Chem. Rev. 1992, 92, 395–410

Analysis of the Interactions Responsible for Long-Range Through-Bond-Mediated Electronic Coupling between Remote Chromophores Attached to Rigid Polynorbornyl Bridges

KENNETH D. JORDAN* and MICHAEL N. PADDON-ROW*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, and School of Chemistry, University of New South Wales, Kensington, NSW, Australia 2033

Received October 11, 1991 (Revised Manuscript Received January 7, 1992)

Contents

I. Introduction

Over the past few years a wide body of experimental[1-3] and theoretical[4-8] data have become available demonstrating that through-bond (TB) coupling,[9] or equivalently, superexchange,[10] can lead to rapid electron transfer (ET) and hole transfer (HT) in donor–bridge–acceptor (D–B–A) compounds. An important development in this area has been the design, synthesis, and characterization of series of rigid D–B–A compounds such as 1–5 shown in the Chart I.[2] In the nonadiabatic weak-coupling limit the rates for ET and HT are given by

$$k_e = 2\pi/\hbar H_e^2\{\mathrm{FCWD}\} \qquad (1)$$

and

$$k_h = 2\pi/\hbar H_h^2\{\mathrm{FCWD}\} \qquad (2)$$

where {FCWD} is a Franck–Condon weighted density of states and H_e and H_h give the electronic coupling between the donor and acceptor groups for electron transfer and hole transfer, respectively.[7,8,11]

We have advocated the use of symmetric model compounds, e.g., 6–10, shown in the inset, for developing a detailed understanding of the factors important for the variation of the electronic coupling on the length and other characteristics of the bridge.[4,12,13] The model compounds offer two advantages over the more complex D–B–A compounds in that they are more amenable to theoretical characterization and their ionization potentials (IP's) and electron affinities (EA's) (at least for those compounds in which the electronic couplings are sufficiently large) can be determined by means of photoelectron spectroscopy (PES) and electron transmission spectroscopy (ETS), respectively.

Figure 1 depicts the relevant potential energy curves for ionization of (or electron attachment to) a symmetrical chromophore–bridge–chromophore system, e.g., one of the dienes 6–10. The ion states are shown in both the diabatic (charge-localized) and adiabatic representations. The techniques of PES and ETS give the splittings between the adiabatic states of the ions (ΔIP and ΔEA for the cations and anions, respectively) at the geometry of the neutral molecule. The ΔIP and ΔEA values, thus determined, may be associated with $2H_h$ and $2H_e$, respectively. These associations are only approximate because the ΔIP and ΔEA values are determined at the geometry of the neutral molecule, while the splittings between the ions at the geometry of the ground-state ion in its symmetric, charge-delocalized structure are usually used to calculate the electronic couplings in eqs 1 and 2. We assume here that the errors introduced by the differences in the geometries are small.

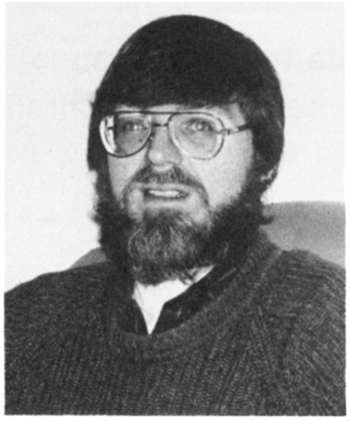
When interpreting experimental data it is often assumed that the electronic coupling for ET or HT in D–B–A compounds falls off exponentially with the "length" of the bridge separating the D and A groups.[1,3,7] With the above-mentioned association of ΔIP and ΔEA with $2H_h$ and $2H_e$, respectively, the former quantities would also be expected to display an exponential dependence on the bridge length as expressed in eqs 3 and 4:[5,12]

$$\Delta\mathrm{IP} = A_h \exp(-\beta_h n) \qquad (3)$$

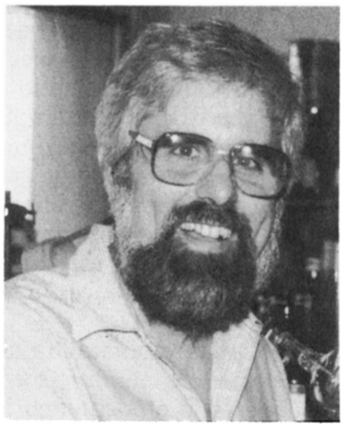
$$\Delta\mathrm{EA} = A_e \exp(-\beta_e n) \qquad (4)$$

where n corresponds to the number of bonds involved in the coupling. For molecules with complex bridges, possessing cross-linkages, e.g., 6–10, there is the question as to how to define n. In this work we associate n with the number of C–C bonds along one side of the main bridges (i.e., those with the shortest paths). For 6–10, the terminal C–C bonds of the bridges do not play a major role in the coupling of the π or π^* orbitals of the ethylenic groups to the bridge, and it is actually more appropriate to view the number of bonds involved in the coupling as ranging from 2 to 10 rather than from 4 to 12. In any case, assuming that eqs 3 and 4 are

0009-2665/92/0792-0395$10.00/0



Kenneth D. Jordan was born in Norwood, MA, in 1948. He received his B.A. from Northeastern University and his Ph.D. in Physical Chemistry from MIT in 1974, under the direction of Robert Silbey. He then spent four years in the Engineering and Applied Science at Yale University, first as a Gibbs Instructor and then as an Assistant Professor. In 1978 he moved to the University of Pittsburgh, where he is a Professor of Chemistry. He has been a visiting scholar at the University of Nebraska and a visiting professor at the University of Utah. In 1984–1985 he served as a Program Director for Theoretical Chemistry at the National Science Foundation. He has received fellowships from the Alfred P. Sloan, Camille and Henry Dreyfus, and Guggenheim Foundations. His research interests include applications of electron transmission and electron energy loss spectroscopy and theoretical studies of long-range intramolecular interactions, electron-transfer processes, properties of atomic and molecular clusters, and chemical reactions on semiconductor surfaces.



Michael N. Paddon-Row was born in Kent, England, in 1942 and received his B.Sc. in Chemistry from King's College, University of London in 1963. He then went "down under" and obtained a Ph.D. in medical chemistry at the Australian National University, Canberra, in 1967, working with Dr. D. J. Brown. After spending a decade at the New South Wales Institute of Technology, he joined the University of New South Wales in 1985, where he is currently a Professor of Chemistry. He has also held visiting professorships at Louisiana State University, Carnegie-Melon University, the University of Pittsburgh, and the University of Amsterdam. His research interests include the synthesis of novel molecules for studying long-range electron and energy transfer, and the application of computational chemistry to problems of molecular structure and reactivity.

valid, the β values are independent of whether or not the terminal C–C bonds are counted. Our recent theoretical studies of **6**–**10** have shown that while ΔIP and ΔEA appear to depend exponentially on n for the compounds with the longer bridges (i.e., **8**–**10**), significant deviations from exponential behavior are found for the dienes with the shorter bridges.[13]

Additional motivation for the study of model compounds such as **6**–**10**, is provided by the expectation

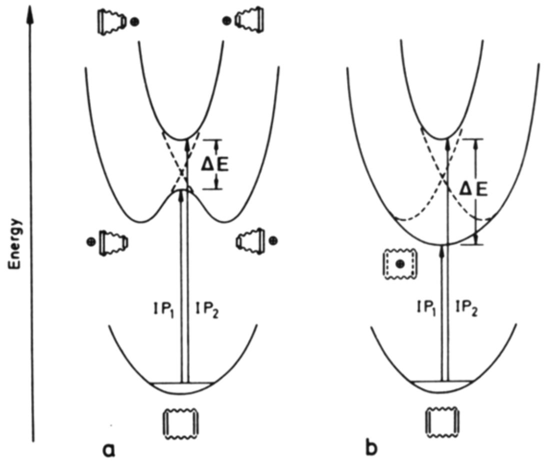


Figure 1. Diabatic (dashed lines) and adiabatic (solid lines) potentials relevant for ionization of a symmetrical ethylene–bridge–ethylene system. The curves on the left represent the weak-coupling limit and those on the right the strong-coupling limit. The reaction coordinate is dominated by the ethylenic C–C stretch. Analogous potentials exist for electron attachment to form the radical anions.

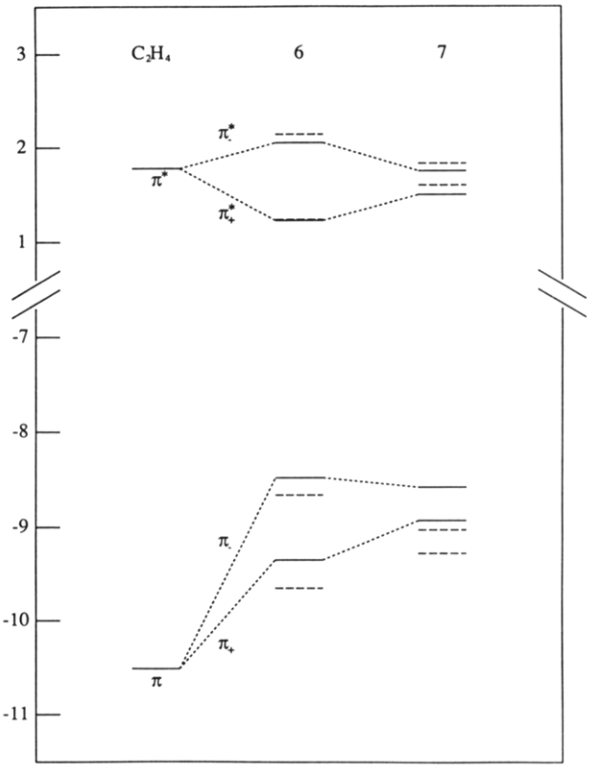
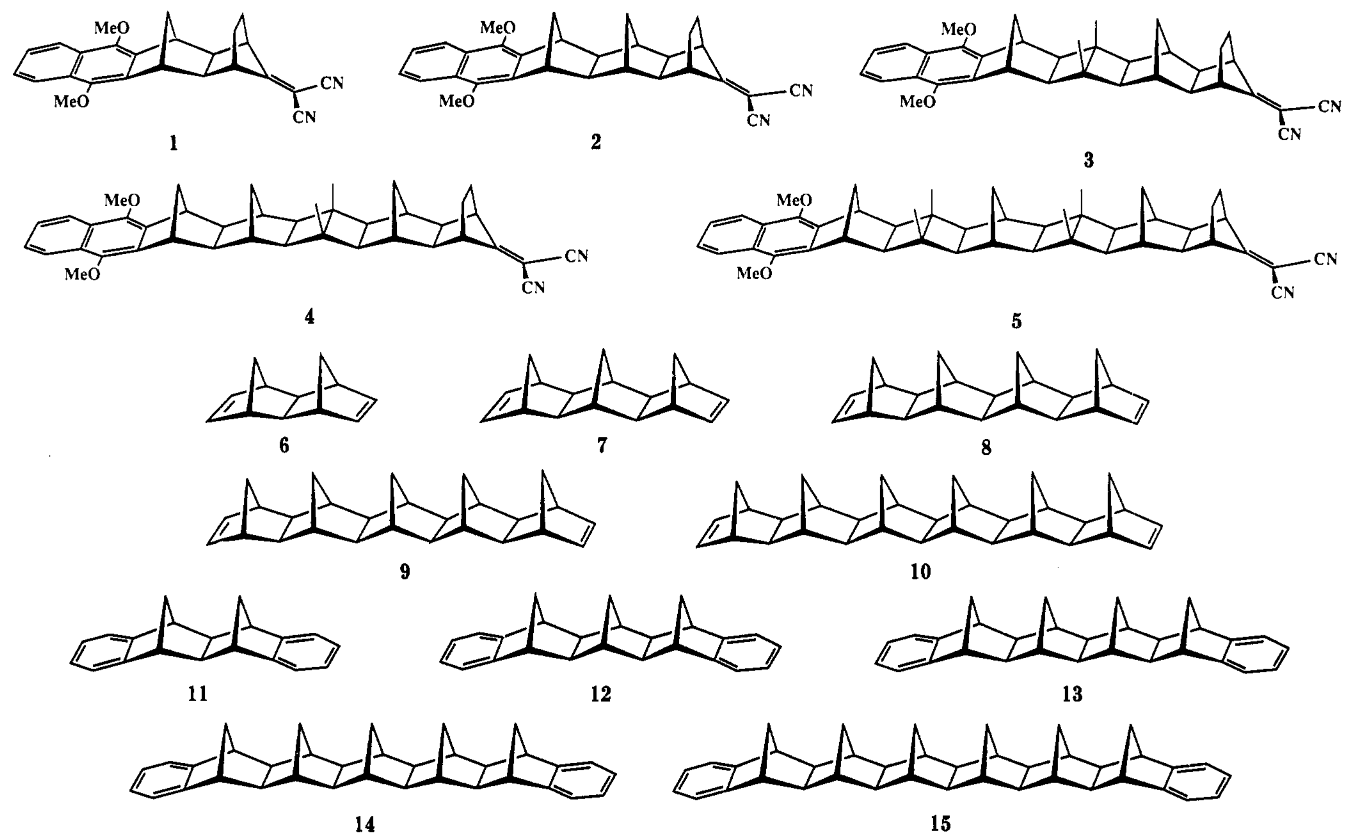


