J. Am. Chem. Soc. 1986, 108, 4321-4326 4321

# Electron Tunneling through Rigid Molecular Bridges: Bicyclo[2.2.2]octane

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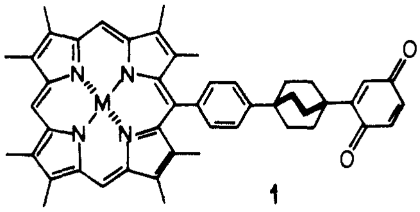
**Abstract**: Electron tunneling through polymers of bicyclo[2.2.2]octane is studied. The repeating nature of the linker allows prediction of the dependence of the tunneling matrix element on distance and electronic energy by a semiempirical method exploiting the translational symmetry of the linker. Specific predictions for the dependence of rate on distance are made for recently synthesized photosynthetic model compounds containing porphyrins and quinones linked by this bridge. A large difference between the decay of rate with distance is predicted for the forward electron transfer in these model compounds compared with the reverse electron transfer. The effects of linker topology on the donor–acceptor interaction in several linkers are compared, and a heuristic rule is quantitated. The ability of the [2.2.2] linker to mediate the donor–acceptor interaction is shown to have an energy dependence determined by the symmetry of the donor and acceptor orbitals *relative* to the linker orbitals.

Electron-transfer reactions between distant weakly interacting sites are of interest in many fields of chemistry.[1] The electronic interaction between donor and acceptor together with the nuclear activation barrier determines the transfer rate. The quantum mechanical expression for the rate when the donor and acceptor weakly interact is[2] as in eq 1 in the Born–Oppenheimer/Franck–Condon formulation. The tunneling matrix element, $T_{ab}$,

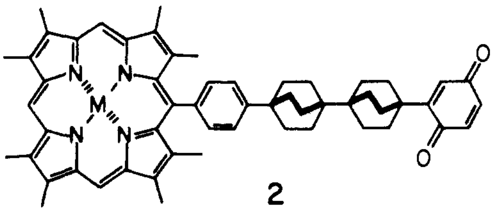
$$k = (2\pi/\hbar)|T_{ab}(E,R)|^2(F.C.) \qquad (1)$$

is the electronic-exchange interaction energy between donor and acceptor. ($F.C.$) is the thermally weighted Franck–Condon factor discussed elsewhere.[2-4] $T_{ab}$ is determined by the distance between donor and acceptor ($R$) and the energy ($E$) of the tunneling electron. $E$ is determined by the orbital energies of the occupied donor and vacant acceptor orbitals, the energetic proximity of these states to the bonding and antibonding state of the isolated bridging orbitals, and the nature of the coupling between electronic and nuclear motion on the donor and acceptor.[2-15] In the Born–Oppenheimer/Franck–Condon formulation of the problem, $T_{ab}$ has a single decay length for a reaction at fixed $\Delta G$, although as $\Delta G$ is changed the decay length may vary.[14,15] In some extremely long distance transfers, this simple separation of electronic and nuclear motion is not possible.[14,15] If the appropriate weighted average of the donor and acceptor orbital energies (determined by the Franck–Condon approximation) is considerably closer to the highest occupied bonding orbital energy than the lowest unoccupied antibonding orbital energy of the isolated bridge, "hole transport" is said to dominate the charge-transfer process.[7,16] If the energy is closer to the lowest antibonding states of the linker, "electron transport" is dominant. When one of these limits obtains, simplified models which generate single "bands" of linker states can often be used to fit the energy dependence of the bridge-mediated donor–acceptor interaction determined by the more detailed calculation described in this paper. When such approximate (often one orbital per repeating bridge unit) models are used, they are only appropriate over limited ranges of electronic energy. Depending on whether the electron or hole tunneling limit is valid, one expects a different relation between the decay of the donor–acceptor interaction with distance in a forward photoinitiated electron transfer compared to the reverse charge recombination.

When the donor–acceptor distance is large and the mediating bridge is linear with identical repeating units, $T_{ab}$ decays approximately exponentially with distance. $T_{ab}(E,R)$ critically depends on the geometry and energetics of the linker.[4] Recent synthesis and measurements of the electron-transfer kinetics in **1** and **2** where M = Zn now make theoretical studies on the bicyclo[2.2.2]octane linker ([2.2.2]) timely.[17-19]



**1**



**2**

## Theoretical Section

**A. General Aspects.** Recently, a method was developed to predict the electronic energy and bridging ligand effects on the distance dependence of nonadiabatic electron-transfer reactions.[7] The method guarantees proper wave function tail decay in the linker region, exploiting the fact that within the linker the electron effectively propagates in a one-di-

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mensional periodic potential. A scale linking the redox potential ($E^\circ$) of the transferring electron with the distance decay[3-12] of $T_{ab}$ was established for several bridging groups.[7] This method can be used to quickly predict the decay of $T_{ab}$ with distance as the chemical properties of the donor, acceptor, and bridge are changed. We now extend this technique to predict the decay of electron-transfer rate with distance between $\pi^*$ and $\pi$ orbitals connected by oligomers of the rigid bicyclo[2.2.2]octane unit. The electron-mediation properties of this bridge are compared with those of linear and spiro-cyclic alkanes. Predictions are made for the distance dependence of forward and reverse electron transfers in the rigid porphyrin–linker–quinone compounds recently synthesized.[17,18] The appeal of this method is that a single calculation predicts the decay of $T_{ab}$ with distance for thermal and photoinitiated electron transfer between appropriate sets of donors and acceptors connected by these linkers. The only experimental parameters needed to calculate the decay lengths of $T_{ab}$ are the redox potentials of the donor and acceptor states.

