| > |\gamma|$. By use of the approximations above, eq 2.4 can be rewritten as eq 2.5.

$$\epsilon + \frac{1}{\epsilon} \simeq \frac{2(E - \beta)\beta}{\gamma\beta} \simeq \frac{E - \beta}{\gamma/2} \tag{2.5}$$

Equation 2.5 is exactly the result we would get from a one orbital per site chain model with the Hamiltonian given in eq 2.6.

$$H_D = \Delta_D a_D{}^{\dagger} a_D + \beta_D(a_D{}^{\dagger} a_1 + a_1{}^{\dagger} a_D) + \sum_{i=1}^{N} \beta a_i{}^{\dagger} a_i + \sum_{i=1}^{N-1} \gamma/2(a_i{}^{\dagger} a_{i+1} + a_{i+1}{}^{\dagger} a_i) \tag{2.6}$$

This Hamiltonian represents a chain of orbitals with self-energy β and nearest-neighbor interaction $\gamma/2$. Now the "orbitals" represent the C–C bonding orbitals rather than the carbon atomic (hybrid) orbitals. This is equivalent to saying that the donor interacts with a chain of bonding orbitals of self-energy β, which form a band of width 2γ. This approximation neglects the donor interaction with an entire band of states, not individual states within a band. In the Appendix we give a comparison of the σ band calculation with the complete calculation for *n*-alkane.

In order to validate the above discussion, we must carefully address two points. The first is that the bridges we are considering are finite, so the infinite chain limit is not exact. The second point is that we assume that the donor weakly interacts with the chain. As in eq 2.2, but for finite N, let us write the (exact) donor wave function for eq 2.6 as eq 2.7, where $\mathcal{N}$ is the normalization factor.

$$\Psi_D = \frac{1}{\mathcal{N}}\{\phi_D + \sum_{i=1}^{N}(a\epsilon^i + b\epsilon^{N+1-i})\phi_i\} \tag{2.7}$$

Here ϕ_j is the jth bond orbital. Also, for reasons of simplification, we fix the zero of the energy scale in the center of the band and define $\gamma' = \gamma/2$. This form for the wave function is completely general as long as the *finite* bridge is periodic except at its edges. Multiplying $H_D\Psi_D = E_D\Psi_D$ by $\phi_j{}^*$ and integrating, we obtain eq 2.8a–d. From eq 2.8c, we obtain the same E–ϵ relation (2.9) that

$$\langle D|: \ \beta_D(a\epsilon + b\epsilon^N) = (E - \Delta_D) \tag{2.8a}$$

$$\langle 1|: \ \beta_D + (a\epsilon^2 + b\epsilon^{N-1})\gamma' = E(a\epsilon + b\epsilon^N) \tag{2.8b}$$

$$\langle i|: \ (a\epsilon^{i-1} + b\epsilon^{N-i+2})\gamma' + (a\epsilon^{i+1} + b\epsilon^{N-i})\gamma' = E(a\epsilon^i + b\epsilon^{N-i+1}) \text{ for } i = 2, N - 1 \tag{2.8c}$$

$$\langle N|: \ (a\epsilon^{N-1} + b\epsilon^2)\gamma' = E(a\epsilon^N + b\epsilon) \tag{2.8d}$$

$$\epsilon + 1/\epsilon = E/\gamma' \tag{2.9}$$

we found for the infinite bridge. Combining eq 2.8d and 2.9, we obtain eq 2.10. From eq 2.10, we see that the coefficient multiplying ϕ_j in Ψ_D is given in (2.11). From eq 2.11 we obtain two

$$a/b = -1/\epsilon^{N+1} \tag{2.10}$$

$$C_j = a\epsilon^j + b\epsilon^{N-j+1} = a\epsilon^j(1 - \epsilon^{2N+2}/\epsilon^{2j}) \tag{2.11}$$

conclusions. First, the infinite chain approximation becomes worse near the ends of the chain. Second, the terminal orbital coefficient, C_N, is always equal to the infinite chain result, $a\epsilon^N$, multiplied by $1 - \epsilon^2$, *independent* of N (a is chain length independent in the weak-coupling limit, discussed below). Thus, if we link an acceptor to the Nth bridge unit, the amplitude of the matrix element is proportional to $(1 - \epsilon^2)\epsilon^N$ and therefore shows a distance dependence proportional to ϵ^N. Also, if $\epsilon^2 \ll 1$ (i.e., $1 - \epsilon^{2N+2}/\epsilon^{2j} \approx 1$ for all j), we can neglect backscattering between bonds, and the infinite chain result becomes exact for a finite chain. It is important to stress that the $\epsilon^2 \ll 1$ condition is not necessary to guarantee a chain length dependence of ϵ^N.

Assuming that $\epsilon^N \ll 1$, we obtain from eq 2.8b the results in (2.12). Substituting eq 2.12 into eq 2.8a yields (2.13). Therefore,

$$a\epsilon = \beta_D/(E - \epsilon\gamma') \approx \beta_D/E \tag{2.12}$$

we can assume $E \approx \Delta_D$ as long as $\beta_D{}^2 \ll \Delta_D{}^2$. (Recall that Δ_D is the energy of the donor orbital relative to the center of the band.)

$$E = \Delta_D + \beta_D{}^2/E \tag{2.13}$$

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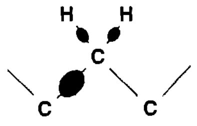

Figure 1. Repeating unit orbitals for valence band of *n*-alkane ($|\epsilon|$).