Figure 2. Correlation diagram of the π IP's and π^* EA's of ethylene, **6**, and **7**. The solid lines represent the negatives of the experimental IP's and EA's (from ref 4) and the dashed lines the STO-3G π and π^* orbital energies. The energies of the π_+ and π_- orbitals of **6** and **7** have been shifted by the amount needed to bring the calculated π orbital energy of ethylene into agreement with the negative of the experimental IP. Likewise the energies of the π_+^* and π_-^* orbitals of **6** and **7** have been shifted by the amount needed to bring the calculated π^* energy of ethylene into agreement with the negative of the experimental EA.

that the distance dependence of the electronic coupling in these model compounds should be similar to that for related molecules with the same bridges but more complicated chromophores, e.g. the dibenzo analogues **11**–**15**, shown in Chart I, or even to that for molecules with closely related, but not necessarily identical, bridges (e.g., **1**–**5**).[12] To the extent that eqs 3 and 4 are

CHART I



valid, strict transferability would require that β be independent of the chromophore.

In this review, we first consider experimental evidence provided by ETS and PES for the importance of TB as well as long-range through-space (TS) interactions. We then consider the McConnell model[14] for TB coupling, which gives an exponential dependence of ΔIP and ΔEA on the bridge length and which provides insight into the validity of the assumption that the β value is transferable (i.e., independent of the nature of the chromophores). This is followed by a discussion of the results of MO calculations for **6**–**10**. We then examine the utility of localized orbitals for dissecting the TB splittings into contributions due to different pathways and use these results to test the McConnell-type model and to identify the most important corrections to this model.

II. ETS and PES Studies

A. Results for the 4-Bond and 6-Bond Dienes 6 and 7

ETS and PES measurements have proven particularly valuable for elucidating TB interactions in **6** and **7** and in a large number of other molecules.[4,15,16] However, because the splittings between the anion states and between the cation states in **8** and the longer dienes should certainly be too small to be determined by these techniques, the difficult syntheses of these compounds was not undertaken.

Figure 2 presents a correlation diagram of the experimental IP's and EA's of ethylene, **6**, and **7**. This figure also includes the energies[12] for the π and π^* orbitals obtained from Hartree–Fock (HF) calculations on the neutral molecules using the STO-3G basis set.[17] In the Koopman's theorem (KT) approximation[18] the energies of the appropriate cation and anion states are associated with the negatives of the energies of the filled and unfilled orbitals, respectively. The orbital energies have been shifted by the amounts needed to bring the theoretical π and π^* orbital energies of ethylene into agreement with the experimental IP and EA, respectively. The experimental ΔIP and ΔEA values of **6** are 0.87 and 0.80 eV, respectively, while the corresponding results for **7** are 0.32 and 0.25 eV.[4] These splittings are much larger than those that would result if only TS interactions were important, thus demonstrating the importance of TB interactions in these molecules. Particularly striking is the excellent agreement between the experimental and the KT/STO-3G values of the splittings. Although there are sizable errors in the IP's and EA's calculated at this level of theory (due to basis set deficiencies and the neglect of relaxation and correlation corrections), these errors prove relatively unimportant for the splittings. However, it should be noted that there is a sizable uncertainty in the experimental ΔEA value of **7**, and that calculations on **7** using larger basis sets give considerably smaller splittings between the π^* orbitals than is found with the STO-3G basis set. Thus, in this case, the good agreement between experiment and theory may be fortuitous.

In interpreting the experimental results, it is convenient to consider the symmetry-adapted semilocalized π_+^{SL} and π_-^{SL} orbitals $\pi_+^{SL} = (1/\sqrt{2})(\pi_L + \pi_R)$ and $\pi_-^{SL} = (1/\sqrt{2})(\pi_L - \pi_R)$, where π_L and π_R are ethylene π orbitals localized on the "right"- and "left"-hand side of the molecules, respectively. The π_+^{SL} and π_-^{SL} orbitals neglect coupling with the σ and σ^* orbitals of the bridge. Similarly, the π_+^{*SL} and π_-^{*SL} orbitals may be expressed as $\pi_+{}^{*SL} = (1/\sqrt{2})(\pi_L{}^* + \pi_R{}^*)$ and $\pi_-{}^{*SL} = (1/\sqrt{2})(\pi_L{}^* - \pi_R{}^*)$.

The TS contributions to the splittings can be estimated from the differences in the energies of the $\pi_+{}^{SL}$ and $\pi_-{}^{SL}$ (or $\pi_+{}^{*SL}$ and $\pi_-{}^{*SL}$) orbitals.[19] For a given molecule, the difference between the TS splitting and the splitting obtained from the MO calculations including the bridge orbitals can be associated with the TB contribution to the splitting. Assuming the validity of Koopmans' theorem, we may associate the splitting between the cation states with that between the π_+ and π_- orbitals and the splitting between the anion states with that between the $\pi_+{}^*$ and $\pi_-{}^*$ orbitals. For **6**–**10** the through-space contributions to the splittings are much smaller than the TB contributions. Hence, experimental measurements of the ΔIP and ΔEA values of these compounds essentially provide a measure of the TB interactions.

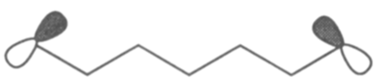
Both the π_+ and π_- orbitals of **6** and **7** are destabilized with respect to the π orbital of ethylene indicating that, as expected, π/σ mixing, which destabilizes the π_+ and π_- orbitals relative to the π orbital of ethylene, is much more important than π/σ^* mixing, which tends to stabilize the π_+ and π_- orbitals relative to the π orbital of ethylene. On the other hand, the $\pi_+{}^*$ and $\pi_-{}^*$ levels of these compounds straddle the π^* MO of ethylene, with the $\pi_-{}^*$ lying above and the $\pi_+{}^*$ lying below that of ethylene. This observation requires that both π^*/σ^* and π^*/σ interactions are important, since the latter are needed to "push" the $\pi_-{}^*$ level of these molecules above that of ethylene. This is a surprising result since the energy separation between the π^* and the σ orbitals is much larger than that between the π^* and σ^* orbitals and, in fact, is comparable to that between the π and σ^* orbitals (and we have already noted that π/σ^* mixing is much less important than π/σ mixing).

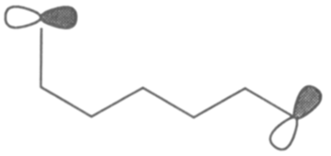
We have suggested that these trends are due to the differences in the magnitudes of the coupling of the π^* (and π) orbitals with the relevant σ and σ^* orbitals of the bridge.[4] Due to the additional node in the localized σ^* than in the σ orbitals, one would expect the matrix element for π^*/σ^* interaction to be smaller than that for π^*/σ interaction.[9b] However, the localized orbital analysis to be presented subsequently, shows that the matrix elements between the π^* MO's with the relevant localized σ and σ^* MO's are comparable.

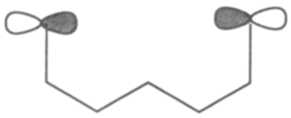
B. Dependence of Through-Bond Interactions on the Bridge Configuration

1. Experimental Demonstration of the All-Trans Rule

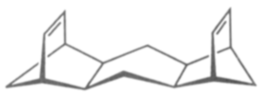
An important consequence of Hoffmann's pioneering extended Huckel studies of through-bond interactions in model α,ω-polyenediyl systems was the finding that the through-bond coupling is sensitive to the configuration of the relaying bridge and is maximized for an all-trans (or antiperiplanar) arrangement of relaying σ bonds (the all-trans rule[4,9]). Thus, the predicted splitting between the π orbitals for the model systems **16**–**18** should decrease in the order **16** > **17** > **18**. PES provides a convincing confirmation of the all-trans rule. For example, for the pair of 4-bond dienes, **6** and **19**, the π_+,π_- splittings are 0.87 and 0.44 eV,[15a,20] respectively, and for the pair of 6-bond dienes, **7** and **20**, the π_+,π_- splittings are 0.32 and 0.17 eV,[15b] respectively.

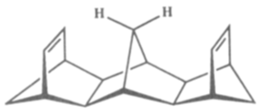

16


17


18


19


20

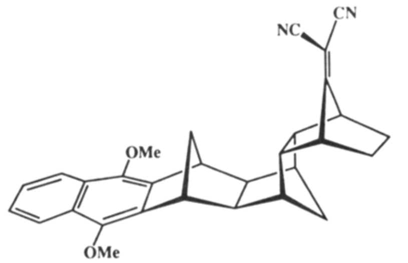


21

KT/STO-3G calculations on these dienes closely reproduce the observed splitting energies, thereby enabling one to explore quickly, and cheaply (in a computational sense) orbital interactions in more complicated dienes, such as the 6- and 8-bond dienes, **22** and **23**.[12] The KT/STO-3G π_+,π_- and $\pi_+{}^*,\pi_-{}^*$ splittings for the all-trans dienes, **7** and **8**, are significantly larger than those for the respective systems, **22** and **23**, containing some gauche arrangements of σ bonds, which are indicated in the structures by bold lines.[12]


22


23



24

25

The dependence of the electronic coupling on the configuration of the bridge is nicely paralleled by the observed rate data for photoinduced intramolecular electron transfer in **2**, **3**, **24**, and **25**.[2d,21] Thus, for the pair of 6-bond species **2** and **24**, photoinduced electron transfer (in MeCN solvent) occurs about 7 times more rapidly in the all-trans system **2** than in **24**, which has a gauche linkage in each relay, and this is similar to the value of 12 for the ratio of the squares of the KT/STO-3G π_+^*,π_-^* splitting energies for the corresponding 6-bond dienes, **7** and **22**.[12] Likewise, for the 8-bond compounds, photoinduced electron transfer (in MeCN solvent) occurs about **14** times more rapidly in **3**, compared to **25**, which has two gauche arrangements of σ bonds in each relay.[2d,21] Again, this ratio is comparable to the KT/STO-3G value of 18 for the ratio of the squares of the π_+^*,π_-^* splitting energies for **8** and **23**.[12] The close correlation between the electron-transfer rate ratios in the naphthalene–spacer–dicyanovinyl systems and the ratios of the squares of the KT/STO-3G π_+^*,π_-^* splitting values for the corresponding dienes strongly suggests that the former are also caused by the variation of through-bond coupling with the configuration of the hydrocarbon bridge, and that this coupling is stronger in **2** than in **24** and in **3** than in **25**.