Neglect of non-nearest-neighbor interactions between orbitals and formulation of the problem in a one-electron (extended Hückel or tight binding) framework provides the donor and acceptor wave functions needed to calculate $T_{ab}$. The linker region is classically forbidden for the donor- and acceptor-localized states. In order to calculate a transfer rate, one needs the eigenfunctions of the donor-plus-bridge Schrödinger equation and the acceptor-plus-bridge Schrödinger equation. One could equally notice that a single "hole" is being transferred from electron acceptor to electron donor and calculate "hole" wave functions to determine the matrix element. Working with electronic states, the decay of the donor-localized electronic state within the linker is parametric in $E$, the donor electronic energy at which the Franck–Condon approximation tell us to calculate the tunneling matrix element (accounting for the energy of the vacant acceptor orbital and the vibronic coupling on both sites).[13] Once the donor wave function distance decay is known as a function of energy, the decay of the rate is also known. The "direct" donor–acceptor interaction is generally assumed to be much smaller than the orbital-meditated interaction in bonded systems. As such, the donor–acceptor interaction is mediated by mixing of the localized states with the bonding and antibonding linker orbitals. The terms "electron" and "hole" tunneling are used when the donor–acceptor interaction is mediated predominantly by the antibonding or bonding states of the linker, respectively. Such a dominance can be understood from perturbation theory. Mixing of the donor orbitals with the linker involves, to first order, orbital amplitudes on the $i$th bridge molecular which scale as $1/[E(\text{donor}) - E_i(\text{bridge})]$. If, say, the energies of the antibonding linker states are much further from the donor and acceptor orbital energies than are the bonding states, one could model the process with a single group (band in the long chain limit) of linker orbitals. In this case one would have to consider many electrons and *one* hole. Because of the single hole, this exchange is referred to as "hole transport" even though any transport process formally involves an electron moving in one direction and a hole in the opposite direction. Such a simplification was not employed in this work, but the terminology is indeed useful.

The analysis of [2.2.2] closely follows the previous study of electron mediation by spiroalkane linkers. The critical assumption is that oligomers of the linker create a periodic potential in which the well-localized electron propagates in its low probability "tail". One can use a periodic potential representation because the propagation of a wave function in a region does not depend on the potential outside of that region. The fact that the linker is of finite length does not complicate the problem if the wave function decay per unit of the bridge is large.

The dependence of the tunneling matrix element on distance in thermal electron transport reactions has been found in related systems by calculating the symmetric/antisymmetric splitting of the electronic states at the point on the reagent and product nuclear potential energy surfaces determined by the Franck–Condon approximation.[7] A golden-rule/perturbation approach also gives the proper distance dependence of the rate.[3] The latter formulation is more convenient at present.

**B. Donor-plus-Bridge Wave Functions and $T_{ab}$.** Wave functions in *finite* molecular systems with regions of one-dimensional and repeating bridge units of size $|\vec{a}|$ are of the form of eq 2 in the region of translational symmetry.[13,20] $\vec{x}$ is the electronic coordinate, and $\epsilon(E)$ is an energy-de-

$$\psi^{\text{bridge}}(\vec{x}) = \sum_{j=1}^{N} \{b_E \epsilon(E)^j + c_E \epsilon(E)^{N-j+1}\} \phi_j(\vec{x} - j\vec{a}) \tag{2}$$

pendent constant. In the tight-binding (LCAO) approximation, $\phi_j$ is a linear combination of atomic orbitals centered on the atoms of the $j$th bridge unit. The wave function involves growing and decaying parts for the same reason that the wave function in a constant potential region between square wells includes growing and decaying exponentials regardless of the relative depths of the wells. In the limit that the number of bridging orbitals ($N$) becomes very large, $c_E \rightarrow 0$ and $\epsilon$ is the Bloch factor by which the wave function changes upon translation by one repeating unit ($|\epsilon| = 1$ for delocalized states and $|\epsilon| < 1$ for the localized states of interest).[13] In this case, wave function propagation in the bridge behaves like the orbital analogue of wave function propagation in a Kronig–Penney potential.[20] $\epsilon(E)$ may be real or complex depending on the energy of the donor localized state. The $\epsilon - E$ relation is determined by the energetics and topology of the bridge's repeating unit and is calculated in Appendix sections 2 and 3 for the [2.2.2] and other linkers. To the extent that electron traps perturb this otherwise periodic system in a localized region and edge effects are not large (valid when $\epsilon^N \ll 1$), the functional form of $\Psi$ (donor + bridge) becomes eq 3. $\Phi^d(\vec{x})$ is the

$$\Psi(\vec{x}) = \Phi^d(\vec{x}) + \zeta\psi^{\text{bridge}}(\vec{x}) \simeq \Phi^d(\vec{x}) + \zeta \sum_{j=1}^{N} \epsilon(E)^j \phi_n(\vec{x} - n\vec{a}) \tag{3}$$

donor molecular orbital in the absence of the bridging group. Edge effects are especially small if the electron has a small probability of residing near the "wrong" trap in the initially prepared state. Independent of whether the $c_E$ term in eq 2 may be neglected to write eq 3, the $E$–$\epsilon$ relation derived for an infinite chain of bridging units is also valid for finite one-dimensional systems.

At this point a divergence between this method and other perturbational approaches for wave function calculation is apparent. Here the requirements of Bloch's theorem are built into the wave functions. A single calculation of $E$ vs. $\epsilon$ for a given linker produces all wave function tails of interest for a given linker. Most variational approaches form the donor wave function from a linear combination of ground and excited bridge states and donor orbital(s) and find the orbital coefficients by energy minimization. This method can give basis-set-dependent results which are not easily compared for different compounds.