The normalization factor of eq 2.7 is given in eq 2.14. In the weak-coupling limit, if $\beta_D \ll E$, then $a\epsilon \ll 1$, so $\mathcal{N}^2 \approx 1$. In this limit the normalization constant is chain length independent.

$$\mathcal{N}^2 = 1 + \sum_{j=1}^{N} |C_j|^2 \tag{2.14}$$

From eq 2.11, we see that if $\epsilon^2 \ll 1$, we can neglect backscattering and the wave function can be described as decaying by the factor γ'/E per bond (orbital). Because γ' is negative and E is positive for hole tunneling, the ratio γ'/E is always negative, and the sign of this ratio is important for interference effects between tunneling pathways, discussed in Section III. For electron rather than hole tunneling, the signs of both parameters are reversed and the ratio is still negative. More generally, if we have a chain with varying orbitals where the periodic condition is not necessarily applicable, we can define decay per bond as in (2.15),

$$\epsilon(\text{bond } i) = \gamma_{i,i-1}/(E - \alpha_i) \tag{2.15}$$

where $\gamma_{i,i-1}$ is the exchange interaction between orbitals (bonds) i and $i-1$, α_i is the bond orbital energy, and E is the energy of the tunneling electron. The result in eq 2.15 has been thoroughly discussed for electron tunneling through a saturated bridge.[1c] Note that because all γ's are of the same order of magnitude, after the one orbital per site approximation was made, eq 2.15 could have been obtained from the first term in the perturbation series for the wave function.

For nonlinear (cyclic) bridges, the results obtained by neglecting backscattering agree with the exact result for the leading term in powers of γ/E. However, in such systems other corrections, besides backscattering, appear. They are basically constructive interference of pathways of the same length or destructive interference of pathways whose lengths differ by one bond. This is shown in Section III and in the Appendix.

III. Topological Effects on Valence Band Tunneling through Hydrocarbon Linkers

For a qualitative treatment of bridge-mediated electron tunneling through hydrocarbons, the basis set of bonding orbitals (hole tunneling) or antibonding orbitals (electron tunneling) is a reasonable approximation. To include all of the states (bonding and antibonding) in the calculation is entirely possible. However, it would not permit a transparent comparison of the results (especially sources of interference) for different bridging groups—the main goal of this section. As discussed in Section II, this approximation is appropriate for saturated hydrocarbons because the bonding–antibonding energy gap ($2\beta \sim 17$ eV) is much larger than the energetic distance between the tunneling electron and the center of the relevant band (<5 eV). In this section we include the CH bonds in our Hamiltonians because their influence on the matrix elements is comparable to many topological effects (e.g., those arising from having cyclic rather than linear bridges) as shown later in this section.

We begin this section by listing the exact E–ϵ relations for some real and imagined hydrocarbon chains. We then show that the leading terms in the relation can be identified with the tunneling pathways in the bridge. The negative sign of γ/E leads to interference between connected pathways differing in length by one bond. For this reason, edge-fused hydrocarbon states of symmetry that minimize side routes are particularly important for charge mediation. A comparison of matrix element decay with distance is made for a chain composed of cyclic hydrocarbons fused on an edge vs. those fused at a single atom.

For the following systems we define the decay per unit cell or bond as ϵ or ϵ'. The value of γ used in this section is half of the valence bandwidth discussed in Section II. When discussing the parity of the bridge states, one should recall that the states contribute to the tunneling matrix element only if the donor and acceptor are of the proper symmetry to mix with them (i.e., β_D and $\beta_A \neq 0$).

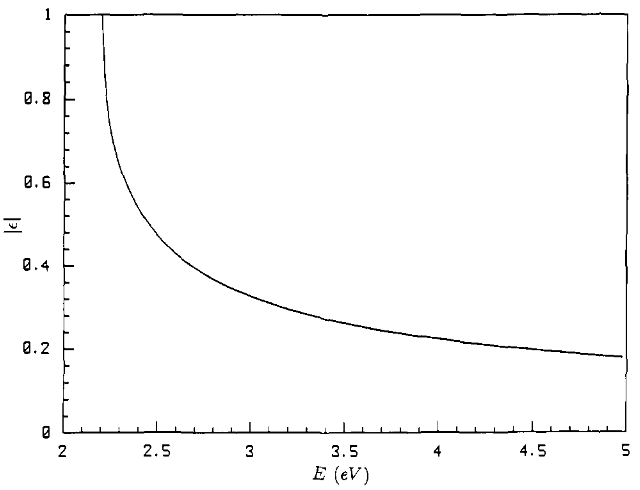

Figure 2. Decay per repeating unit (per CC bond) in *n*-alkane. The energies shown are tunneling energies above the band. The zero of the energy scale is the CC σ bond energy.

A. Linear Alkane.[1b] The simplest molecular model for extended *n*-alkane is composed of one CC bond and two CH bonds per "unit cell" (see Figure 1). In this case, eq 3.1a holds. This was obtained

$$\epsilon + \frac{1}{\epsilon} = \frac{E}{\gamma}\left[\frac{1 + 4\gamma^2/E(\alpha + \gamma - E)}{1 - 2\gamma/[\alpha + \gamma - E]}\right] \tag{3.1a}$$

by expanding the determinate that relates E to ϵ (eq 3.1b).

$$\det\begin{pmatrix} \gamma/\epsilon + \gamma\epsilon - E & 2\gamma/\epsilon + 2\gamma \\ \gamma + \gamma\epsilon & \alpha + \gamma - E \end{pmatrix} = 0 \tag{3.1b}$$

Figure 2 shows ϵ vs. E in the gap (above the band) for this linker ($\gamma = -1.1$ eV and α, the CH bond energy relative to the CC bond energy, is -0.5 eV). Solving eq 3.1b for $\epsilon + 1/\epsilon$ and expanding the quotient for small γ, we obtain eq 3.1c. Since $-2\gamma/(E - \alpha)$

$$\epsilon + \frac{1}{\epsilon} \simeq \frac{E}{\gamma}\left[1 - \frac{2\gamma}{E - \alpha} + \ldots\right] \tag{3.1c}$$

is positive, $|\epsilon|$ is *decreased* due to the CH bonds (recall that without any CH bonds $\epsilon + 1/\epsilon = E/\gamma$). This correction can be attributed to amplitude that has made a single excursion into the two CH bonds interfering with amplitude, which has propagated directly along the CC backbone. Higher order terms in the expansion can be connected with more convoluted tunneling pathways. This destructive interference is a general effect, in hydrocarbons, of bonds adjacent to the tunneling pathway.