It has also been found that the KT/STO-3G splitting energies of dienes serve as useful predictors of electron transfer rates in an extended series of donor–acceptor systems, including **1**–**5**. For example, the square of the KT/STO-3G π_+^*,π_-^* splitting energies for a series of polynorbornyl dienes, including **6**–**8**, was found[12] to follow an approximate exponential decay with increasing number, n, of σ bonds in the relay:

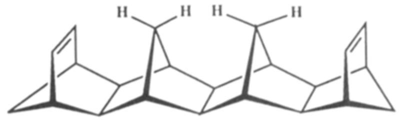
$$\Delta EA^2 = 16.3 \exp(-1.20n). \tag{5}$$

The exponent (1.20) in this expression is very close to those deduced from the rate constants for photoinduced ET in **1**–**5** and related systems, which range from 0.92 (in THF) to 1.00 (in EtOAc) to 1.23 (in MeCN).[2,12] This, admittedly crude approach to estimating ET rates should be of general use.[12]

A similar dependence of electron-transfer rate on the configuration of the bridge has also been observed for thermal electron transfer in anion radicals of 1,4-diarylcyclohexanes,[1] and for photoinduced electron transfer in some porphyrin–quinone molecules.[3i] On the theoretical front, Ohta et al. have calculated matrix elements for electron transfer between two methylene groups across a cyclohexane bridge as a function of stereochemistry.[22] In accordance with the all-trans rule, they found that the matrix element was largest when the two methylene groups adopted the equatorial conformation, corresponding to an all-trans arrangement of the C–C bonds.

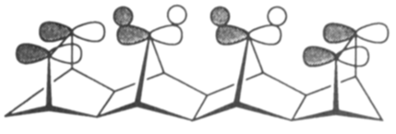
2. Laticyclic Hyperconjugation

The experimental π_+,π_- splitting energy for the 6-bond diene **21** (0.52 eV[15b]) is considerably larger than that found for the all-trans 6-bond diene, **7**, even though the bridge in the former molecule has two gauche arrangements of bonds in each relay. The π_+,π_- splitting energy found for the 8-bond diene **26** is 0.27 eV, which is a very large value indeed, when one recognizes that the two double bonds in this diene are separated by about 9 Å! The origin of the large π_+,π_- splittings in **21** and **26** is attributed to a variant of hyperconjugation, termed laticyclic hyperconjugation[23] in which the π orbitals of the double bonds overlap with the pseudo-π orbital(s) of the intervening methano bridges, as shown schematically by **27** and **28**. The X-ray crystal structures of chlorinated derivatives of **21** and **26** show that the carbon atoms of the methylene bridges are about 3 Å from the nearest double bond and, consequently, reasonably strong interorbital overlap of the kind shown by **27** and **28** should be obtained. An estimate of the contribution of orbital interactions through the 6-bond relays to the π_+,π_- splitting in **21** is provided by the PES split of 0.17 eV for diene **20**. Subtracting this value from the observed π_+,π_- splitting of **21** gives an estimate of 0.35 eV for the laticyclic hyperconjugative interactions in **21**.



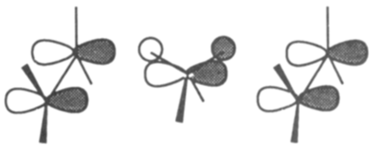
26

27



28

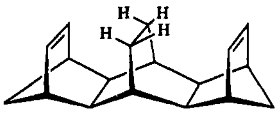
It has been found that laticyclic interactions in these systems can be nicely modeled by means of KT/STO-3G calculations on ethene/$(CH_4)_n$/ethene sandwiches, in which the ethene molecules are in van der Waals contact with a "chain" of CH_4 molecules spaced 3 Å apart, as in **29**. The computed π_+,π_- split of 0.39 eV for **29**, with a single intervening CH_4 moiety, is in good agreement with the value of 0.32 eV estimated from the PES data for dienes **20** and **21**.[15d,23] Laticyclic hyperconjugation therefore accounts for about 75% of the total experimental π_+,π_- splitting energy found for **21**. In a similar fashion, the KT/STO-3G laticyclic hyperconjugative split for the 8-bond diene is found to be 0.17 eV, accounting for 63% of the total experimental splitting energy.[23]



29

The long-range nature of these laticyclic hyperconjugative interactions is exemplified by a calculated KT/STO-3G π_+,π_- splitting energy of 0.025 eV for both the ethene/$C_{12}H_{26}$/ethene complex (in which $C_{12}H_{26}$ is a straight chain hydrocarbon) and the ethene/$(CH_4)_6$/ethene complex, in both of which the ethene molecules are placed ca. 21 Å apart! Such splits could correspond to positive hole-transfer rates within the cation radical of these complexes as fast as 10^{11} s^{-1}. This is several orders of magnitude larger than electron-transfer rates found in (modified) biological systems, in which the donor and acceptor sites are separated by comparable distances (14–25 Å).[25-28] These predictions find some support from the recent ESR investigation of the cation radical of **21** at 77 K.[29] The ESR spectrum of this species revealed a symmetrical triplet with a hyperfine splitting (hfs) of 30 G, which became a doublet with the same hfs value in the ESR spectrum of the corresponding cation radical in which the central bridging CH_2 group was replaced by a CHD group. These data suggest substantial accumulation of unpaired spin density on the central CH_2 bridge and that the hole migration rate between the double bonds is very rapid on the ESR time scale (i.e., $> 10^8$ s^{-1}). In fact, given the magnitude of the electronic coupling, the hole is probably delocalized.

The ETS spectrum of **21** yields a single peak at low energy, indicating that the splitting between the π^* orbitals is less than 0.2 eV (confirmed by HF/STO-3G and HF/3-21G calculations).[4] Laticyclic hyperconjugation is unimportant for the π^* orbitals because they cannot mix with the methylene C–H orbitals (at least not in a minimum basis set picture) due to symmetry. However, if the methylene bridge were replaced with an ethano bridge (to give **30**), laticyclic hyperconjugation would also be possible in the π^* manifold. Indeed, KT/STO-3G calculations on **30** bear out this expectation, giving π_+,π_- and π_+^*,π_-^* splittings of 0.43 and 0.25 eV, respectively. Moreover, KT/STO-3G calculations on the model ethene/ethane/ethene sandwich, whose geometry mimics that of **30**, give a π_+,π_- splitting of 0.29 eV and a π_+^*,π_-^* splitting of 0.19 eV.[23] Thus in **30**, the major contribution to both the π_+,π_- and π_+^*,π_-^* splittings is due to laticyclic hyperconjugation through the ethano bridge.



30

Compounds, such as **21** and **26** may be viewed as models for the interaction between two ethylene molecules with methane "solvent" molecules sandwiched in between. The MO calculations on the model ethene/$(CH_4)_n$/ethene complexes described above give a distance dependence of the π_+,π_- splitting surprisingly close to that found for **6–10**, indicating that significant coupling can be relayed through a series of "solvent" molecules (at least in the ideal geometrical alignments enforced in the model molecules). These preliminary studies have important ramifications for long-range electron-transfer processes in that they suggest that solvent molecules can greatly facilitate rapid ET through a laticyclic type of mechanism. Of course, in practice, solvent molecules will not normally obligingly align themselves so as to maximize laticyclic hyperconjugative interactions. Nevertheless, random orientations of solvent molecules occupying the space between two chromophores may still result in significant electronic coupling. This aspect is being actively explored by us. We note that one can achieve near optimal alignment for laticyclic interactions by using Langmuir–Blodgett films.[2g]

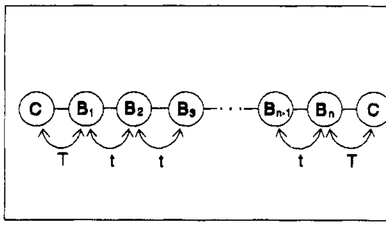


Figure 3. Schematic representation of the McConnell model for a symmetric chromophore–bridge–chromophore system. The chromophores are denoted as C's. The identical bridge subunits are denoted $B_1, B_2, ..., B_n$. The coupling of the chromophores to the adjacent bridge subunits (B_1 and B_n) is given by T, and the coupling between adjacent bridge subunits is given by t.

C. Long-Range Through-Space Interactions

ETS studies have shown that through-space interactions extend over greater distances in anion states than in cation states, at least for the gas-phase species.[30] Perhaps the most clear-cut example of this is provided by *cis*- and *trans*-1,3,5-hexatriene. The ET spectra show that the second EA's of the two isomers differ by about 0.6 eV, with the anion being more stable in the cis isomer. In an orbital picture this means that the π_2^* orbital is 0.6 eV more stable in the cis than in the trans isomer. This can be understood from the facts that this orbital has large coefficients on the C_2 and C_5 atoms and that the C_2–C_5 distance is much smaller in the cis than in the trans isomer. MO calculations using the STO-3G basis set give nearly the same energy for the π_2^* orbital in the two isomers, due to the inability of this basis set to describe interactions occurring over distances much greater than 2.5 Å.[30] With the 3-21G basis set, on the other hand, the π_2^* orbital is predicted to be appreciably more stable in the cis isomer, in agreement with experiment.

In a Huckel model the occupied π_2 MO of hexatriene has the same magnitude coefficients on the C_2 and C_5 atoms as does the π_2^* MO. However, both PES studies[31] and MO calculations indicate that the energy of the π_2 orbital is nearly the same in the cis and trans isomers. These results demonstrate that long-range interactions tend to be more important in anion than in cation states, and they indicate the need of employing sufficiently flexible basis sets in theoretical studies of such interactions.

III. McConnell Model

A simple model which leads to the exponential dependence of the splittings on the number of bonds in the bridge, consistent with eqs 3 and 4, is that forwarded by McConnell to explain the coupling in the anion states of phenyl–bridge–phenyl systems.[14] The essence of the McConnell model is illustrated in Figure 3 for a symmetric system with two identical chromophore units (C) and n identical bridge subunits $\{B_1, B_2, ..., B_n\}$.

This model includes explicitly only a single orbital on each chromophore and on each of the identical bridge subunits and assumes that only nearest neighbor interactions are important. Typically, the orbitals on the chromophores could be occupied π (or unoccupied π^*) orbitals and those on the bridge occupied σ (or unoccupied σ^*) orbitals. This model gives the following expression for the splitting, $\Delta E = \epsilon_{\pi_-} - \epsilon_{\pi_+}$ (or $\epsilon_{\pi_-}{}^* - \epsilon_{\pi_+}{}^*$), between the "−" and "+" orbitals of the chromophores, due to mixing with the orbitals of the bridge:

$$\Delta E = -2(T^2/\Delta)(t/\Delta)^{n-1} \tag{6}$$

where T gives the coupling of the chromophores to the adjacent subunits (B_1 or B_n), t gives the coupling between two adjacent bridge subunits, and Δ is the energy gap between the relevant orbital of the chromophore and that of the bridge subunit.

In addition to the above-mentioned assumptions, the derivation of eq 6 assumed that (1) the bridges are "simple" in the sense of lacking branches or cross-linkages, (2) the splitting of the band of orbitals associated with the bridge is small compared to Δ, and (3) $|t/\Delta| \ll 1$. An excellent discussion of the McConnell model and of generalizations of this model is given in the recent review of Newton.[8]

ΔE has been defined so that a positive sign is consistent with the so-called natural ordering of the "+" and "−" orbitals, in which the $\pi_+(\pi_+^*)$ level lies below the $\pi_-(\pi_-^*)$ level in energy. Other authors (see, for example, ref 8) have adopted the opposite sign convention, in which case the minus sign in eq 6 would be absent. The energy gap, Δ, is defined to be positive for both π/σ and π^*/σ^* mixing. Moreover, t is assumed to be negative. For TB interactions involving coupling of π orbitals via intervening σ orbitals, eq 6 leads to a positive value of ΔE for even n and a negative value for odd n. This means that for even values of n, the π_+ combination lies below the π_- combination in energy. The levels therefore follow the natural sequence of orbitals, which also obtains for sequences arising from pure TS interactions.[33] In contrast, for odd n, π_- lies below π_+, and this is the basis of the so-called parity rule,[9] which has been confirmed experimentally.[4] A similar analysis for the π^* orbitals leads us to expect π_+^* to be more stable than π_-^* for even n and π_-^* to be more stable than π_+^* for odd n.

Equating eq 6 with eqs 3 and 4 gives

$$\beta_h, \beta_e = -\ln|t/\Delta| \tag{7}$$

and

$$A_h, A_e = 2T^2/t \tag{8}$$

where the subscripts "h" and "e" that should be associated with T, t, and Δ in order to distinguish the electron (anion) and hole (cation) cases, have been supressed.