The tunneling matrix element in the Born–Oppenheimer separation is calculated for the electronic states which solve the Schrödinger equations (4a) and (4b). $T_e$ is the electronic kinetic energy operator, and $V$

$$H_D{}^{el}\Psi_D = E_D{}^{el}\Psi_D; \qquad H_D{}^{el} = T_e + V_B + V_D \tag{4a}$$

$$H_A{}^{el}\Psi_A = E_A{}^{el}\Psi_A; \qquad H_A = T_e + V_B + V_A \tag{4b}$$

is the potential on the donor (D), acceptor (A), or bridge (B). Neglecting overlap we find eq 5. $|V_A\ \Psi_A>$ is localized in the acceptor region and is, to an excellent approximation, distance independent. The distance-

$$T_{ab} \simeq <\Psi_D|V_A|\Psi_A> \propto \epsilon(E)^N \tag{5}$$

dependent part of this matrix element is, then, proportional to $\epsilon(E)^N$. $N$ is the number of repeating units in the bridge. In the LCAO approach, the perturbation which promotes transfer is $\beta'(a_N{}^\dagger a_{\text{acceptor}} + a_{\text{acceptor}}{}^\dagger a_N)$ and the $\epsilon^N$ decay of $T_{ab}$ with distance is nearly exact.[13] $a^\dagger$ and $a$ are the fermion creation and annihilation operators. Their subscripts define the orbital on which the electron is created or destroyed (e.g., $a_N{}^\dagger$ creates an electron on the $N$th [2.2.2] unit in the bridge adjacent to the acceptor). The donor-bridge and acceptor-bridge interactions are transfer distance *independent* and enter $T_{ab}$ only as constant prefactors. Being only interested in the *change* of rate with distance, we are not concerned with the actual magnitudes of these interactions. Delocalization of the excited porphyrin electron into the meso phenyl group is also independent of linker length.

The value of $E$ specified by the Franck–Condon approximation ($E^\ddagger$) is some value between $E_d$ and $E_a$, the electronic orbital energies of the unperturbed donor and acceptor.[5] $E^\ddagger$ is the average of these energies if the vibronic couplings on the donor and acceptor are identical. This is likely a good approximation when the transfer occurs between structurally similar molecules. However, since both inner- and outer-sphere reorganization energies scale with molecular size, $E^\ddagger$ need not be proportional to the average of the donor and acceptor redox potentials (see eq 7).[15]

**C. Wave Function Symmetry and Decay in Bicyclo[2.2.2]octane.** Following ref 7 the dependence of the wave function decay on energy is found for propagation through bicyclo[2.2.2]octane chains. It was shown for linear and spiroalkanes that the decay constant may, to an excellent approximation, be found by considering the carbon backbone orbitals only. Within the weak donor-bridge interaction approximation, the donor orbital mixes with the bridging orbitals through the nearest atomic orbitals of the two subunits which have a non-zero interaction. The porphyrin–linker interaction is determined by the $\pi$ symmetry of the electron donor. There is a symmetry axis joining the two quaternary carbons in each [2.2.2] unit. If the terminal donor orbital were even with respect to rotations about this axis (e.g., s or $d_{z^2}$ atomic orbitals), it would mix

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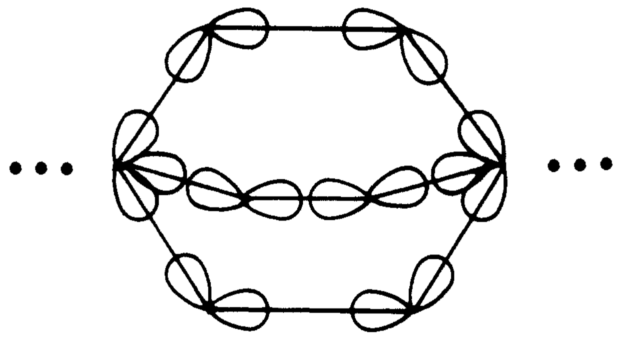

**Figure 1.** Carbon backbone orbitals participating in electron transfer of **1** and **2**.

**Table I.** Redox Potentials for Model Zinc Porphyrin and Quinone[a]

| solvent | $E_{1/2}$ (Q/Q$^{-\bullet}$) NHE, V | $E_{1/2}$ (P/P$^{+\bullet}$) NHE, V |
|---|---|---|
| acetonitrile | −0.40 | +0.74 |

[a] Calculated from experimental data measured vs. a ferrocene/ferrocenium reference.[18]

directly with the sp$^3$ carbon orbital of the [2.2.2] bridgehead and electron mediation would proceed with equal amplitude and sign along the three pathways of the linker (see Appendix section 3). However, the porphyrin excited state is not cylindrically symmetryic, and mixing of the donor with the three pathways is not equal. In the coordinate system shown in Figure 1 the donor p orbital may mix only with the two p orbitals at the bridgehead orthogonal to the axis between quaternary carbons. It is simpler to speak of the associated sp$^3$ hybrid bridge orbitals. These bridge orbitals in turn interact with adjacent sp$^3$ backbone orbitals. The size of the $p_z$(donor)–sp$^3$(bridge) interaction varies with the angle between the bridgehead orbitals and the donor orbital according to eq A1. The appendix shows that decay with *distance* is identical in both the staggered and eclipsed chains of [2.2.2].