Far from the band ($|E|$ large), the destructive interference is unimportant. Recall that we cannot use these models for tunneling energies so far from the valence band that mediation by other bands becomes important. The presence of CH or other bonds with energy lower than that of CC bonds decreases hole tunneling, i.e. *decrease* $|\epsilon|$ (wave function decay becomes more rapid).

To illustrate further complications that arise from geometric effects of the linker, we consider chains with four-membered rings. These chains have pedagogical value as well as relevance to bridges described in ref 10 and 12. We then consider six-membered rings of current experimental relevance, namely fused norbornanes and fused cyclohexanes.

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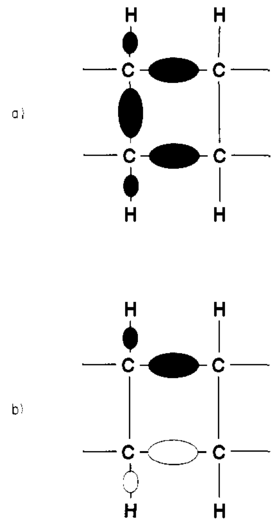

Figure 3. (a) Same as Figure 1 for the even states of edge-fused cyclobutane. (b) Same as (a) for the odd states.

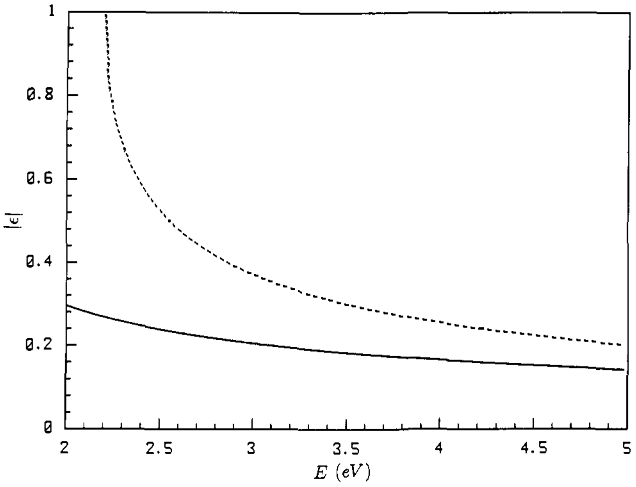

Figure 4. Same as Figure 2 for edge-fused cyclobutane. The solid (dashed) line shows the decay for the odd (even) states.

B. Poly(edge-fused cyclobutane). For the even states (Figure 3a) we find eq 3.2a and for small γ we find eq 3.2b. Interference

$$\epsilon + \frac{1}{\epsilon} = \frac{E}{\gamma}\left[\frac{(\alpha - E)(1 - 2\gamma/E) + 4\gamma^2/E}{\alpha - E - \gamma}\right] \tag{3.2a}$$

$$\epsilon + \frac{1}{\epsilon} = \frac{E}{\gamma}\left[1 - \frac{2\gamma}{E} - \frac{\gamma}{E - \alpha} + \ldots\right] \tag{3.2b}$$

arises from the CC bond connecting the two parallel σ pathways as well as from the CH bond. Equations for the odd states (Figure 3b) of the valence band (eq 3.3a) and for small γ (eq 3.3b) are found as well. In this case, interference arises only from the CH

$$\epsilon + \frac{1}{\epsilon} = \frac{E}{\gamma}\left[\frac{\alpha - E + 2\gamma^2/E}{\alpha - E - \gamma}\right] \tag{3.3a}$$

$$\epsilon + \frac{1}{\epsilon} = \frac{E}{\gamma}\left[1 - \frac{\gamma}{E - \alpha} + \ldots\right] \tag{3.3b}$$

bonds because there is no interaction between the parallel σ bonding pathways. Figure 4 shows the E–ϵ relation for the even and odd states of this unit cell.

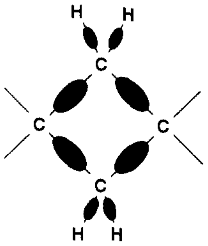

Figure 5. Same as Figure 1 for the even states of spirocyclobutane.

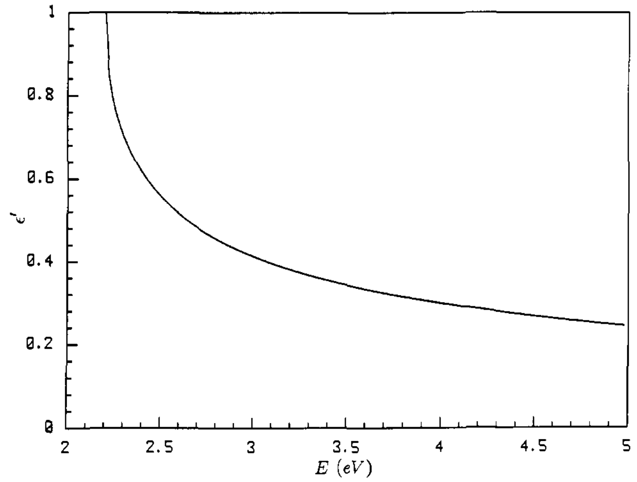

Figure 6. Same as Figure 2 for spirocyclobutane (even states). In all the following molecules there are two CC bonds per repeating unit. The decay per bond is shown ($\epsilon' = |\epsilon|^{1/2}$).