The McConnell model leads to a very appealing physical interpretation in that the splitting is a product of a factor due to the coupling of the chromophores to the bridge $2(T^2/\Delta)$ and a factor of t/Δ for each relay between bridge subunits. From eq 7 it is seen that β_h and β_e depend on the energy gap between the relevant orbitals of the chromophore and the bridge subunit. As a result, the β value determined from calculations or experimentally for a specific chromophore can be directly used to predict the distance dependence of the splittings for a different chromophore only if the energies of the relevant orbitals of the two chromophores are very close. However, from the McConnell model one can derive the following result:

$$\beta' = \beta - \ln(\Delta/\Delta') \tag{9}$$

where β and β' are the exponents for the two chromophores and Δ and Δ' are the corresponding energy gaps. For **6–10**, Δ, as determined from the STO-3G calculations, is of the order of 8.4 and 9.0 eV for the filled and unfilled orbital spaces, respectively. Using these Δ values and the differences between the first IP's and between the first EA's of ethylene and benzene, we predict using eq 9 that β_h and β_e for **11–15** should be smaller than the corresponding exponents for **6–10** by about 0.14 and 0.06, respectively. The change predicted for β_h is greater than that for β_e because the difference between the first IP's of ethylene and benzene is 1.3 eV, while the difference in the first EA's in these molecules is only 0.6 eV. (These energy differences are determined from the experimental IP's and EA's). Of course, β values estimated in this manner will be reliable only to the extent that the McConnell model itself is valid.

From the McConnell model one can also derive the following relation between the ratio of the splittings for two chromophore–bridge–chromophore systems with different chromophores but identical bridges. If Δ is

$$\Delta E/\Delta E' = (T^2/T'^2)(\Delta'/\Delta)^n \tag{10}$$

approximately equal to Δ', then a rough estimate of $\Delta E/\Delta E'$ is provided by the ratio of the squares of the MO coefficients of the two chromophores at their sites of attachment to the relay.

Compounds **6–10** may be viewed as having two main bridges with multiple cross-linkages. In the absence of coupling between the bridges, the McConnell model would still hold, providing that the various criteria discussed above are valid. In this case, the only modification needed to accomodate the presence of two bridges is the inclusion of an additional factor of 2 in the expression for the splitting, giving

$$\Delta E = -4(T^2/\Delta)(t/\Delta)^{n-3} \tag{11}$$

where the exponent in eq 11 is $n-3$, rather than $n-1$ as in eq 6 because we have allowed for the fact that the coupling of the chromophores is primarily to the C_2–C_3 and C_{N-1}–C_{N-2} bonds of the two main bridges, and we have neglected the coupling of the σ NBO's associated with the terminal C–C bonds of the main bridge with the other σ NBO's of the bridges. One might expect that both the interactions between the two parallel main bridges as well as those between nonadjacent bonds within the main bridges are important, thus, causing significant deviations from the behavior predicted by the McConnell model. The ETS and PES data alone do not permit us to resolve this issue since results are available for only the first two molecules in the series. (For the molecules with the longer bridges the splittings should be much too small to be determined by these techniques.) Therefore, in determining the range of validity of simple models for the TB interactions, electronic structure calculations can prove particularly valuable.

IV. Ab Initio Results for 6–10

In this section we consider the results of ab initio calculations for **6–10**.[12,13] It has already been noted that for **6** and **7** good agreement is found between the orbital splittings calculated at the KT/STO-3G level of theory and the experimentally determined splittings between the anion and between the cation states. Thus, we believe that this approach should also provide a qualitatively (and, perhaps even, semiquantitatively) correct

TABLE I. β **Values Determined from Exponential Fits to the Splittings for Successive Pairs of Dienes**[a]

	β(ΔIP-KT)			β(ΔIP-SCF)			β(ΔEA-KT)			β(ΔEA-SCF)		
pair	STO-3G	3-21G	D95v	STO-3G	3-21G	D95v	STO-3G	3-21G	D95v	STO-3G	3-21G	D95v
6,7	0.51	0.48	0.49	0.58	0.58	0.54	0.69	0.75	0.68	0.68	0.75	0.60
7,8	0.45	0.42	0.41	0.54	0.48	0.49	0.60	0.35	0.22	0.65	0.45	0.41
8,9	0.39	0.33	0.34	0.50	0.46	0.47	0.59	0.52	0.59	0.66	0.56	0.59
9,10	0.40	0.34	0.35	0.50	0.47	0.48	0.60	0.55	0.65	0.66	0.58	0.64

[a] In determining the β values for the **6,7** pair of molecules, the TB rather than the net splittings are used for **6**.

description of the TB coupling in the longer members of this series. However, it is possible that in the longer dienes, interactions which are longer range than can be accounted for with the STO-3G basis set are important, and for this reason it is instructive to examine also results obtained using more flexible basis sets.

Before proceeding, we note that the anion states of **6**–**10** all lie in the continuum of the neutral molecule plus a free electron. As a result the anion states are temporary in nature, and may be viewed as descrete states coupled to a continuum.[32] In such cases, care must be exercised in equating the virtual orbitals obtained from HF calculations on the neutral molecules with the anion states, since with sufficiently flexible basis sets, some of the low-lying unfilled orbitals will correspond to approximations to continuum functions rather than to approximations to anion states in the KT sense. In was shown in ref 13, that for the basis sets considered here, the lowest a_2 and b_1 π^* orbitals do correspond to anion states in a KT sense, and that the splittings between these unfilled orbitals can be meaningfully correlated with those between the anion states. Further justification of this approach was provided by comparison of the trends in the energies of the π^* orbitals of **6**, calculated with the STO-3G, 3-21G, and D95v basis sets, with those from more rigorous stabilization calculations[32] using more flexible basis sets.

Table I summarizes β values derived assuming validity of eqs 3 and 4 and using the splittings calculated for consecutive pairs of dienes. The geometries of the dienes were all optimized in the HF approximation, using the 3-21G basis set, within the C_{2v} symmetry constraint. Results are presented for three different basis sets[17]—STO-3G, 3-21G, and D95v—of increasing flexibility as well as at both the KT and ΔSCF levels of theory. The splittings in the ΔSCF approximation are obtained from differences of the Hartree–Fock energies of the ion states. The KT/STO-3G results are considered first.

Several important conclusions can be drawn from these results. First, neither the β_e nor the β_h values are constant along the series of compounds. For example, the β_h values determined from the KT/STO-3G splittings for the (**6**, **7**), (**7**, **8**), (**8**, **9**), and (**9**, **10**) pairs of molecules are 0.51, 0.45, 0.39, and 0.40, respectively, while the corresponding β_e values are 0.69, 0.60, 0.59, and 0.60. Secondly, as one progresses to longer bridges, both the β_e and β_h values approach constant values. Thirdly, the β_e values are consistently larger than the β_h values. We have suggested that the variations in the β values with bridge length could be due to multiple TB pathways, the contributions from which fall off at different rates with the bridge length.[13] This possibility will be examined in the next section of the review.

To the extent that interactions occurring over distances larger than about 2.5 Å are important, one might expect that the STO-3G basis set would prove to be inadequate. It is of interest, therefore, to examine the β_h values obtained using the 3-21G and D95V basis sets (still focusing on the KT results). The β_h values are reduced upon going from the STO-3G to the 3-21G basis set, with the reduction being greatest for the β_h values deduced from the splittings of the longer dienes: For the (**9**, **10**) pair of molecules the reduction is 15%. On the other hand, nearly identical β_h values are obtained with the 3-21G and the more flexible D95v basis sets. These results suggest that pathways other than those involving interactions between adjacent bonds must be important, but that interactions which skip over three or more bonds are apparently unimportant, at least for the coupling of the π orbtials.

Nearly the same β_e values are determined from the π_+^*,π_-^* splittings for the (**6**, **7**), (**8**, **9**), and (**9**, **10**) pairs of molecules when using the D95v basis set as when using the STO-3G basis set. (However, the "intermediate" 3-21G basis set yields β_e values which differ by about 10% from those obtained with the STO-3G and D95v basis sets.) This is a surprising result since it was anticipated that the use of flexible basis sets would be more important for describing the interactions in the π^* than in the π manifold. The β_e value determined from the π_+^*,π_-^* splittings for **7** and **8** proves to be much more sensitive to the basis set, being 0.60, 0.35, and 0.22 with the STO-3G, 3-21G, and D95v basis sets, respectively. The rather different behavior found for these β_e values is due to the fact that the π_+^*,π_-^* splitting of **7** decreases rapidly, with increasing flexibility of the basis set, being 0.23, 0.18, and 0.11 eV in the STO-3G, 3-21G, and D95v basis sets, respectively. The reason for the anomalous behavior of **7** is not known. It is expected that a pathway analysis similar to that discussed below for the π orbitals will prove useful in identifying the origin of this behavior.

The β_e and β_h values obtained in the ΔSCF approximation are generally larger and show less variation along the series of molecules than do those obtained in the KT approximation. The inclusion of electronic relaxation effects is particularly important for the β_h values, leading to increases of as much as 38%. For the β_e values the inclusion of relaxation effects is of major importance only for that determined for the (**7**, **8**) pair of molecules, and only then when using the 3-21G and D95v basis sets, in which case the ΔSCF β_e values are, respectively, 30 and 95% larger than the corresponding KT values.

The experimental ΔIP values of **6** and **7** are consistent with a β value of 0.50 which is actually closer to the values determined in the KT approximation than in the ΔSCF approximation for each of the basis sets considered. Hence, the KT approximation may actually be more reliable for predicting the distance dependence

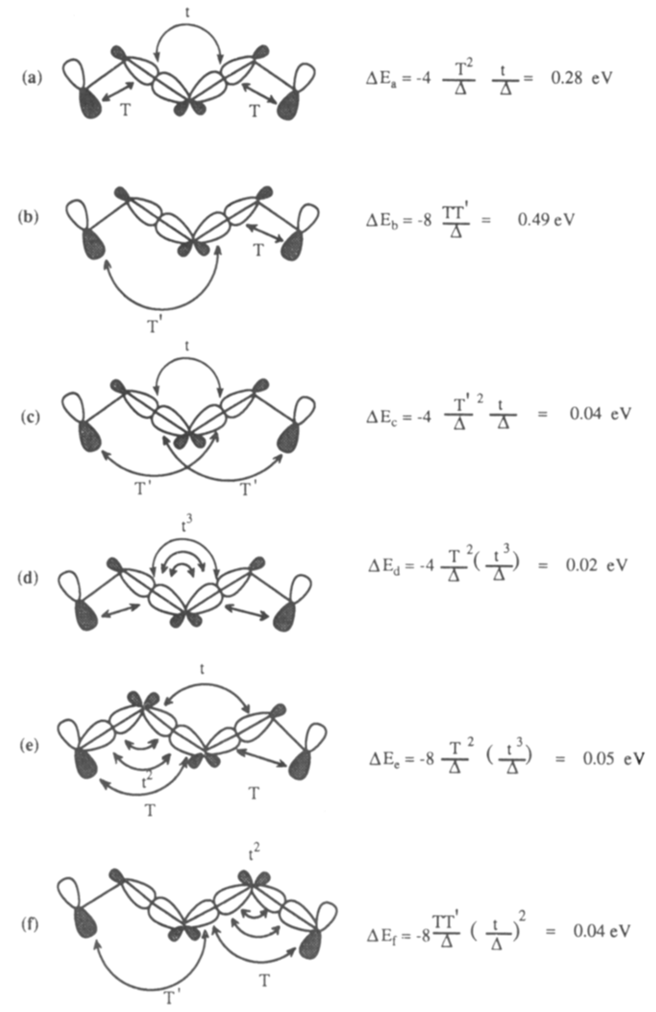


Figure 4. Pathways contributing to the π_+,π_- splitting in **6**. The presence of equivalent pathways has been accounted for in numerical prefactors. The various interaction terms are determined in terms of the NBO's obtained using the STO-3G basis set. The dominant pathways are a and b which do not involve retracing interactions. All contributions have been computed using $t = -2.68$ eV and $\Delta = 8.45$ eV. This t value is that giving the coupling between the C_2–C_3 and C_3–C_4 σ NBO's.

of the TB coupling than is the ΔSCF approximation. This hypothesis could be tested by performing high quality Cl calculations on the ion states of **6**–**10**.