Little mixing of the porphyrin excited donor state occurs with the $\sigma$ bond joining linker to porphyrin. Hence little direct $\sigma$ interaction between bridgeheads occurs. Such a bridgehead-to-bridgehead pathway may be more important with $\sigma$ symmetry donors and acceptors joined by similar linkers.[21]

Analysis of experimentally measured electron-transfer rates as a function of distance may require that the data first be corrected for effects expected due to a change in reaction energetics with distance. Outer-sphere reorganization energies and donor–acceptor Coulombic interactions are transfer distance dependent. Direct comparisons of transfer rates from the *singlet* excited state may not be made with rates from the *triplet* excited state without correcting for the rate difference arising from the different reaction free energies. Using the connection between the Hückel parameters and the redox potentials,[7] the donor-state wave function decay per linker unit ($\epsilon(E)$) is predicted in Appendix section 2 for [2.2.2].

The redox properties of the donors and acceptors have been measured.[18] The outer-sphere reorganization energy arising from solvent reorientation near a trap scales as the reciprocal of the trap's radius if Coulombic interactions are neglected. The inner-sphere reorganization energy scales as the reciprocal of the number of bonds over which the electron is delocalized. The smaller the reorganization energy associated with a given site, the closer the energy of transfer will be to the redox potential of that isolated species.[5,15] Table I shows the redox properties of the model compound in acetonitrile. The properties vary somewhat with solvent, but not in ways that alter the calculated $\epsilon(E^\ddagger)$ significantly.

The spectral function for electron removal from the donor when damping is strong enough so that the density of states is continuous is in eq 6[5,15] where $\lambda_d$ is the donor reorganizational energy and $T_{\text{eff}}$ is a function of donor vibrational frequency and temperature. If the frequency of the mode on the acceptor is identical, replacing $\lambda_d$ with $-\lambda_a$ in the exponential and $\lambda_d$ with $\lambda_a$ elsewhere, the acceptor electron insertion spectral function $D_a'(E)$ is generated.

$$D_d(E) \propto (2\pi\sigma_d^{\,2})^{-1/2} \exp[-(E - E_d + \lambda_d)^2/(2\sigma_d^{\,2})]$$

$$\sigma_d^{\,2} = \lambda_d T_{\text{eff}} \tag{6}$$

Assuming that $\lambda_d$ and $\lambda_a$ are inversely proportional to molecular size, the peak of $D_d(E)D_a'(E)$ occurs at the position shown in eq 7 and has been further estimated for the experimental systems. This is the $E^\ddagger$ specified by the Franck–Condon approximation.

$$E^\ddagger = \frac{\lambda_a E_d + \lambda_d E_a}{\lambda_a + \lambda_d} \simeq \frac{2}{3}E^\circ(\text{P}^*) + \frac{1}{3}E^\circ(\text{Q}) \tag{7}$$

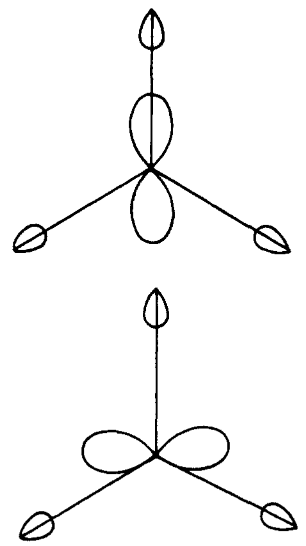

**Figure 2.** View along the donor–linker bond. The two terminal donor (phenyl substituent) atomic p orbitals into which the donor atomic orbital nearest the bridge may be decomposed are shown.

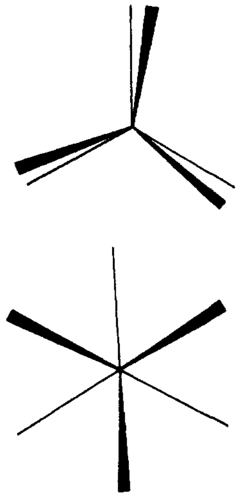

**Figure 3.** Staggered and eclipsed geometries of adjacent repeating [2.2.2] units.

**Table II.** $E^\ddagger$ for Model Zinc Porphyrin and Quinone[a]

| solvent | $\Delta G_\infty^{\text{for}}(\text{S}_1)$, eV | $E^\ddagger(\text{S}_1)$ NHE, V | $\Delta G_\infty^{\text{for}}(\text{T}_1)$, eV | $E^\ddagger(\text{T}_1)$ NHE, V |
|---|---|---|---|---|
| acetonitrile | −1.01 | −1.1 | −0.66 | −0.84 |

[a] Calculated from Table I and eq 7. $\Delta G_\infty$ neglects electrostatic interactions between donor and acceptor. S and T refer to transfer from the lowest excited singlet and triplet states of the porphyrin.

**Table III.** Energies of Reverse Electron Transfers

| solvent | $\Delta G_\infty^{\text{rev}}$, eV | $E^\ddagger$ NHE, V |
|---|---|---|
| acetonitrile | −1.14 | 0.36 |

**Table IV.** Decay Constants for Forward and Reverse Electron Transfer

| parameter | $(\text{S}_1)E_{\text{for}}^{\ddagger} =$ −1.0 V[a] | $(\text{T}_1)E_{\text{for}}^{\ddagger} =$ −0.84 V | $E_{\text{rev}}^{\ddagger} =$ +0.36 V |
|---|---|---|---|
| $\epsilon^{1/4}$ | 0.40 | 0.42 | 0.60 |
| $\epsilon^2 = k_{\text{LL}}/k_{\text{L}}$[b] | $1500^{-1}$ | $1000^{-1}$ | $59^{-1}$ |
| $\alpha_{\text{av}}$, Å$^{-1}$ | 0.91 | 0.87 | 0.51 |

[a] vs. NHE. [b] LL refers to compound **2** and L to compound **1**.