C. Poly(spirocyclobutane).[1b,10] To illustrate the difference between edge- and corner-fused cyclic alkanes, we now consider spirocyclobutanes. There are two CC bonds per unit cell and two *convergent* pathways for tunneling. One finds for the even states (Figure 5) eq 3.4a holds. This equation was used to plot the E–ϵ

$$\epsilon + \frac{1}{\epsilon} = \frac{(\gamma - E)^3 - 9\gamma^2(\gamma - E) + \alpha(\gamma - E)^2 + 4\gamma^3 - 5\alpha\gamma^2}{2\gamma^2(\gamma - E) + 2\gamma^2\alpha - 4\gamma^3} \tag{3.4a}$$

relation in Figure 6. Expanding this for small γ, we obtain eq 3.4b. The convergent pathways give a prefactor of 2 in the decay

$$\epsilon + \frac{1}{\epsilon} = \frac{1}{2}\left(\frac{E}{\gamma}\right)^2\left[1 - \frac{2\gamma}{E} - \frac{2\gamma}{E - \alpha} + \ldots\right] \tag{3.4b}$$

per unit cell, which enhances tunneling. Destructive interference arises from the CH bonds and the interactions between bonds to the quaternary carbon atoms. Far from the band, the factor of 2 dominates and wave function propagation per CC bond is $2^{1/2}$ times as efficient as in n-alkane. However, near the band edge, the extra destructive interference at the quarternary carbon is significant and the full $2^{1/2}$ enhancement relative to n-alkane is not realized.

From the equations for these and other unit cells we see that the valence band is split into a few closely lying bands. The one-band approximation discussed in the previous section cannot be applied further to these bands because the gaps are smaller than the energetic distance of the transfer state to the bands. The sole inclusion of CC σ bonds, however, remains valid and is discussed further in the Appendix. The bridge states, odd with respect to either mirror plane of spirocyclobutane, give zero contribution to electron tunneling due to the molecular symmetry.[1b]

D. Poly(edge-fused cyclohexane). A model for the steroidal and cyclohexyl donor–acceptor linkers of Closs and co-workers[11] is a chain of edge-fused cyclohexane rings (Figure 7). As in the edge-fused cyclobutanes, the leading term in the $\epsilon + 1/\epsilon$ equation is E/γ raised to the power of the number of bonds in the unit cell along the most direct tunneling route. The next higher order terms arise from the destructive interference due to the CH bonds and the one-bond connection between the two parallel direct tunneling routes. The $2\gamma/E$ factor arises from destructive interference

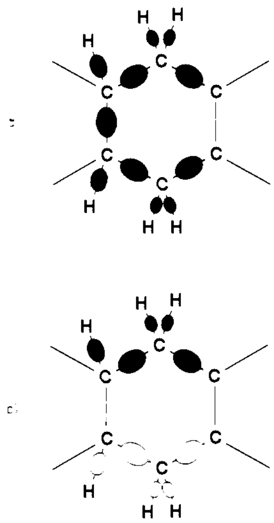

Figure 7. Same as Figure 3 for edge-fused cyclohexane.

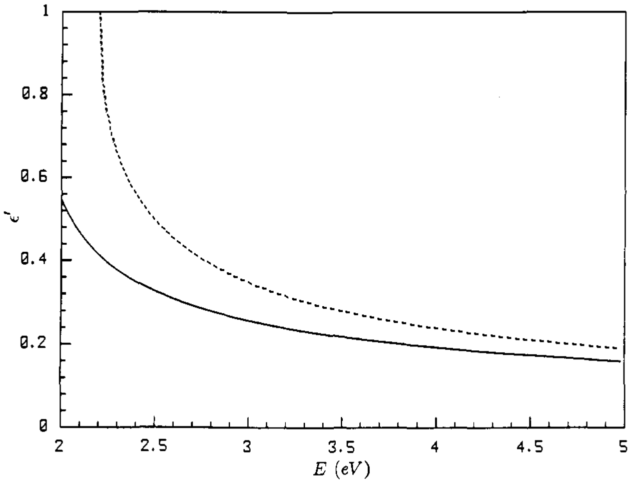

Figure 8. Same as Figure 4 for edge-fused cyclohexane.

between amplitude propagating along the edge of the molecule with that propagating between the two edge pathways (for even bridge states). For the even states, we solved (Figure 8) eq 3.5a, and for small γ, found eq 3.5b. For the odd states, the decay

$$\det\begin{pmatrix} \alpha - E & \gamma & \gamma & 0 & \gamma/\epsilon \\ 2\gamma & -E & 2\gamma & 0 & 2\gamma/\epsilon \\ \gamma & \gamma & -E & 2\gamma & \gamma/\epsilon + \gamma \\ 0 & 0 & \gamma & \gamma + \alpha - E & \gamma \\ \gamma\epsilon & \gamma\epsilon & \gamma + \gamma\epsilon & 2\gamma & -E \end{pmatrix} = 0 \qquad (3.5a)$$

$$\epsilon + \frac{1}{\epsilon} = \left[\frac{E}{\gamma}\right]^2\left(1 - \frac{3\gamma}{\mathrm{E} - \alpha} - \frac{2\gamma}{E} + ...\right) \qquad (3.5b)$$

per unit cell is given (Figure 8) by eq 3.6a. For these odd states,

$$\det\begin{pmatrix} -E & \gamma/\epsilon + \gamma & 2\gamma & \gamma/\epsilon \\ \gamma\epsilon + \gamma & -E & 2\gamma & \gamma \\ \gamma & \gamma & \alpha + \gamma - E & 0 \\ \gamma\epsilon & \gamma & 0 & \alpha - E \end{pmatrix} = 0 \qquad (3.6a)$$

the bridge functions as two independent *n*-alkane chains with one less CH bond every other carbon atom. For small γ, we obtain eq 3.6b.

$$\epsilon + \frac{1}{\epsilon} = \left[\frac{E}{\gamma}\right]^2\left(1 - \frac{3\gamma}{E - \alpha} + ...\right) \qquad (3.6b)$$

E. Poly(norbornane).[12] In this case (shown in Figure 9), a model for the linkers of Verhoeven and co-workers, the propagation is similar to that through fused cyclohexane. The differences arise (to first order) from the presence of two CC bonds in the place of two CH bonds in the unit cell.