V. Localized Orbital Analysis of the Through-Bond Interactions

The MO calculations, by themselves, do not provide much insight into the factors responsible for the observed trends in the splittings. However, the canonical MO's can be transformed to localized orbitals, in terms of which the π_+,π_- and π_+^*,π_-^* splittings can be dissected into contributions due to various pathways. This approach was pioneered by Heilbronner and co-workers and by Imamura and Ohsaku.[33] It was later used by us in conjunction with natural bond orbitals (NBO's)[34] as the orthogonalized localized orbitals in studies of the role of TB interactions in the π_+,π_- and π_+^*,π_-^* splittings of 7-silanorbornadiene, 7-germanobornadiene, and 7-stannanobornadiene.[35] The NBO approach has recently been applied by Naleway, Curtis, and Miller[36] to examine pathways for electronic coupling in the butane-1,4-diyl and 1,4-dimethylenecyclohexane anions and by Liang and Newton[37] in studies of other systems.

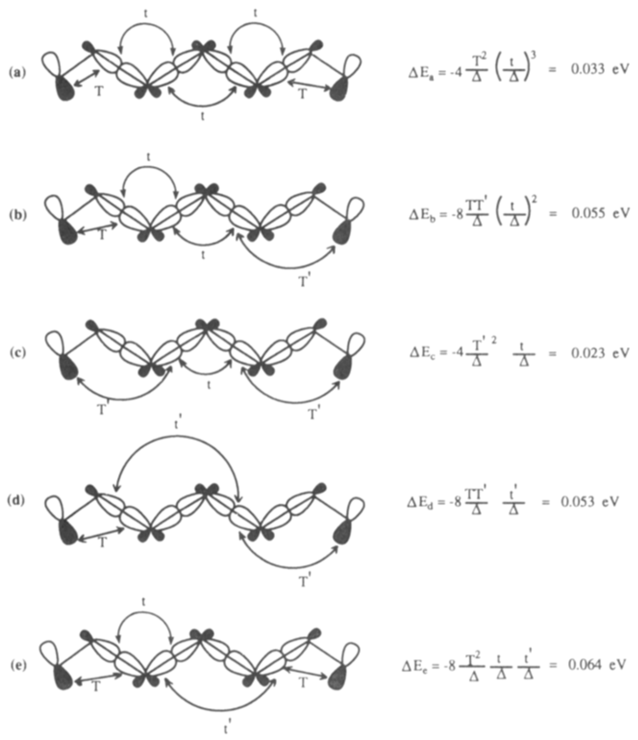


Figure 5. Pathways contributing to the π_+,π_- splitting in **7**. No retracing pathways have been computed. The various interaction terms are determined in terms of the NBO's obtained using the STO-3G basis set. These contributions have been computed using an average value for t of -2.82 eV and an average value of Δ of 8.45 eV.

In the present study, we focus on results obtained from NBO analyses of the TB pathways in **6**–**10**. Due to space constraints, we consider in detail only the results obtained with the STO-3G basis set and, further, focus on the π_+,π_- splittings. The pathways important for the π_+^*,π_-^* splitting will be considered only briefly. A more detailed analysis of the role of localized orbitals in analyzing the TB interactions in **6**–**10** will be presented elsewhere.[38] Other approaches to examining the role of pathways for long-distance electron transfer in proteins and other systems are being explored by Beratan and co-workers,[39] Siddarth and Marcus,[40] and Ratner.[41]

A. McConnell and Extended McConnell Perturbative Models

Figures 4 and 5 depict various pathways important for the TB coupling between the localized π NBO's of **6** and **7**, respectively. Part a of these two figures shows the so-called McConnell pathway for the TB interaction between the localized π NBO's, in which coupling along the bridge is assumed to occur only between adjacent C–C bonds, and the localized π NBO's are assumed to couple to the bridge via mixing with the σ orbitals associated with the C_2–C_3 and C_{N-1}–C_{N-2} bonds. (The number of bonds, n, in the main bridges is equal to N–1.) As noted above, the coupling of the π NBO's to the C_1–C_2 and C_N–C_{N-1} bonds is ignored because of the relatively poor overlap in this case. In addition, in the pathway analysis based on the McConnell model and its extensions, we also ignore the coupling of the C_1–C_2 and C_N–C_{N-1} NBO's with the other σ NBO's. Although such coupling introduces sizable shifts in the energies of the π_+ and π_- orbitals, it proves relatively unimportant for the distance dependence of the splittings.

The effects of these interactions are discussed in the Appendix. With these approximations, the effective bridge length is then n–2 rather than n.

Using the matrix elements and the π/σ energy separation obtained in the NBO analysis of **6** we have

$$T^2/\Delta = (1.39)^2/8.45 = 0.229 \text{ eV} \qquad (12)$$

$$t/\Delta = -2.68/8.45 = -0.306 \qquad (13)$$

$$\Delta E_a(\mathbf{6}) = -4(T^2/\Delta)(t/\Delta) = 0.280 \text{ eV} \qquad (14)$$

where T, t, and Δ are in electron volts, and $\Delta E_a(\mathbf{6})$ gives the π_+,π_- splitting for **6** due to the McConnell-type pathway depicted in Figure 4a. (With the sign conventions adopted, T and Δ are positive and t is negative.) The resulting splitting, ΔE_a, is about 3.7 times smaller in magnitude than that found in the MO calculations.[42] Clearly, this simple model is inadequate for accounting for the TB coupling in this molecule.

From the π_+,π_- splittings of **6** and **7** determined from the MO calculations one can derive the following results:

$$(T^2/\Delta)_{\text{MO}} = 0.75 \text{ eV} \qquad (15)$$

and

$$(t/\Delta)_{\text{MO}} = -0.575 \qquad (16)$$

$(T^2/\Delta)_{\text{MO}}$ and $(t/\Delta)_{\text{MO}}$ are much larger in magnitude than the corresponding quantities obtained assuming that only pathway a is important. Comparison of the results in eqs 12 and 15 leads to the conclusion that the π orbitals couple to orbitals of the bridge other than those associated with the C_2–C_3 and C_{N-1}–C_{N-2} bonds, and comparison of the results in eqs 13 and 16 shows that pathways other than those allowing for coupling between adjacent σ bonds of the main bridges are important for relaying the interaction. This conclusion was also reached by Naleway et al.[36]

Pathway b, depicted for **6** and **7** in Figures 4b and 5b, respectively, allows for the coupling of the π NBO's with the σ orbitals of the C_3–C_4 and C_{N-3}–C_{N-4} bonds of the bridges. Although the relevant matrix element, denoted by T', is about 3.7 times smaller than T, this mechanism of coupling to the bridge is more important than that due to pathway a because T' is nearly equal to $T(t/\Delta)$ and because there are two pathways that involve T' coupling at one end of the bridge and T coupling at the other end. For **6** these pathways lead to a contribution of

$$\Delta E_b = -8T'T/\Delta = 0.49 \text{ eV} \qquad (17)$$

to the π_+,π_- splitting. The net contribution of pathways a and b to the splitting is 0.77 eV, only 0.23 eV smaller in magnitude than that in the MO calculations.

Because the derivation of eq 17 and of the contributions of the other pathways considered here may not be obvious, we believe it to be instructive to present a derivation of eq 17. For **6**, the symmetry-adapted semilocalized orbitals of interest are π_+, π_-, $\sigma_+ = 1/2(\sigma_1 + \sigma_2 + \sigma_1' + \sigma_2')$ and $\sigma_- = 1/2(\sigma_1 - \sigma_2 + \sigma_1' - \sigma_2')$, where the σ_1 and σ_2 localized orbitals are associated, respectively, with the C_2–C_3 and C_3–C_4 bonds of one of the main bridges and σ_1' and σ_2' are the corresponding orbitals of the other, parallel, main bridge. In second-order perturbation theory, the shift in the energy of the π_+ orbital due to mixing with the σ_+ orbital is given by

$$\Delta E(\pi_+) = [(1/\sqrt{8})\langle(\pi_L+\pi_R)|H|(\sigma_1+\sigma_2+\sigma_1'+\sigma_2')\rangle]^2/(\epsilon_{\pi_+} - \epsilon_{\sigma_+}) \qquad (18)$$

and that in the π_- orbital due to mixing with σ_- is given by

$$\Delta E(\pi_-) = [(1/\sqrt{8})\langle(\pi_L-\pi_R)|H|(\sigma_1-\sigma_2+\sigma_1'-\sigma_2')\rangle]^2/(\epsilon_{\pi_-} - \epsilon_{\sigma_-}) \qquad (19)$$

With the definitions $\langle\pi_L|H|\sigma_1\rangle = T$, $\langle\pi_L|H|\sigma_2\rangle = T'$, $\epsilon_{\pi_L} - \epsilon_{\sigma_1} = \Delta$, and $\langle\sigma_1|H|\sigma_2\rangle = t$, and the assumption that the TS coupling between the π_L and π_R orbitals is negligible so that $\epsilon_{\pi_+} = \epsilon_{\pi_-} = \epsilon_{\pi_L} = \epsilon_{\pi_R}$, these equations may be simplified to give

$$\Delta E(\pi_+) = (2T^2 + 4TT' + 2T'^2)/(\Delta - \text{t}) \qquad (20)$$

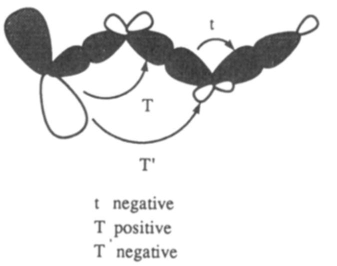
and

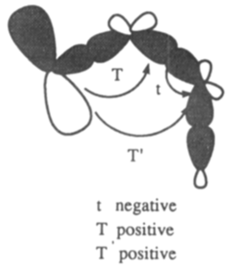
$$\Delta E(\pi_-) = (2T^2 - 4TT' + 2T'^2)/(\Delta + t) \qquad (21)$$

where we have made use of the fact that $\epsilon_{\sigma_+} = \epsilon_2 + t$ and $\epsilon_{\sigma_-} = \epsilon_2 - t$, with ϵ_2 being the energy of the σ NBO associated with C_2–C_3 (and of the symmetry equivalent NBO's). With the further assumption that $|t/\Delta| \ll 1$, the t's in the denonimators can be neglected. In this case, subtraction of eq 20 from eq 21, gives $-8TT'/\Delta$, the result expressed in eq 17. Moreover, if we expand the denominators in powers of t/Δ, i.e., $(\Delta - \text{t})^{-1} = \Delta^{-1}(1 + t/\Delta + ...)$ and $(\Delta + t)^{-1} = \Delta^{-1}(1 - t/\Delta + ...)$, and keep only terms through t/Δ, we obtain

$$\Delta E = -(4T^2/\Delta)(t/\Delta) - (4T^2/\Delta)(t/\Delta) - 8TT'/\Delta \qquad (22)$$

which includes the contribution from the McConnell pathway (Figure 4a) as well as contributions due to the "retracing" term (shown in Figure 4c) and to the "TT'" pathway (Figure 4b). The T′ interaction, describing the coupling of the π_L orbital with the C_3–C_4 σ NBO, is negative when the C_1–C_2, C_2–C_3, and C_3–C_4 bonds have a trans orientation, as shown in Figure 4b, but positive when these bonds are arranged in a cis or gauche, manner as shown.





The dependence of the sign of T' on the orientation of the σ bonds is a major factor leading to the diminished π_+,π_- (and π_+^*,π_-^*) splittings in **19** compared to **6**[15a,20] and in **20** compared to **7**.[15d] For **6** for which both t and T' are negative and T is positive, all three contributions enhance the π_+,π_- splitting.

The general expression for the π_+,π_- splitting of the dienes **6**–**10** due to pathways a and b is

$$\Delta E_a + \Delta E_b = -4(T^2/\Delta)(t/\Delta)^{n-3} - 8(TT'/\Delta)(t/\Delta)^{n-4} \qquad (23)$$

which may be rearranged to give

$$\Delta E_a + \Delta E_b = -4(T^2/\Delta)(1 + 2T'\Delta/Tt)(t/\Delta)^{n-3} = -4\tilde{T}^2/\Delta(t/\Delta)^{n-3} \quad (24)$$

From eq 24 it may be seen that the presence of two mechanisms for coupling to the bridge can be viewed as giving an effective T value

$$\tilde{T} = T\sqrt{(1 + 2T'\Delta/Tt)} \quad (25)$$

or, alternatively, a modified pre-exponential factor in eq 3. In this model the introduction of the longer range coupling between the chromophore and the bridge does not modify the propagation of the interaction along the bridge.