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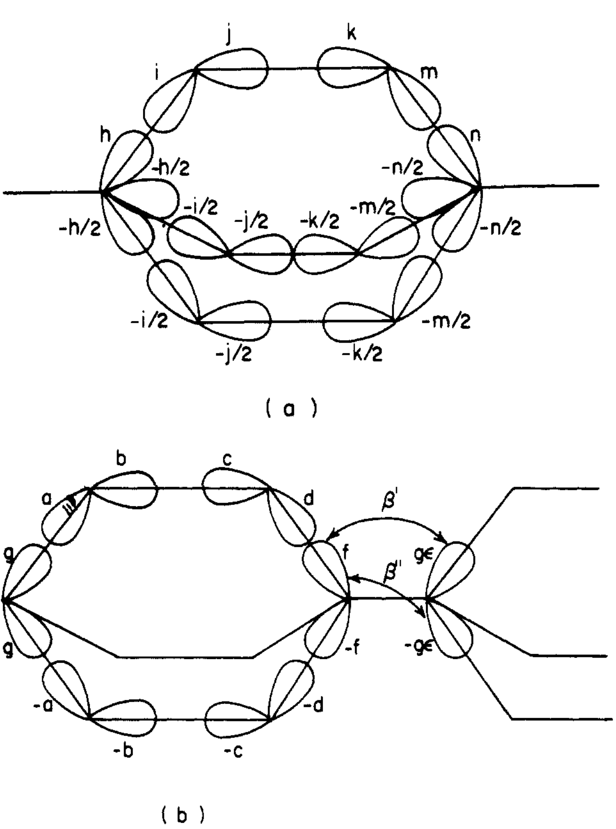

Figure 4. Bridging orbitals included in the calculation for (a) even symmetry and (b) odd symmetry donors and acceptors with respect to a plane containing one of the three parallel pathways of the linker.

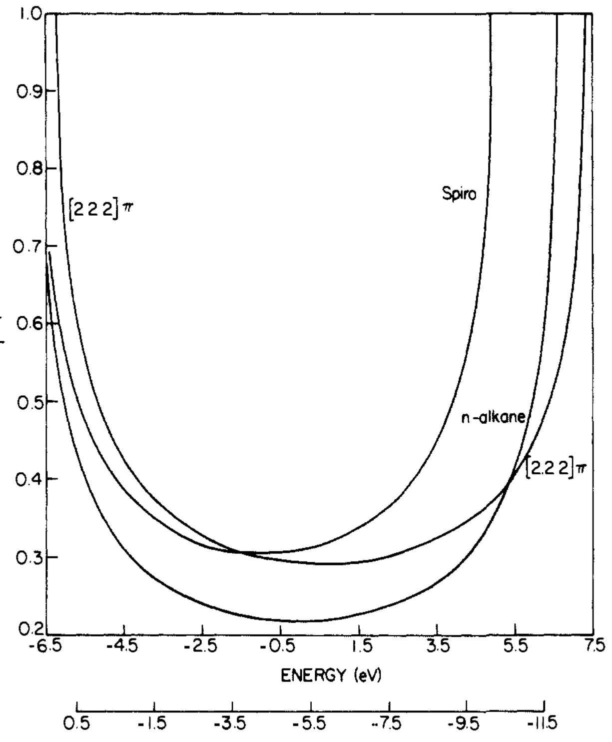

Figure 5. $\epsilon' = \epsilon_{\text{alkane}}, \epsilon_{\text{spiro}}^{1/2}$, and $\epsilon_{[2.2.2]}^{1/4}$ as a function of energy. The calculation is relevant to odd symmetry donors and acceptors for [2.2.2] but even symmetry donors and acceptors for the other linkers. The center of the band gap for [2.2.2] is found to be different from that of the other linkers.

The first excited singlet porphyrin state is ~2.15 eV above the ground state. The lowest triplet state is ~1.8 eV above the ground state.[18] The values of $E^{\ddagger}$ (eq 7) and $\epsilon(E)$ (Figures 5 and 6) for the two excited porphyrin states in acetonitrile, and forward and reverse electron transfer

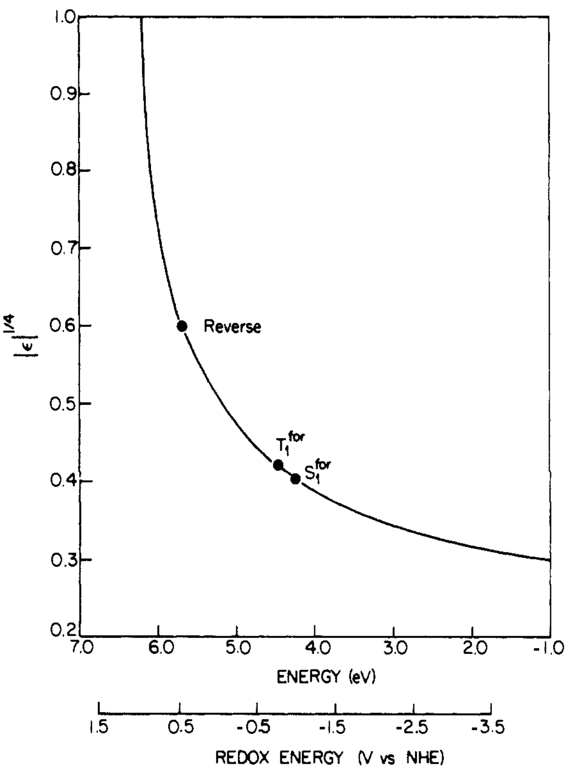

Figure 6. $E$–$\epsilon^{1/4}$ relation for [2.2.2] in the range of experimental interest. The energies of forward transfer from the singlet and triplet P* states are shown as well as the energy for $Q^{-\bullet}$ to $P^{+\bullet}$ transfer. $k_{LL}/k_L \propto (\epsilon^{1/4})^8$ for the reactions in the model systems.

are shown in Tables II and III. Table IV shows the corresponding rate predictions. In principle, entropic effects can enter the electronic factor by changing the choice of $E^{\ddagger}$.