For the even states (Figure 10), eq 3.7a and 3.7b are obtained.

$$\det \times \begin{pmatrix} -E & 2\gamma & 2\gamma & 0 & 0 & 2\gamma/\epsilon & 0 \\ \gamma & \alpha - E & \gamma & 0 & 0 & \gamma/\epsilon & 0 \\ \gamma & \gamma & -E & \gamma & \gamma & \gamma + \gamma/\epsilon & 0 \\ 0 & 0 & \gamma & \alpha - E & \gamma & \gamma & 0 \\ 0 & 0 & \gamma & \gamma & \gamma - E & \gamma & 2\gamma \\ \gamma\epsilon & \gamma\epsilon & \gamma + \gamma\epsilon & \gamma & \gamma & -E & 0 \\ 0 & 0 & 0 & 0 & 2\gamma & 0 & \gamma + \alpha - E \end{pmatrix} = 0 \qquad (3.7a)$$

$$\epsilon + \frac{1}{\epsilon} = \left[\frac{E}{\gamma}\right]^2\left(1 - \frac{2\gamma}{E - \alpha} - 3\frac{\gamma}{E} + ...\right) \qquad (3.7b)$$

For the odd states (Figure 10), eq 3.8a and 3.8b are obtained. As in the case of fused cyclohexanes, the odd states assist electron transport more than the even ones due to the absence of destructive interference from the bond common to adjacent rings. The presence of the CC bond in place of the CH bond compared to cyclohexane decreases the electron propagation.

$$\det\begin{pmatrix} \alpha - E & \gamma & 0 & 0 & \gamma/\epsilon \\ \gamma & -E & \gamma & \gamma & \gamma + \gamma/\epsilon \\ 0 & \gamma & \alpha - E & \gamma & \gamma \\ 0 & \gamma & \gamma & -\gamma - E & \gamma \\ \gamma\epsilon & \gamma + \gamma\epsilon & \gamma & \gamma & -E \end{pmatrix} = 0 \qquad (3.8a)$$

$$\epsilon + \frac{1}{\epsilon} = \left[\frac{E}{\gamma}\right]^2\left(1 - \frac{2\gamma}{\mathrm{E} - \alpha} - \frac{\gamma}{E} + ...\right) \qquad (3.8b)$$

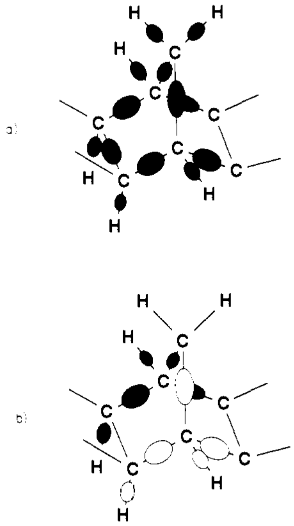

Figure 9. Same as Figure 3 for norbornane.

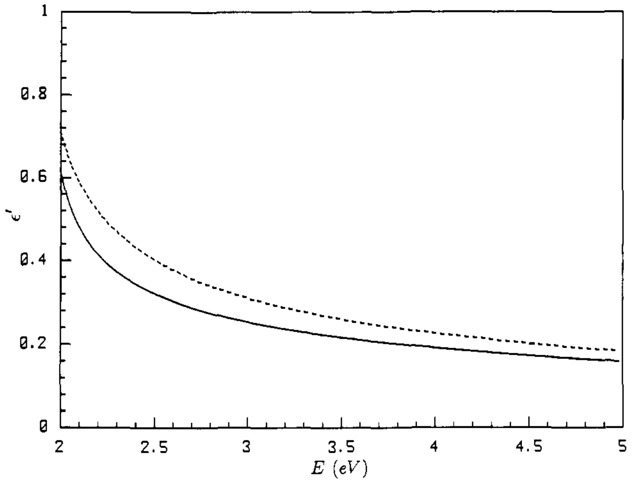

Figure 10. Same as Figure 4 for norbornane.

We now discuss the simple interpretation of the above results. Let us assume that the shortest pathway in the unit cell is composed of x CC bonds. If we neglect pathways with more than x bonds, the decay can be written as in eq 3.9a, where $\mathcal{P}$ is the

$$\epsilon + \frac{1}{\epsilon} = \frac{1}{\mathcal{P}}(\gamma/E)^x \tag{3.9a}$$

number of convergent pathways in the unit cell. This factor $\mathcal{P}$ enhances the rate due to constructive interference of multiple pathways x bond in length. The next correction we can include in eq 3.9a arises from the destructive interference of pathways of length x with those of length $x + 1$. To this order of correction, the decay can be written as in eq 3.9b, where the sum on i extends

$$\epsilon + \frac{1}{\epsilon} = \frac{1}{\mathcal{P}}(\gamma/E)^x[1 - \sum_i \gamma/(E - \alpha_i)] \tag{3.9b}$$

over the extra bond of all $x + 1$ bond pathway. α_i is zero if this extra bond is CC and −0.5 eV if it is CH. Equation 3.9b yields exactly the first-order expansions presented in this section up to this point.

It is important to recall that these corrections arise from the several possible tunneling pathways, not from backscattering. As discussed in Section II, the backscattering corrections for periodic systems are the corrections to the approximation $\epsilon + 1/\epsilon \approx 1/\epsilon$.