In deriving eq 23 it was assumed that the energies of the various localized σ orbitals are nearly identical and that the matrix elements ($H_{i,i+1}$) between the different pairs of adjacent C–C bonds are also nearly identical (for all the molecules in the series). Examination of the NBO matrices reveals that, although the first assumption is justified, the second is questionable. In particular, the interactions between adjacent σ orbitals when both orbitals derive from the same norbornyl ring differ appreciably from those in which the two orbitals derive from adjacent norbornyl rings. The former matrix elements have a value of around 3.1 eV, and the latter 2.6 eV. For example, for **9** the H_{12}, H_{23}, H_{34}, and H_{45} matrix elements between consecutive pairs of σ NBO's of the main bridge are 3.16, 2.56, 3.10, 2.56, and 3.10 eV, respectively. Thus, to a good approximation, the nearest-neighbor matrix elements alternate between these two values as one progresses down the bridge. In such a case, it can be shown that an exponential dependence of the splitting on n is still obtained. The values of the two matrix elements in question are sufficiently close that their mean yields a β value quite close to that derived from a proper treatment allowing for the alternation in the couplings. In the following discussion we will ignore the alternation of the values of the matrix elements along the bridge.

For the 6-bond diene, **7**, and the longer dienes, there is a third contribution to the splitting

$$\Delta E_c = -4(T'^2/\Delta)(t/\Delta)^{n-5} \quad (26)$$

With the inclusion of this term, the pathway for which is shown in Figure 5c, the net π_+,π_- splitting for **7** and for the longer dienes is

$$\Delta E_a + \Delta E_b + \Delta E_c = -\{4T^2/\Delta + 8(TT'/\Delta)(\Delta/t) + 4(T'^2/\Delta)(\Delta/t)^2\}(t/\Delta)^{n-3} \quad (27)$$

and the effective T becomes

$$\tilde{T} = T\{1 + (T'/T)(\Delta/t)\} \quad (28)$$

Note that an interaction of the form $-4(T'^2/\Delta)(t/\Delta)$ is also found for the 4-bond diene, **6**, as shown in Figure 4c. However, this contribution to the splitting has a different origin in **6** and **7**. In the former it is due to a "retracing" pathway, whereas in the latter, it is due to a pathway that does not involve retracing. From the results summarized in Figure 4, it is seen that this retracing pathway in **6** is relatively unimportant compared to contributions due to pathways not involving retracing interactions.

Although the inclusion of pathways b and c in addition to a leads to an enhanced coupling of the π groups to the bridge, there is still the problem that the splittings decrease much too rapidly with increasing bridge length, compared to those from the HF calculations. The obvious refinement to the McConnell-type model is to include next-nearest-neighbor interactions along the bridge. The relevant matrix element is denoted t'. (The variations in the $H_{i,i+2}$ matrix elements along the bridge are negligible, being less than 1%.) In a model neglecting coupling to the σ NBO's associated with the terminal C–C bonds, t' interactions cannot contribute to the π_+,π_- splitting of **6**. The changes brought about by allowing for coupling to the terminal C–C bonds is considered in the Appendix.

For **7**, inclusion of pathways involving interactions between next-nearest-neighbor C–C σ bonds gives contributions to the splitting of

$$\Delta E_d = -8(TT'/\Delta)(t'/\Delta) \quad (29)$$

and

$$\Delta E_e = -8(T^2/\Delta)(t'/\Delta)(t/\Delta) \quad (30)$$

shown in Figures 5d and 5e, respectively. (t' is positive, so these two terms have the same sign as those in eq 27). Although t'/Δ is about 3.6 times smaller in magnitude than t/Δ, pathways involving t' prove important for the splitting because each occurrence of a t' interaction replaces two interactions via t and t'/Δ is comparable in magnitude to $(t/\Delta)^2$.

The interactions considered thus far give rise to five pathways (ignoring those with retracing) contributing to the π_+,π_- splitting of **7**. No one of these dominates; individually the contributions of the various pathways range from 0.025 to 0.058 eV. The two largest contributions (d and e) to the π_+,π_- splitting of **7** involve t' interactions that "skip over" one of the σ bonds. These do not have counterparts in **6**.

The inclusion of pathways involving next-nearest-neighbor interactions introduces a nonexponential distance dependence into the splittings. Consider, for example, the case whereby the coupling to each end of the bridge occurs via T'. Because t'/Δ and $(t/\Delta)^2$ are of comparable magnitude, all terms of the form $(t/\Delta)^l(t'/\Delta)^i$, $l + 2i + 5 = n$, should be included in calculating the coupling along the bridge. However, to illustrate the origin of the nonexponential behavior, we focus (for simplicity) on pathways in which the matrix element t occurs only once, with the remaining transfers along the bridge occurring via t' "hops" and in which retracing is not permitted. The general form of the contribution of such pathways to the π_+,π_- splitting of **7** and the longer dienes is

$$\Delta E_f = -4\{(n - 4)/2\}(T'^2/\Delta)(t/\Delta)(t'/\Delta)^{(n-6)/2} \quad (31)$$

Equation 31 does not pertain to **6** because, in this case, T' coupling of both π NBO's to the bridge would require a retracing interaction along the bridge, and we have excluded such pathways. Because of the $(n - 4)/2$ factor, which gives the number of possible locations of the t' relay, eq 31 leads to a nonexponential distance dependence of the splitting. However, for large n, this term exhibits nearly exponential behavior. In the more general case in which all pathways involving various combinations of t and t' are included, it is not clear that

TABLE II. π_+,π_- Splitting Energies (eV) Calculated in Various Models for 6–10[a]

	model[b]					
molecule	I	II	III	IV	V	Hartree–Fock
6	0.257	0.735	0.744 (0.602)	0.745 (0.603)	0.610	0.990 (1.107)
7	0.032	0.111	0.263 (0.234)	0.293 (0.254)	0.188	0.350 (0.372)
8	0.004	0.014	0.096 (0.090)	0.130 (0.127)	0.057	0.141 (0.165)
9	0.000	0.002	0.036 (0.035)	0.058 (0.063)	0.019	0.065 (0.085)
10	0.000	0.000	0.013 (0.014)	0.026 (0.032)	0.006	0.029 (0.043)

[a] Results in parentheses are obtained using the 3-21G basis set. All other results are obtained using the STO-3G basis set. [b] Model I includes only *T* type coupling of the π NBO's to the bridge and *t* type coupling along the bridge. Model II includes *T'* coupling to the bridge as well as *T* and *t* interactions. Model III includes *T*, *T'*, *t*, and *t'* interactions. Model IV includes *T*, *T'*, *t*, *t'*, and *t''* interactions. Model V includes all interactions between the occupied valence NBO's.

an exponential distance dependence should result even in the limit of large *n*. Thus, it is especially noteworthy that the ab initio calculations are consistent with a nearly exponential dependence of the splittings on *n* for large *n*.

The above analysis shows that there are two reasons that the β values deduced from the splittings for the shorter dienes deviate from those deduced for the longer dienes: first, there are interactions involving nonadjacent bonds that give rise to nonexponential couplings, and secondly, there are pathways that are important in the molecules with the longer bridges but which do not have counterparts in 6. Indeed, with the inclusion of still longer range interactions, there will be pathways for 8–10 that will not have counterparts in either 6 or 7.

B. Nonperturbative Calculations of β_h Values

In order to obtain quantitative assessments of the importance of various pathways for the π_+,π_- splittings, we have adopted an approach employed previously by us in analyzing the TB interactions in a series of substituted norbornadienes.[35] In the current application of this approach, we start with the full STO-3G–Fock matrix expressed in terms of NBO's. We then delete from this matrix various subsets of off-diagonal matrix elements. Five different models are considered. In each of these, all interactions involving the nonvalence core NBO's and those involving the unoccupied NBO's are deleted. Unlike the simplified perturbation theoretical analysis presented above, none of the models considered here assumes special relationships between matrix elements (e.g., except when dictated by symmetry, the various $H_{i,i+1}$ matrix elements are not necessarily equal).

Models I and II allow only for nearest-neighbor coupling (*t*) along the main bridge. These two models differ in that model I allows coupling to the bridge only via *T*, while model II allows for coupling to the bridge via both *T* and *T'* interactions. Models III and IV both allow for next-nearest interactions (*t'*) along the main bridge as well as for the various interactions present in model II. Model IV includes as well interactions along the main bridge that "skip over" two σ bonds (so-called *t''* interactions). For each of these models the terminal C–C σ bonds are permitted to couple via *t'* and *t''* interactions with the other C–C σ bonds of the main bridges. Model V is obtained by diagonalizing the NBO matrix, retaining all interactions between occupied NBO's.

In Table II we summarize π_+,π_- splittings obtained from diagonalization of the NBO matrices for each of the models as well as for the full ab initio calculations.

TABLE III. β_h Values for 6–10 Obtained Using the STO-3G and 3-21G Basis Sets[a]

pair of	model[b]					Hartree–
molecules	I	II	III	IV	V	Fock
(6, 7)	1.05	0.95	0.52 (0.48)	0.47 (0.43)	0.59	0.51 (0.48)
(7, 8)	1.06	1.05	0.48 (0.48)	0.41 (0.35)	0.58	0.45 (0.42)
(8, 9)	1.03	1.06	0.47 (0.47)	0.41 (0.35)	0.55	0.39 (0.33)
(9, 10)	1.04	1.08	0.48 (0.47)	0.42 (0.34)	0.55	0.40 (0.33)

[a] Results obtained using the 3-21G basis set are given in parentheses. [b] Model I allows for *T* and *t* interactions; model II for *T*, *T'*, and *t* interactions; model III for *T*, *T'*, *t*, and *t'* interactions; model IV for *T*, *T'*, *t*, *t'*, and *t''* interactions; and model V for all interactions between occupied NBO's.

The β_h values derived from the splittings for consecutive pairs of dienes for each of these models are summarized in Table III. For models III and IV and for the full HF calculations, results obtained with the 3-21G basis set are presented in addition to the STO-3G results.

We first consider the results obtained using the STO-3G basis set. As expected, based on the perturbation theoretical analysis, the splittings are much too small (compared to the HF results) and fall off much too rapidly with increasing bridge length in models I and II. The splittings obtained in models III–V are appreciably larger and fall off more slowly with bond length. Particularly striking are the findings that the inclusion of the *t'* interactions leads to a reduction of the β_h values by about a factor of 2 and that interactions that hop over two bonds are also important, leading to 10–16% reductions in the β_h values. The β_h values obtained from model IV are in very good agreement with those of the full ab initio calculations, even though interactions between the two parallel main bridges, interactions involving the methylene bridges and the C–H bonds, and interactions involving σ^* orbitals are neglected. It is clear from the π_+,π_- splittings and the β_h values obtained from model IV, model V, and the HF calculations that the good agreement of the results of model IV with the HF predictions is, in part, fortuitous. In fact, the splittings obtained from model V are appreciably larger than the HF splittings and the corresponding β_h values, are larger by about one-third than those obtained from model IV or from the HF method. This implies that the net effect of pathways involving σ^* NBO's is to decrease the π_+,π_- splittings and to cause them to drop off more slowly with distance, leading to decreased β_h values. The good agreement of the β_h values obtained from model IV with the HF results, is due to the fact that there is considerable cancellation between contributions due to the various pathways neglected in model IV but present in the HF calculations.

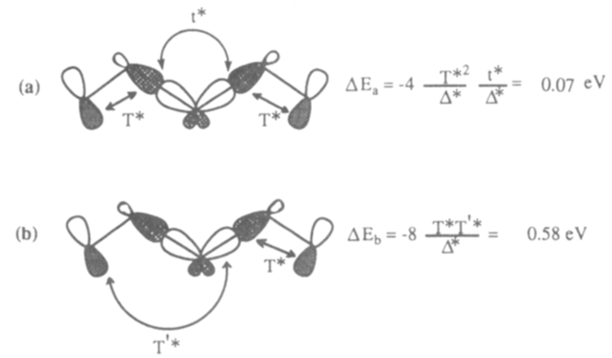


Figure 6. Pathways contributing to the TB coupling of the π^* NBO's of **6** via σ^* NBO's of the bridge.