$\epsilon(E)$ is calculated for the [2.2.2] linker in Appendix sections 2 and 3. The only parameter, $E^{\ddagger}$, needed to predict the distance dependence of the transfer rate is found by using the electrochemical data and the estimated relative reorganization energies of the donor and acceptor. The connection between the calculated orbital energies and the redox potentials was established in ref 7. Since $\alpha \approx a^{-1} \ln [(\epsilon(E^{\ddagger})]$ where $T_{ab} = A \exp(-\alpha R)$, the decay of the tunneling matrix element with distance may be read directly from Figure 6 for tunneling between $\pi$ symmetry donors and acceptors through [2.2.2] oligomers. $\epsilon(E)$ for electron transport from singlet or triplet states of other porphyrins to quinones is also readily found. $E^{\ddagger}$ is first calculated by using eq 7 and $E°(P^*)$ estimated as $E_{1/2}(P) + h\nu$ where $h\nu$ is estimated from the porphyrin optical absorption spectrum.[18] This calculation of $E°(P^*)$ neglects entropic contributions to the free energy of reaction due to differences in the geometry of the ground and excited potential energy surfaces. Based on the extreme symmetry of porphyrin absorption and emission spectra, such contributions to the free energy of reaction are likely to be quite small. For the zinc porphyrin, the decay of $T_{ab}$ with distance is not predicted to be drastically different for the singlet and triplet transfers. $\epsilon(E)$ was also calculated for $\sigma$ symmetry donors and acceptors (see eq A5 and Figure 7).

## Discussion

Electron tunneling following porphyrin excitation is mediated principally by the bonding states of the linker based on the known electrochemical data for the donors and acceptors. Figure 6 shows the relative energetics of the donor, acceptor, and bridge. This energetic situation results because the porphyrin is excited with a quantum of energy small compared to the HOMO-LUMO energy gap of saturated alkane. In this case, as in the case of the intervalence and thermal transfer between bridged metallic species,[22-24] the transfer mechanism is expected to be "hole tunneling" or superexchange via the occupied binding levels of

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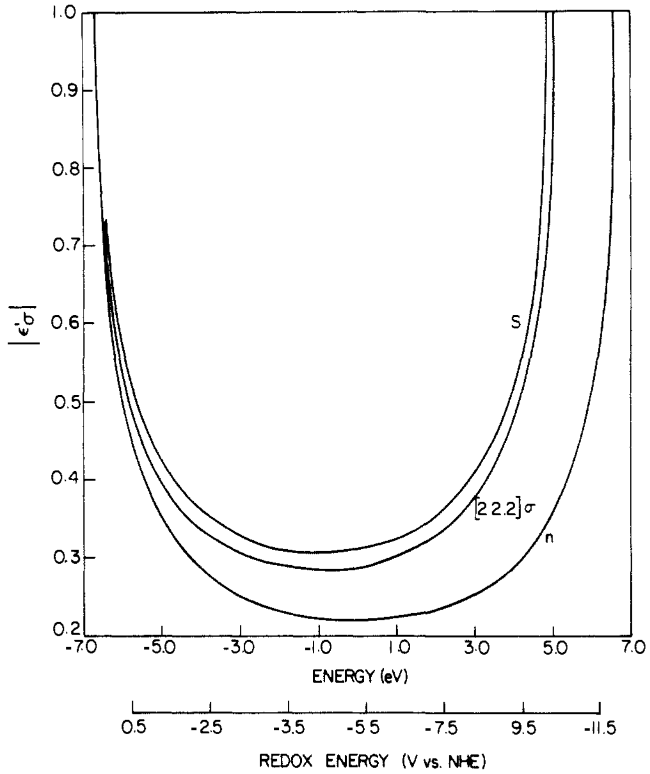

**Figure 7.** Even symmetry donor $E$–$\epsilon$ relations for $n$-alkane, spiroalkane, and [2.2.2].

the bridge.[25] This prediction can be tested experimentally. Raising the energy of the excited porphyrin moves the energy of the tunneling electron away from the linker bonding states and is expected to cause $T_{ab}$ to decay more *quickly* with distance. The absolute rate, however, may be quite different due to a change in the reaction exothermicity. This prediction runs counter to the notion that the more excited a state is, the more "loosely" bound is its electron. Here "looseness" arises only from favorable wave function overlap with the bridge and is decreased by an increase in the energy of the donor state. The reverse rate ($Q^{-\bullet}$ to $P^{+\bullet}$) is predicted to decay *much more slowly* with distance than the forward rate for the same reason. An alternative test of hole tunneling would involve initially reducing the quinone and measuring the back transfer from $Q^{-\bullet}$ to $P^*$ by fluorescence or phosphorescence quenching following a light flash. Writing $T_{ab} = A\ \exp(-\alpha R)$, $\alpha^{for}/\alpha^{rev} \simeq 1.8$ for the ZnPL$_n$Q model system.