The leading terms in the expansions for small γ may not be adequate for calculating ϵ in some experimentally important cases because γ/E need not be small compared to one, and prefactors of these and higher order terms may need to be included. However, they give a qualitative indication of which bridges are more favorable for mediating electron transfer at a given tunneling energy. The discussion to first order about constructive and destructive interference can be generalized. Pathways that differ by an odd number of bonds interfere destructively, but those that differ by an even number of bonds interfere constructively. Convergent tunneling routes, such as those in spirocyclobutane (rings fused at a single atom), give $\epsilon + 1/\epsilon$ a prefactor equal to the number of these routes. Parallel pathways joined occasionally, such as in edge-fused cyclohexane or cyclobutane, introduce destructive interference due to paths one bond longer than the "main" path. For σ band tunneling, the odd states in edge-fused molecules assist tunneling more than the even states. For *electron* tunneling through the antibonding bands, the reverse is true (i.e., even states assist tunneling more than odd states in that case).

IV. Discussion

We have seen that different destructive and/or constructive interference for different bridges leads to different matrix elements. Because of destructive interference, odd (even) states for edge-fused single-ring hydrocarbons have a slower (faster) decay than n-alkane. Norbornane, due to the additional CC bridging bonds, is the least favorable bridge considered within a few electronvolts of the valence band. Donor and acceptor states may mix with both even and odd bridge states. At large transfer distances, the wave function amplitude will be dominated by the odd symmetry bridge states. Constructive interference is important in spiro cyclic alkanes, and it will always slow the matrix element decay with distance.

Figure 11 shows the energy dependence of the average wave function decay per bond for the linkers discussed in the previous section (odd symmetry states). Normal donors and acceptors lie a few electronvolts from the band edge. At these energies the relative mediation efficiencies can be understood from the interference effects described in the previous section. The constructive interference in spirocyclobutane makes it the most effective hydrocarbon charge mediator that we have considered.

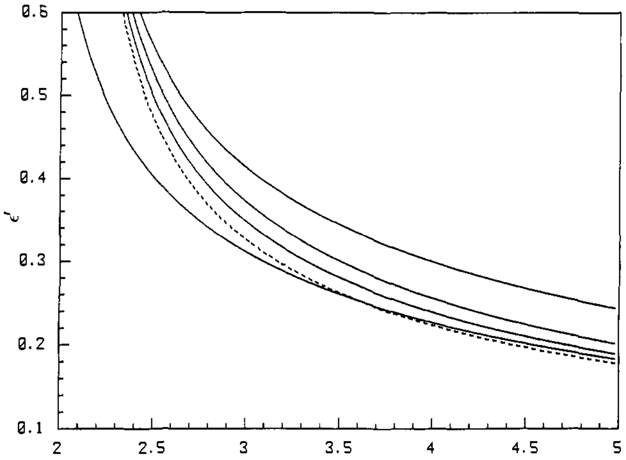

Figure 11. Decay per bond for n-alkane (dashed line), for even states of spirocyclobutane, and for odd states of all other linkers. The solid curves, from top to bottom, correspond to spirocyclobutane, edge-fused cyclobutane, edge-fused cyclohexane, and edge-fused norbornane.

Experimental results show that the model systems are in the range of 1–3 eV from the band edge. The electronic tunneling energy is determined by the redox potentials of the donor and acceptor.[1a,b] Therefore, in order to determine the tunneling energy more precisely, we need the full study of the distance dependence at several redox potentials. The free energy for the transfer reaction at a fixed distance, ΔG, depends on the redox potential difference between donor and acceptor plus other electrostatic corrections. Because of these electrostatic corrections, ΔG for the transfer reactions may be distance dependent. To first order, this adds a constant correction term to ΔG for each distance. To determine this electrostatic term, a ΔG analysis at several distances is required. Such a series of experiments would allow a separation of the matrix element distance dependence from the Franck–Condon terms. (Assuming that we have donors and acceptors with similar reorganization energies, the Franck–Condon factor is only a function of ΔG.) Once the ΔG dependence on distance is understood, experiments that fix ΔG but move *both* the donor and acceptor energies (moved up or down in the absolute sense) would be particularly useful. Such experiments would determine the electronic tunneling energy relative to the band. From these experiments, it will be possible to obtain ϵ as a function of electronic energy and ΔG. This will permit connection of the redox energy scale with the energetic distance to the band. For systems where the donor and acceptor are both initially neutral, the importance of the ΔG study is even greater. Here ΔG is especially transfer distance dependent due to the charge-pair interaction in the final state (i.e., ΔG is smaller for longer transfer distances). This problem appears in the norbornyl model systems (actually, these systems are composed of both edge-fused norbornyl and cyclobutyl groups) of Verhoeven and co-workers.[12] For the recently reported systems of Closs and co-workers[11] (biphenyl radical anion donor, fused cyclohexyl bridges, and naphthylene acceptor), we expect the tunneling energy to be about 2.5 eV on our energy scale. This result is preliminary, and a real quantitative prediction should include all of the bridge orbitals and will require more experiments.

If a full experimental study as prescribed above were performed, it would permit us to quantify precisely the redox energy scale. Comparison of the results for spirocyclobutane, fused norbornanes, and fused cyclohexanes for fixed donors and acceptors would allow a check of the effectiveness of this calculation. Also, the ΔG–distance study would permit a test of our early prediction that hole tunneling (valence band) rather than electron tunneling (conduction band) dominates the charge mediation process in most hydrocarbons.