For model III the π_+,π_- splittings and the β_h values obtained with the 3-21G basis set are nearly the same as those obtained with the STO-3G basis set. This is not surprising, since the longest range interactions permitted in this model are those that skip over one bond. On the other hand, for model IV, which also includes t'' interactions, that skip over two bonds, the β_h values obtained with the 3-21G basis set are appreciably smaller than those obtained with the STO-3G basis set. The β_h values obtained from the full HF calculations undergo similar reductions when the 3-21G basis set is used in place of the STO-3G basis set, once again showing that model IV "captures" many of the essential features of the full HF calculations.

We now consider briefly the interactions responsible for the splittings between the π^* orbitals. For **6** the π_+,π_- splitting obtained for the "classic" McConnell-type pathway, shown in Figure 6a, is about a factor of 12 smaller than that obtained from the MO calculations. A significant increase in the π_+^*,π_-^* splitting results from inclusion of coupling of the π^* NBO's to the C–C σ^* NBO's three bonds removed, as shown in Figure 6b. In fact, for **6** the contribution of pathway b ($\Delta E_b^* = -8T'^*T^*/\Delta^* = 0.58$ eV) is about two-thirds as large as the ab initio splitting of 0.86 eV. The T^* and T'^* interaction matrix elements (shown in Figure 6) are the analogues of T and T' and give the coupling of the localized π^* orbitals with the C–C σ^* orbitals of the bridge. Δ^* is the energy gap between the π^* and C–C σ^* NBO's.

Interactions along the bridge that skip over bonds are more important in the σ^* manifold than in the σ manifold. In fact, the matrix elements between the next-nearest-neighbor σ^* orbitals are actually somewhat larger in magnitude than those between the nearest-neighbor σ^* orbitals (i.e., $t'^* > t^*$), and the matrix elements (t''^*) between σ^* orbitals two bonds removed are about 60% as large (in magnitude) on the average as the t^* interactions. Even t'''^* interactions (those skipping over three bonds) between σ^* NBO's are sizable. It should be noted that t^* is about 8 times smaller than t, t'^* is comparable to t' in magnitude, and t''^* is about 2.5 times larger than t'' in magnitude. Thus, although $(t/\Delta)^2$ and t'/Δ are comparable in magnitude, (t'^*/Δ^*) is about 1 order of magnitude greater than $(t^*/\Delta^*)^2$. Examination of the STO-3G and 3-21G Fock matrices in terms of NBO's reveals that although the t^* and t'^* matrix elements actually decrease somewhat in magnitude upon going from the STO-3G to the 3-21G basis sets, the t''^* and t'''^* matrix elements are significantly larger in magnitude in the 3-21G basis set. Thus, as expected, the use of basis sets more flexible than STO-3G is particularly important for describing the coupling between σ^* NBO's more than two bonds removed.

Although the above discussion shows that long-range interactions (i.e., those skipping over one or more bonds) are very important in the σ^* manifold, we have also noted that the β_e values derived from the π_+^*,π_-^* splittings for the (**8**, **9**) and (**9**, **10**) pairs of molecules are relatively insensitive to the basis set. These two observations appear to be inconsistent, but can be reconciled by the fact that there is considerable cancellation between various pathways contributing to the π_+^*,π_-^* splittings in these compounds.

As was noted above, the MO calculations on **6** and **7** show that for these species, the π_+^* orbital is stabilized and the π_-^* orbital destabilized with respect to the π^* orbital of ethylene. This indicates that interactions involving σ NBO's must also be important for the π_+^*,π_-^* splittings. The NBO analysis shows that the matrix elements coupling the π_L and the π_L^* NBO's with the C_2–C_3 σ and σ^* NBO's are all comparable in magnitudes, as are the matrix elements coupling the π_L and the π_L^* NBO's with the C_3–C_4 σ and σ^* NBO's. This is contrary to our earlier hypothesis,[4] that matrix elements coupling the localized π and π^* orbitals with the nearby localized σ orbitals should be appreciably larger than those coupling the localized π and π^* orbitals to the corresponding localized σ^* orbitals. The greater importance of π^*/σ than π/σ^* mixing, in fact, appears to be due to differences in how the different interactions are propagated along the bridges. A detailed analysis of this phenomenon will undoubtedly require consideration of coupling between σ and σ^* NBO's associated with different bonds. With the STO-3G basis set the matrix elements between σ and σ^* NBO's associated with adjacent C–C bonds are about 1 eV in magnitude as are those between σ and σ^* NBO's separated by one bond.

VI. Conclusions

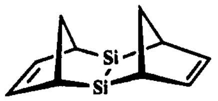
In this work we have examined the π_+,π_- splittings of a series of dienes with the ethylenic groups separated by saturated bridges containing 4–12 C–C σ bonds. The calculated splittings display small, but significant, deviations from an exponential dependence on the number of bonds in the bridge, with the deviations being most important for the shorter bridges.

An analysis of the pathways important for the π_+,π_- splittings has been carried out using NBO's. This analysis revealed that nonexponential distance dependence of the splittings can originate from pathways that skip over bonds, both because some of these pathways have an intrinsically nonexponential distance (i.e., n) dependence and because certain pathways that are important for the longer bridges do not have counterparts for the shorter bridges. The inclusion of pathways that allow for interactions that skip over bonds is important, not only to account for the deviations of the splittings from an exponential distance dependence, but also for obtaining even qualitatively accurate splittings. Interactions skipping over one or more bonds of the bridge are more important for describing TB coupling involving localized σ^* than localized σ MO's. It should be stressed that this behavior has been observed for other saturated bridges, including those involving *n*-alkanes, cyclohexane, [1.1.1]bicyclopentane, and [2.2.2]bicyclooctane units.[36,37]

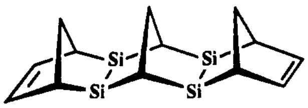
The analysis used in examining the role of various pathways (e.g., eqs 24, 27, and 28) contributing to the TB coupling in the π manifold was based on perturbation theory and would cease to be valid if t/Δ or T/Δ were not much less than 1 in magnitude. For **6**–**10**, T/Δ is approximately equal to $^1/_6$ and the various t/Δ terms are close to $^1/_3$ in magnitude. These coupling constants are large enough that the corrections to the simple perturbation treatment involving retracing interactions are non-negligible. However, as shown in the Appendix, some of the corrections to the perturbation theoretical approach described in the main body of the paper are positive and others are negative, with the result that there is appreciable cancellation between these terms.

A nonperturbative approach, in which one retains only subsets of the matrix elements over NBO's, was also considered. This approach accounts for retracing terms to all orders and is applicable even if the various t/Δ or T/Δ quantities are not small. Within this scheme, we presented a simple model (designated model IV) which, although it retains only a small subset of the possible interactions, accounts in a semiquantitative manner for the π_+,π_- splittings and their distance dependence. However, even in this case, the success of the model depends, in part, upon the fact that the contributions of various neglected pathways tend to cancel.

So far we have focused our attention on the distance dependence of TB interactions. Although this dependence has great relevance to electron- and energy-transfer processes, another important factor is the strength of the interactions for a given distance. We have initiated theoretical studies to obtain a better understanding of the factors that determine the coupling strength and with the goal of designing bridges which would be more effective for electron and energy transfer. Our preliminary studies have focused on appropriately substituted polysilanorbornyl systems such as **31** and **32**.[43] The reason for choosing these species is that the replacement of carbon atoms by silicon atoms at the indicated positions should greatly increase T^2/Δ, both because the C–Si σ NBO has a higher energy than the C–C σ NBO and because the C–Si NBO is polarized toward the C atom, which should lead to an enhanced overlap with the π NBO over that for the C–C σ NBO in the corresponding hydrocarbons. Similarly, we expect enhanced coupling of the π^* NBO's, with the C–Si σ^* and σ NBO's. Indeed, calculations on **31** and **32**, which are Si-substituted analogues of **6** and **7** show that the introduction of the Si atoms leads to enhanced π_+,π_- and π_+^*,π_-^* splittings. With the STO-3G basis set, the π_+,π_- splittings of **31** and **32** are 1.91 and 1.53 eV, respectively, approximately 2 and 5 times larger than the π_+,π_- splittings of **6** and **7**, respectively. The calculated π_+^*,π_-^* splittings of **31** and **32** are 1.43 and 0.44 eV, respectively, again much larger than those of the corresponding hydrocarbons. An examination of the Fock matrix over NBO's reveals that both T/Δ and some of the t/Δ interactions are appreciably larger in magnitude in the silicon derivatives than in the parent hydrocarbons. Consequently, a perturbative approach is of little value in analyzing the contributions of various pathways in **31** and **32**. However, the procedure described in section V, in which one diagonalizes NBO matrices, retaining various subsets of the possible interactions, is still applicable.



31



32

In addition to providing a more detailed understanding of the factors determining the splittings in D–B–A compounds, the NBO procedure provides a method of predicting the π_+,π_- and π_+^*,π_-^* splittings of molecules with long bridges by using matrix elements determined from ab initio calculations on smaller molecules. This is possible because the matrix elements over NBO's are, to a very good approximation, transferable. For example, the matrix element giving the coupling between the σ NBO's of the C_2–C_3 and C_3–C_4 bonds is nearly the same for each of the dienes **6**–**10**. The transferability of localized orbitals and their utility for studying through-bond interactions was noted well over a decade ago by Heilbronner and co-workers and by Imamura and Ohasaku,[33] but it is only over the past few years that various researchers have begun to use this technique for elucidating the factors contributing to the electronic coupling responsible for electron and hole transfer in donor–bridge–acceptor systems.[35–38]

From the examination of the NBO matrices it is seen that the interaction elements between NBO's separated by four or more bonds are very small even in the case of the σ^* NBO's. Hence it should be possible to ignore all such matrix elements without introducing sizable errors in the π_+,π_- or π_+^*,π_-^* splittings. Moreover, due to the transferability of the matrix elements between molecules, we conclude that one could determine all matrix elements needed for accurately predicting the splittings of **9**, **10**, and longer members in this series from a Hartree–Fock/NBO analysis of **8**, or perhaps even **6**. It should also be possible to obtain all matrix elements needed for predicting the π_+,π_- (or π_+^*,π_-^*) splittings in **11**–**15** by combining the matrix elements describing the coupling to the bridge (T, T', etc.) from a HF/NBO analysis of **11** with the various matrix elements describing propagation along the bridge (t, t', t'', etc.) obtained from the NBO analysis of **8**. This approach for predicting the electronic couplings in such molecules requires orders of magnitude less computational time than would ab initio electronic structure calculations.

Acknowledgments. This work was supported by the National Science Foundation (K.D.J.) and the Australian Research Council (M.P.R.). We acknowledge insightful discussions with Drs. D. Beratan, J. Miller, and M. Newton and with D. Abramovitz.

Appendix: Influence of the Terminal C–C Bonds

In the perturbative analysis interactions involving the C_1–C_2 and C_{N-1}–C_N bonds of the main bridge were neglected. From examination of the STO-3G NBO matrix of **6** it is seen that the matrix elements between the π_L NBO and the σ_1, σ_2, and σ_3 NBO's are 0.48, 1.38, and −0.38 eV, respectively. The latter two matrix elements are T and T', considered in the main body of the paper. The matrix element between π_L and σ_1 NBO's (or between π_R and σ_4), denoted as T^+, is comparable in magnitude to T'. However, the T^+ coupling to the bridge proves important for the π_+,π_- splitting only if the σ_1 and σ_4 NBO's are allowed to couple to the other σ NBO's of the bridge, which leads to additional factors of $(t/\Delta)^2$ or t/Δ not present when the coupling to the bridge occurs via T'. Thus, both the relatively small magnitude of T^+ and the fact that coupling to the bridge via T^+ rather than via T or T', effectively lengthens the bridge along which the coupling must occur, requiring additional relays, tend to make these interactions small in magnitude.