Only staggered or eclipsed geometries of the $\pi$ cloud with one of the three electron-transfer pathways of the bridge were considered. Decay with distance is identical in each case. Any donor configuration may be decomposed into a linear combination of these geometries. Thus, the decay with distance of the donor state along the linker obeys the same $E$–$\epsilon$ relation independent of donor–acceptor orientation. No interference effects occur. Aside from the jumps between bridghead orbitals, the parallel pathways assist transfer compared to a purely linear network.

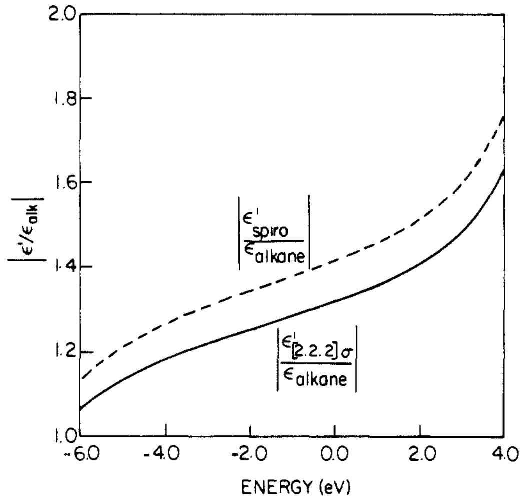

**Figure 8.** Even symmetry donor and acceptor $E$–$\epsilon$ relation compared for alkane, spiroalkane, and [2.2.2]. The gap center occurs at $E = 0$.

A direct comparison of tunneling predictions for spherically symmetric donors[7] is not meaningful because the p orbitals of the donor and acceptor cannot mix with all atomic orbitals of the linker. This causes a shift in the energy of the apparent HOMO–LUMO gap center because energetically different linker states are involved with the electron mediation. Figure 8 shows a calculation for $n$-alkane, spiroalkane, and bicyclo[2.2.2]octane linkers where only even symmetry (with respect to all mirror planes) donors and acceptors were considered. Appendix section 3 gives the determinantial equation relating $E$ to $\epsilon$ in that case. This is not the case of current experimental interest. A heuristic rule for the relative values of $\epsilon'$ (*decay per C–C bond* in the linker unit) might have been as shown in eq 8 based on the topology of the unit cells. These relationships are true *only* in the center of

$$\epsilon'(\text{alkane}) = x$$

$$\epsilon'(\text{spiroalkane}) = x2^{1/2}$$

$$\epsilon'(\text{bicyclo[2.2.2]octane}) = x3^{1/4} \qquad (8)$$

the band gap for the $\sigma$ symmetry donors. However, the *relative* values of $\epsilon$ for spiro and [2.2.2] hold throughout the band gap (Figures 7 and 8). Comparison is not made between the even symmetry alkane and spiroalkane chains and the odd symmetry [2.2.2] system because the inter-unit cell interactions are qualitatively different (as noted above). A test of the relative $\sigma$ mediation by these linkers awaits construction of rigid systems with $\sigma$ symmetry donors and acceptors.

## Conclusions

Predictions of the decay of the tunneling matrix element with distance for electron mediation by bicyclo[2.2.2]octane have been made assuming that the linker creates a periodic potential between donor and acceptor with one or two repeating units. Mediation by CH bonds and non-nearest-neighbor interactions was neglected. Predictions for the thermal electron-transfer rate dependence on the number of bicyclo[2.2.2]octane linkers were made for transfer in zinc *meso*-phenyloctaethyl-linker$_n$-benzoquinone. Hole transfer is predicted to dominate in these systems, suggesting that the reverse transfer will decrease more slowly with distance than the forward transfer. Porphyrins with higher energy excited states are expected to have more rapid wave function decay with distance in the linker. Writing $T_{ab} \propto \exp(-\alpha R)$ with $\alpha$ in inverse angstroms and distance measured through space, $\alpha^{for} \simeq 0.9$ Å$^{-1}$ and $\alpha^{rev} \simeq 0.51$ Å$^{-1}$ for ZnPL$_n$Q. No drastic effect of solvent on $\alpha$ is predicted. A slowing of the forward rate from the singlet excited state by a factor of 1500 per [2.2.2] unit is expected. The reverse rate is expected to slow only by a factor of about 60 per linker unit. These predictions come from the parametric dependence of wave function decay in a given linker on the redox potentials of the donor and acceptor. Since $\alpha = -a^{-1} \ln \epsilon(E^{\ddagger})$, predictions for other donors and acceptors separated by [2.2.2] can be made directly from Figures 6 and 7.

**Acknowledgment.** Thanks are due to J. J. Hopfield for discussion of all aspects of this work. I am also grateful to P. B. Dervan, A. D. Joran, and B. A. Leland for making the electrochemical data available prior to publication. This work was supported in part by NSF Grant PCM-8406049.