Other complex bridges of biological relevance can be studied with similar techniques. They do not necessarily need to be composed of hydrocarbon for this method to be useful. Such an example has been given for electron transfer through a protein backbone.[1c] Indeed, these methods can be extended and applied to aperiodic systems if backscattering can be neglected.[1c]

If the donor is weakly coupled to the bridge, the tunneling matrix element decay is strictly exponential in the number of bridge groups independent of the size of ϵ. This finding runs counter to clains of Hush[4] and Schipper,[5] that matrix element decays such as $1/R^m$ with $m \simeq 3$ are anticipated. Although the origin of the Hush result is unclear, the $1/R^3$ prediction of Schipper arises from assumption of a finite bridge and a shallowly bound donor state. The wave function amplitude on unmixed bridge molecular orbital j at the Nth (terminal) bridge site in a one orbital per bridge unit representation is[13] given by (4.1).

$$[2/(N+1)]^{1/2} \sin (jN\pi/(N+1)) \qquad (4.1)$$

Considering electron (rather than hole) transfer through this band, the energetically nearest state is the $j = 1$ state, and as a function of N, the amplitude on the Nth site is given in eq 4.2. As the

$$C_{1,N} \propto 1/(N+1)^3 \text{ as } N \rightarrow \infty \qquad (4.2)$$

chain length increases, the density of states near the band edge changes and one expects many bridge states to mix with the donor and acceptor. The $1/R^3$ result would have meaning only if the bridge states were so well separated that only the interaction of the nearest bridge state with the donor and acceptor dominated the interaction. For the parameters considered here, this is certainly not the case, even for short chains. Formally, the assumption of interaction with a single state is invalid for any set of parameters as $N \rightarrow \infty$, and we know that the *exact* result in this limit[14] for the amplitude of the donor localized wave function at the Nth bridge site is given by eq 4.3a and 4.3b. Hence, in

$$C_N \propto \epsilon^{N-1} \qquad (4.3a)$$

$$\epsilon + 1/\epsilon = E/\beta \qquad (4.3b)$$

the long-chain limit the *analytical* form for the localized wave function (and hence the tunneling matrix element) decay is a pure exponential. This is the case even if backscattering cannot be ignored (ϵ^2 not much smaller than 1), in which case we solve the E–ϵ quadratic equation exactly. That the decay must be exponential in the long-chain limit is known from Bloch's theorem. It is of interest that neglect of an entire band with energy far from the donor, acceptor, and "relevant" band does not introduce functional errors to the modeling. Indeed, if the interaction parameters are judiciously chosen and the band gaps are large enough, quite satisfactory results can be obtained from one orbital per bond models.

Finally, we emphasize the fundamental energy and orbital symmetry dependence of the tunneling matrix element. Its value depends on the tunneling energy and so, for a given linker, depends on the donor and acceptor energetics and vibronic coupling. Individual calculations of the tunneling splitting cannot be used to predict the distance dependence of the tunneling matrix element for *different* donors and acceptors on the same bridge. Sources of both constructive and destructive interference in saturated tunneling bridges can be readily identified. Generally speaking, pathways of equal length converging at a single atom enhance the matrix element more than if these pathways converge at a bond.

Appendix

This Appendix shows the validity of the σ band approximation and presents preliminary results for tunneling through unsaturated linkers. First, we show the validity of separating the saturated linker tunneling problem into independent bonding and antibonding mediated transport problems. That is, we show that the use of just the bonding CC and CH orbitals reproduces the band structure of the bonding states obtained from the more "complete" calculation, which uses a full set of atomic orbitals and finds both the bonding and antibonding bands. Second, we discuss tunneling in unsaturated periodic linkers.

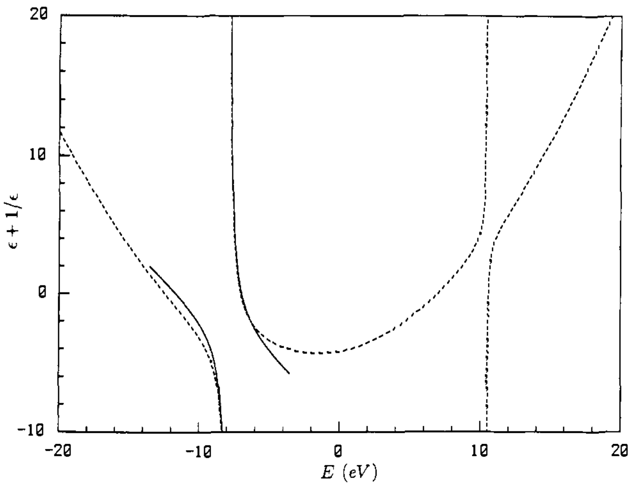

Figure 12. Band structure determined for *n*-alkane using only bonding orbitals (dashed line) and band structure determined for *n*-alkane[1a] including both bonding and antibonding states (solid line). The structure of the bonding bands determined with the simple model (solid line) reasonably reproduces that determined from the full model. Recall that for $-2 < \epsilon + 1/\epsilon < 2$ the states are delocalized over the bridge. The σ band energies were shifted by 8.5 eV for direct comparison with the full model.

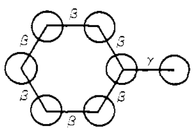

Figure 13. Geometry and interactions in the para-poly(phenyl) chains.

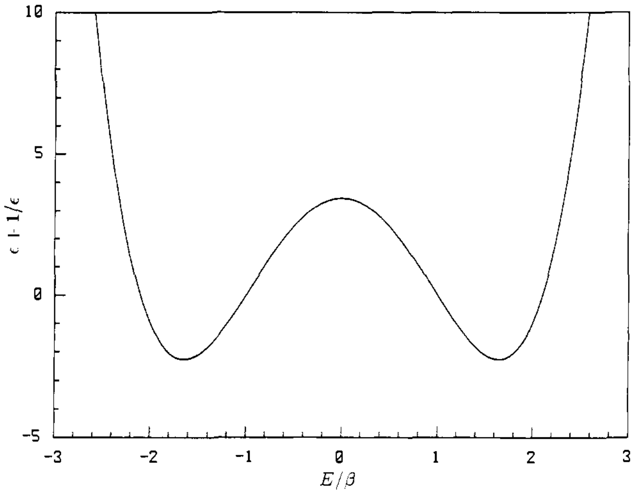

Figure 14. $\epsilon + 1/\epsilon$–E/β relation for para-poly(phenyl) when $\nu = \cos 50°$. ν is the ratio of the inter-ring (γ) to intra-ring exchange (β) interactions.