In order to estimate the importance of terms involving T^+ coupling to the bridge, it suffices to restrict our attention to the case in which propagation along the main bridge occurs via nearest-neighbor (i.e, t-type) interactions. For **6**, the following terms involving T^+ coupling contribute to the π_+,π_- splitting: $-8(TT^+/\Delta)(t/\Delta)^2$, $-4(T^{+2}/\Delta)(t/\Delta)^3$, and $-8(T'T^+/\Delta)(t/\Delta)$, where multiplicative factors accounting for the presence of equivalent pathways have been included. Of these, the first and third terms, which are negative, dominate. Combined, the contribution to these three terms to the π_+,π_- splitting is about 14% as large (in magnitude) as that due to the sum of the interactions given in eq 14 and 17. Although, the net effect of these interactions terms involving T^+ is to decrease the splitting, there are other interactions involving the terminal σ bonds, to be discussed below, which act so as to increase the π_+,π_- splitting.

The π_+,π_- splitting obtained by adding the generalized form of the above three interactions to eq 27 is

$$\Delta E = -4(T^2/\Delta)(t/\Delta)^{n-3} - 8(TT'/\Delta)(t/\Delta)^{n-4} - 8(TT^+/\Delta)(t/\Delta)^{n-2} - 4(T^{+\,2}/\Delta)(t/\Delta)^{n-1} - 4(T'^2/\Delta)(t/\Delta)^{n-5} - 8(T'T^+/\Delta)(t/\Delta)^{n-3} \quad \text{(A1)}$$

All of the terms on the right hand side of A1 equation can be combined to give an expression of the form $-4(\tilde{T}^2/\Delta)(t/\Delta)^{n-3}$, where $\tilde{T} = (T + T'\Delta/t + T^+t/\Delta)$ is an effective coupling to the bridge. Hence, providing that coupling pathways along the bridge that skip over bonds and those which involve retracing are ignored, the additional interactions involving T^+ coupling do not influence the distance dependence of the splittings.

Even in the absence of the T^+ coupling mechanism, the terminal C–C bonds of the main bridges are expected to influence the π_+,π_- splittings since they raise the energies of the high-lying delocalized σ orbitals. In order to illustrate the nature of such interactions, we again restrict ourselves to the case that the coupling along the chain occurs via nearest-neighbor (i.e., t) interactions and coupling to the bridge occurs via T and T' interactions. In this case for **6**, there are two additional contributions to the π_+,π_- splitting, $-8(T^2/\Delta)(t/\Delta)^3$ and $-8(TT'/\Delta)(t/\Delta)^2$, which are shown in Figure 4, parts e and f, respectively. Both of these terms involve retracing interactions with the σ_1 (or σ_4) NBO's, and thus are smaller by factors of $2(t/\Delta)^2$ and $(t/\Delta)^2$, respectively, than the $-4(T^2/\Delta)(t/\Delta)$ and $-8TT'/\Delta$ contributions considered previously. Moreover, both of these terms are positive, and thus act so as to increase the π_+,π_- splitting in **6**. In the general case, the effect of these additional interactions involving the terminal σ bonds can also be absorbed into an effective T coupling and, hence, are not expected to prove important for the distance dependence of the splittings (i.e., for determining the β values).

If one includes the coupling of the terminal C–C σ bonds to the other σ bonds of the main bridge, then for consistency, one should also include other interactions involving retracing, e.g., between σ_3 and σ_4 in **6**. However, the number of such terms depends on the length of the bridge. Thus, these pathways are analogous to those involving interactions that skip over bonds, in that their presence introduces deviations from exponential behavior and prevents a perfect factorization of the splitting into a term describing the coupling to the bridge and a term describing the propagation along the bridge.

Registry No. **6**, 83602-18-0; **7**, 83830-72-2; **8**, 83797-20-0; **9**, 128300-59-4; **10**, 138060-37-4.

VII. References

(1) Calcatera, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1988**, *105*, 670. Closs, G. L.; Calcatera, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673.

(2) (a) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258. (b) Penfield, K. W.; Miller, J. R.; Paddon-Row, M. N.; Cotsaris, E.; Oliver, A. M.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 5061. (c) Warman, J. M.; de Haas, M. P.; Paddon-Row, M. N.; Cotsaris, E.; Hush, N. S.; Oevering, H.; Verhoeven, J. W. *Nature* **1986**, *320*, 615. (d) Oliver, A. M.; Craig, D. C.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1988**, *150*, 366. (e) Warman, J. M.; Smit, K. J.; de Haas, M. P.; Jonker, S. A.; Paddon-Row, M. N.; Oliver, A. M.; Kroon, J.; Oevering, H.; Verhoeven, J. W. *J. Phys. Chem.* **1991**, *95*, 1979. (f) Antolovich, M.; Keyte, P. J.; Oliver, A. M.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W.; Jonker, S. A.; Warman, J. M. *J. Phys. Chem.* **1991**, *95*, 1933. (g) Paddon-Row, M. N.; Verhoeven, J. W. *New. J. Chem.* **1991**, *15*, 107. (h) Warman, J. M.; Mom, M.; Paddon-Row, M. N.; Oliver, A. M.; Kroon, J. *Chem. Phys. Lett.* **1990**, *172*, 114.

(3) (a) Connolly, J. S.; Bolton, J. R. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part D, p 303. (b) Wasielewski, M. R. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part A, p 161. (c) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596. (d) Gust, D.; Moore, T. A. *Science* **1989**, *244*, 35. (e) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090. (f) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571. (g) Joran, A. D.; Leland, B. A.; Felker, P. M.; Zewail, A. H.; Hopfield, J. J.; Dervan, P. B. *Nature (London)* **1987**, *327*, 508. (h) Gust, D., Moore, T. A., Eds.; "Covalently Linked Donor-Acceptor Species for Mimicry of Photosynthetic Electron and Energy Transfer", Tetrahedron Symposium-in-Print No. 39. *Tetrahedron* **1989**, 45. (i) Wasielewski, M. R.; Niemczyk, M. P.; Johnson, D. G.; Svec, W. A.; Minsek, D. W. *Tetrahedron* **1989**, *45*, 4785.

(4) (a) Balaji, V.; Ng, L.; Jordan, K. D.; Paddon-Row, M. N.; Patney, H. K. *J. Am. Chem. Soc.* **1987**, *109*, 6957. (b) Paddon-Row, M. N.; Jordan, K. D. In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988.

(5) Broo, S.; Larsson, S. *Chem. Phys.* **1990**, *148*, 103.

(6) Onuchic, J. N.; Beratan, D. N. *J. Chem. Phys.* **1990**, *92*, 722.

(7) Mikkelsen, K. V.; Ratner, M. D. *Chem. Rev.* **1987**, *87*, 113 and references therein.

(8) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767.

(9) (a) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (b) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (c) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696. (d) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245. (e) Martin, H.-D.; Mayer, B. *Angew. Chem., Int. Ed. Engl.*

1983, *22*, 283. Gleiter, R.; Schaefer, W. *Acc. Chem. Res.* **1990**, *23*, 369.

(10) Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884. Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.

(11) Levich, V. G. In *Electrochem. Electrochem. Eng.* **1966**, *4*, 249. Dogonadze, R. R.; Kuznetsov, A. M. *Elektrokhim.* **1967**, *2*, 1324. Marcus, R.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. Newton, M. D.; Sutin, N. *Ann. Rev. Phys. Chem.* **1984**, *35*, 437 and references therein.

(12) Paddon-Row, M. N.; Wong, S. S. *Chem. Phys. Lett.* **1990**, *167*, 432.

(13) Jordan, K. D.; Paddon-Row, M. N. *J. Phys. Chem.* **1992**, *96*, 1188.

(14) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508. See also, Halpern, J.; Orgel, L. *Discuss. Faraday Soc.* **1960**, *29*, 32.

(15) (a) Paddon-Row, M. N.; Patney, H. K.; Brown, R. S.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5575. (b) Paddon-Row, M. N.; Jorgensen, F. S.; Patney, H. K. *J. Chem. Soc., Chem. Commun.* **1983**, 573. (c) Jorgensen, F. S.; Paddon-Row, M. N. *Tetrahedron Lett.* **1983**, 5415. (d) Paddon-Row, M. N.; Patney, H. K.; Peel, J. B.; Willett, G. D. *J. Chem. Soc., Chem. Commun.* **1984**, 564.

(16) Falcetta, M. F.; Jordan, K. D.; McMurry, J. E.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1990**, *112*, 579. Balaji, V.; Jordan, K. D.; Gleiter, R.; Jahne, G.; Muller, G. *J. Am. Chem. Soc.* **1985**, *107*, 7321. Morrison, H.; Singh, T. V.; de Cardenas, L.; Severance, D.; Jordan, K. D.; Schaefer, W. *J. Am. Chem. Soc.* **1986**, *108*, 3862.

(17) (a) For a discussion of the STO-3G and 3-21G basis sets as well as citations to the original references, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons, Inc.: New York, 1986. (b) D95v basis sets: Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(18) Koopmans, T. *Physica* **1934**, *1*, 104.

(19) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Chem. Soc., Perkin Trans. 2* **1990**, 425.

(20) Martin, H.-D.; Schwesinger, R. *Chem. Ber.* **1974**, *107*, 3143.

(21) Kroon, J.; Oliver, A. M.; Paddon-Row, M. N.; Verhoeven, J. W. *Recl. Trav. Chim.* **1988**, *107*, 509.

(22) Ohta, K.; Closs, G. L.; Morokuma, K.; Green, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 1319.

(23) Paddon-Row, M. N. *J. Chem. Soc., Perkin Trans. 2* **1985**, 257.

(24) Paddon-Row, M. N.; Englehardt, L. M.; Skelton, B. W.; White, A. H.; Jorgensen, F. S.; Patney, H. K. *J. Chem. Soc. Perkin Trans. 2* **1987**, 1835.

(25) McGourty, J. L.; Blough, N. V.; Hoffman, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 4470.

(26) Crutchley, R. J.; Ellis, Jr.; W. R.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 5002.

(27) Gray, H. B. *Chem. Soc. Rev.* **1986**, *15*, 17.

(28) Liang, N.; Kang, C. H.; Ho, P. S.; Margoliash, E.; Hoffman, B. M. *J. Am. Chem. Soc.* **1986**, *108*, 4665.

(29) Oliver, A. M.; Paddon-Row, M. N.; Symons, M. C. R. *J. Am. Chem. Soc.* **1989**, *111*, 7259.

(30) Burrow, P. D.; Jordan, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 5247.

(31) Beez, M.; Bieri, G.; Bock, H.; Heilbronner, E. *Helv. Chim. Acta* **1973**, *56*, 1028.

(32) Falcetta, M. F.; Jordan, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 2903 and references therein.

(33) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936. Imamura, A.; Ohsaku, M. *Tetrahedron* **1981**, *37*, 2191.

(34) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736.

(35) (a) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Am. Chem. Soc.* **1990**, *112*, 1710. (b) Paddon-Row, M. N.; Jordan, K. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1508. (c) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Chem. Soc. Perkin Trans. 2* **1990**, 417.

(36) Naleway, C. A.; Curtis, L. A.; Miller, J. R. *J. Phys. Chem.* **1991**, *95*, 8434.

(37) Liang, C.; Newton, M. *J. Phys. Chem.*, submitted for publication.

(38) Abramovitz, D.; Jordan, K. D.; Paddon-Row, M. N., to be submitted for publication.

(39) Onuchic, J. N.; de Andrade, P. C. P.; Beratan, D. N. *J. Chem. Phys.* **1991**, *95*, 1131.

(40) Siddarth, P.; Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 2985.

(41) Ratner, M. A. *J. Phys. Chem.* **1990**, *94*, 4877.

(42) It might be more appropriate to compare the quantity ΔE_a with the π_+,π_- splitting obtained by diagonalizing the NBO matrix including all interactions between filled (noncore) NBO's, but neglecting interactions with core and unfilled NBO's, rather than that obtained by diagonalizing the full NBO matrix including all filled and unoccupied NBO's. The quantity ΔE_a is about 2.1 times smaller than the π_+,π_- splitting obtained neglecting all interactions with σ^* and core NBO's.

(43) Jordan, K. D.; Paddon-Row, M. N., to be submitted for publication.