## Appendix

**1. Interaction of Porphyrin and Quinone with [2.2.2].** Mixing of the porphyrin and quinone states with the bridge is presumed to occur via the adjacent quaternary carbon orbitals. The in-

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[25] Halpern, J.; Orgel, L. *Discuss. Faraday Soc.* **1960**, *29*, 32–41.

teraction between the four $sp^3$ orbitals at the center of a tetrahedron pointed in the (1, 1, 1), (−1, 1, −1), (−1, −1, 1), and (1, −1, −1) directions (a, b, c, and d, respectively) with a p orbital ($p_\perp$) at (1, 1, 1) normal to hybrid a is given by eq A1. $\theta$ is the

$$\langle p_\perp | sp^3(a) \rangle = 0$$

$$\langle p_\perp | sp^3(b) \rangle = -[2/(6^{1/2})] \sin\theta$$

$$\langle p_\perp | sp^3(c) \rangle = -[1/(2^{1/2})] \cos\theta + [1/(6^{1/2})] \sin\theta$$

$$\langle p_\perp | sp^3(d) \rangle = [1/(2^{1/2})] \cos\theta + [1/(6^{1/2})] \sin\theta \quad \text{(A1)}$$

angle between the axes of cylindrical symmetry of the transformed p orbital and one of the p orbitals on the central site normal to the C–C axis. These results were obtained by transforming the hybrid orbitals into s orbitals and p orbitals perpendicular or parallel to the (0, 0, 0)–(1, 1, 1) axis. The transformation equations are (A2).

$$\begin{bmatrix} p_x \\ p_y \\ p_z \end{bmatrix} = \begin{bmatrix} 1/(3^{1/2}) & 1/(2^{1/2}) & 1/(6^{1/2}) \\ 1/(3^{1/2}) & -1/(2^{1/2}) & 1/(6^{1/2}) \\ 1/(3^{1/2}) & 0 & -2/(6^{1/2}) \end{bmatrix} \begin{bmatrix} p_\sigma \\ p_{\pi a} \\ p_{\pi b} \end{bmatrix} \quad \text{(A2)}$$

**2. Propagation in the Linker.** The donor(acceptor) p orbital adjacent to the linker may be converted to a linear combination of p orbitals staggered and eclipsed with the ring. When only the two geometries in Figure 2 are considered, the wave function of the donor plus bridge must be odd with respect to the nodal plane of the donor p orbital (see also eq A1). Propagation between neighboring [2.2.2] units is identical when the neighboring rings are fully eclipsed or fully staggered (recall that the only bridgehead orbitals contributing to the wave function are the p orbitals perpendicular to the bridgehead axis).

The determinential equation in *both* cases which determines the $E$–$\epsilon$ relation is eq A3.

The relation is identical for the even and odd wave functions as can be seen in Figure 4. Writing the orbitals on the lower half of the unit cell as symmetrized combinations shows this.

From previous calculations the parameters were chosen as $\beta = -8.47$ eV, $\gamma = -1.85$ eV, and $\beta_{p\pi} = \beta' - \beta'' = -1.325$ eV. $\gamma$ is the energy difference between a p and $sp^3$ orbital.

$$\det \begin{bmatrix} -E & \gamma & 0 & 0 & 0 & \beta \\ \gamma & -E & \beta & 0 & 0 & 0 \\ 0 & \beta & -E & \gamma & 0 & 0 \\ 0 & 0 & \gamma & -E & \beta & 0 \\ 0 & 0 & 0 & \beta & -\gamma - E & (\beta' - \beta'')\epsilon \\ \beta & 0 & 0 & 0 & (\beta' - \beta'')/\epsilon & -\gamma - E \end{bmatrix} = 0 \quad \text{(A3)}$$

The $E$–$\epsilon^{1/4}$ relation corresponding to eq A3 is plotted in Figure 5. The $E$–$\epsilon^{1/4}$ relation shows the average decay of the donor wave function per carbon atom in the linker. The result is compared to the spiroalkane and *n*-alkane results of ref 7. Figure 6 shows an expanded view of the [2.2.2] plot in the region of experimental interest. The redox scale corresponding to this set of parameters was determined in ref 7. The expanded determinantial equation (eq A3) is eq A4.

$$(\epsilon + 1/\epsilon)\beta^3\gamma^2\beta_\pi = +E^6 + E^5(2\gamma) + E^4(-3\beta^2 - \beta_\pi{}^2 - \gamma^2) + E^3(-4\beta^2\gamma - 4\gamma^3) + E^2(\beta^2\beta_\pi{}^2 + \beta^2\gamma^2 + 2\beta_\pi{}^2\gamma^2 + 3\beta^4 - \gamma^4) + E(2\beta^2\gamma^3 + 2\beta^4\gamma + 2\gamma^5) - \beta_\pi{}^2\gamma^4 - \beta^6 + \gamma^6 \quad \text{(A4)}$$

The p orbital of the donor (or acceptor) may be decomposed into two p orbitals, one staggered and one eclipsed with respect to the bridge. At fixed donor and acceptor orientations, the decay of $T_{ab}$ with linker number is known from Figure 5. Only the transfer-distance-independent prefactor is orientation dependent.

**3. $\sigma$ Symmetry Donors.** The $\epsilon$–$E$ relation for donors interacting equally with all three bridges is eq A5. Figure 7 shows the corresponding $E$–$\epsilon^{1/4}$ relation which might be of use with $\sigma$ symmetry donors and acceptors linked by [2.2.2]. Figure 8 compares propagation through such a [2.2.2] linker with propagation through other saturated linkers.

$$\det \begin{bmatrix} -E & \gamma & 0 & 0 & 0 & \beta & 0 & 0 \\ \gamma & -E & \beta & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta & -E & \gamma & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma & -E & \beta & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta & (2\gamma - E) & 0 & 0 & \gamma \\ \beta & 0 & 0 & 0 & 0 & (2\gamma - E) & \gamma & 0 \\ 0 & 0 & 0 & 0 & 0 & 3\gamma & -E & \beta/\epsilon \\ 0 & 0 & 0 & 0 & 3\gamma & 0 & \beta\epsilon & -E \end{bmatrix} = 0 \quad \text{(A5)}$$