For *n*-alkane, the full (bonding and antibonding) band structure is calculated from eq A.1. β_{CH} is the carbon sp^3 orbital exchange

$$\det \begin{pmatrix} -E & \gamma + \beta/\epsilon & 2\gamma & 0 \\ \gamma + \beta\epsilon & -E & 2\gamma & 0 \\ \gamma & \gamma & \gamma - E & \beta_{CH} \\ 0 & 0 & \beta_{CH} & \alpha_H - E \end{pmatrix} = 0 \qquad (A.1)$$

interaction with hydrogen, and α_H is the diagonal energy of hydrogen relative to carbon sp^3. Figure 12 plots this equation for[1a] $\beta_{CH} = -9.14$ eV, $\beta_{CC} = -8.5$ eV, and $\alpha_H = 0.35$ eV.[1c] Also shown is a plot of eq 3.1a (offset by 8.5 eV).

Para-poly(phenyl) (Figure 13) is a linker of increasing interest.[15,16] It is difficult to obtain quantitative predictions for unsaturated linkers because, in contrast to the saturated linker problem, a consistent set of experiments does not exist on which we can "normalize" ϵ for a given tunneling energy. Also, dynamical effects due to phenyl ring rotation may be significant in

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systems without locked geometries. For para-poly(phenyl) chains we find eq A.2 for the geometry of rings in Figure 14. The interaction between p orbitals in the ring is β, and the interaction between p orbitals on atoms connecting the rings is γ. The ratio of these quantities is $\nu = \gamma/\beta$.

$$\epsilon + \frac{1}{\epsilon} = \frac{(E/\beta)^4 - (E/\beta)^2(5 + \nu^2) + (4 + \nu^2)}{2\nu} \qquad \text{(A.2)}$$

Because the HOMO-LUMO gap is a few electronvolts in these systems and ν is on the order of the cosine of the angle between the rings, the small backscattering approximation is most likely not generally appropriate. Taking $\nu = \cos 50°$, the equilibrium geometry of biphenyl, we find the E-ϵ relation shown in Figure 14. The maximum decay of the rate with distance occurs for the tunneling energy at the center of the gap ($E = 0$) where

$$\epsilon(E = 0) = \nu/2 \qquad \text{(A.3)}$$

For a 50° angle, therefore, the rate is expected to change by no more than a factor of 10 per ring. Because of the relatively small band gap, ϵ (and hence the distance decay of the rate) may be considerably different for (photoinduced) forward transfer compared to reverse (thermally activated) electron transfer in these systems.

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ESR Studies of the Thietane and Thiirane Radical Cations in Freon Matrices. Evidence for Ethylene Molecule Extrusion from the σ^* Thiirane Dimer Radical Cation [$C_2H_4S{-}SC_2H_4^{\cdot+}$]

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Abstract: ESR spectroscopy has been used to study the structures and reactions of the radical cations produced from the three- and four-membered sulfur-containing ring compounds, thiirane and thietane, the radical cations being generated by γ irradiation of dilute solutions of the parent compounds in Freon matrices at 77 K. With use of $CFCl_3$ as the matrix, the monomer radical cations have been identified and characterized as having $^2B_1$ ring-closed structures with the unpaired electron localized on the sulfur atom. The hyperfine coupling to the four equivalent β-hydrogens in the thietane cation (31.1 G) is normal, but the corresponding value for the thiirane cation (16.1 G) is lower by almost a factor of 2, suggesting that hyperconjugation to methylene groups is much reduced in three-membered rings. In the more mobile $CFCl_2CF_2Cl$ and CF_3CCl_3 matrices, dimer radical cations of thiirane and thietane are produced by the combination of a monomer radical cation with a neutral molecule at low temperatures (<100 K). ESR studies show that these dimer species are centrosymmetric, the binding between the molecules resulting from the formation of a 3-electron $\sigma^2\sigma^{*1}$ S-S bond. Both of the dimer cations are unstable above 105 K in the $CFCl_2CF_2Cl$ matrix, the thietane dimer radical cation decomposing to give the 2-thietanyl radical as a result of hydrogen atom or proton transfer, whereas the thiirane dimer radical cation undergoes a novel reaction involving the extrusion of an ethylene molecule. Evidence for ethylene formation in the latter reaction comes indirectly from the ESR observation of secondary radicals with the structure RCH_2CH_2 on annealing γ-irradiated solutions of thiirane in $CFCl_2CF_2Cl$. Similar radicals are also generated in γ-irradiated thiirane solutions in CF_3CCl_3 at 145-150 K, the ESR spectrum being indistinguishable from that of identically treated ethylene solutions. The ethylene extrusion is depicted as a concerted reaction in which the driving force is supplied by the transfer of the unpaired electron from the σ^* (S-S) orbital of the dimer cation to a vacant p orbital on the terminal sulfur atom of the remaining $C_2H_4S_2^+$ moiety.

The radical cations of oxirane and aziridine clearly display the extraordinary reactivity that is commonly associated with strained three-membered rings. Thus, it has been shown by ESR studies[1-4] that the respective $^2B_1$ and $^2A'$ ground states of these species resulting from heteroatom lone-pair ionizations are unstable even at 77 K and undergo C⋯C ring opening to give either delocalized[1,2,4] or localized[3] carbon-centered radicals. A similar conclusion regarding the ease of ring opening in the oxirane cation was reached earlier by means of detailed gas-phase studies,[5-7] and additional evidence for this rearrangement comes from the interpretation of electronic absorption spectra associated with the delocalized forms of the ring-opened oxirane and tetramethyloxirane cations.[8,9] Moreover, high-level theoretical calculations predict that the delocalized ring-opened forms of the oxirane[10] and aziridine[11] radical cations are more stable than their ring-closed forms by 19.6 and 26.5 kcal mol^{-1}, respectively, and that the barrier to the ring opening of the oxirane cation is likely to be less than 3.7 kcal mol^{-1}.[12]

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