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Why Is a Simple *n*-Alkyl Bridge More Efficient Than a Polynorbornyl Bridge at Mediating Through-Bond Coupling?

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Abstract: NBO analyses have been conducted on a series of polynorbornyl dienes and α,ω-divinyl alkanes in an attempt to delineate the destructive interference mechanisms that cause through-bond coupling in the π manifold to display a stronger distance dependence in the former series than in the latter. It appears that two principal mechanisms are responsible for the destructive interference in the polynorbornyl dienes. These are the "cross-links" mechanism, in which interference is caused by the C–C bonds joining the relays, and the "cross-talk" mechanism, in which the interference occurs by way of direct, through-space interactions between the relays. Of these two mechanisms, the "cross-talk" mechanism is found to be more important. The bridge C–H bonds are found to have a negligible effect upon the electronic couplings in the polynorbornyl dienes, although they have a significant influence in the divinyl alkanes.

Introduction

Long range intramolecular electron transfer (ET) and hole transfer (HT) between rigid, covalently linked donor–{saturated hydrocarbon bridge}–acceptor (D-B-A) dyads is a subject of major ongoing experimental study.[1] Bridges that have been used in such studies include bicyclo[2.2.2]octane,[2] triptycene,[3] polyspirocyclobutanes,[4] cyclohexane,[5] decalin,[5] and norbornylogous[6] systems. Studies on such dyads have amply demonstrated that rapid intramolecular ET can take place over large interchromophore separations, presumably by way of a through-bond (TB) coupling mechanism involving the bridge σ and σ^* orbitals.[7] For example, the photoinduced ET rate, k_{et}, for the 12-bond norbornylogous molecule, **1(12)**, was found to be $\approx 10^9$ s^{-1}, even though the interchromophore separation in this molecule is ≈ 13.5 Å.[6a] These experimental observations have generated widespread theoretical interest in determining how bridge characteristics affect the magnitude and distance dependence of the electronic coupling matrix element, H_{el}.[8–16]

For the different D-B-A systems, k_{et} has been found to display an approximate exponential distance decay dependence with increasing number, n, of bridge C–C bonds concerning the two chromophores, i.e.

$$k_{et} \propto \exp(-2\beta^0 n) \tag{1}$$

where β^0 has been found to lie between 0.4 and 0.6 per bond.[1b,2a,4,6a] Given that long range (>7 Å) ET occurs under the nonadiabatic, weak-coupling limit, application of the Golden Rule leads to the following expression for k_{et}

$$k_{et} = \frac{4\pi^2}{h}|H_{el}|^2\mathrm{FCWD} \tag{2}$$

where H_{el} is the electronic coupling matrix element between donor (D) and acceptor (A) and FCWD denotes the Franck–Condon weighted density of states.[14] It is generally assumed that H_{el} falls off approximately exponentially with increasing interchromophore separation:

$$H_{el} = H_{el}^0 \exp(-\beta n) \tag{3}$$

If the FCWD term in eq 2 is not distance dependent, then $\beta = \beta^0$.

Electronic couplings have recently been calculated for the polynorbornyl dienes, **3(*n*)**,[13,15] and α,ω-divinyl alkanes, **2(*n*)**,[16]

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(1) (a) Wasielewski, M. R. *Photoinduced Electron Transfer, Part D*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Chaper 1.4. (b) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (c) Paddon-Row, M. N.; Verhoven, J. W. *New J. Chem.* **1991**, *15*, 107. (d) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(2) (a) Joran, A. D.; Leyland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090. (b) Leyland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571.

(3) Wasielewski, M. R.; Niemcyzk, M. P.; Johnson, D. G.; Svec, W. A.; Minsek, D. W. *Tetrahedron* **1989**, *45*, 4785.

(4) Stein, C. A.; Lewis, N. A.; Seitz, G. J. *J. Am. Chem. Soc.* **1982**, *104*, 2596.

(5) (a) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670. (b) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. (c) Pasman, P.; Mes, G. F.; Koper, N. W.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1985**, *107*, 5839.

(6) (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) Oliver, A. M.; Craig, D. C.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1988**, *150*, 366. (c) Kroon, J.; Verhoeven, J. W.; Paddon-Row, M. N.; Oliver, A. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1358. (d) 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.

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

(8) Larsson, S. *J. Am. Chem. Soc.* **1981**, *103*, 4034.

(9) Newton, M. D. *Int. J. Quantum Chem. Symp.* **1980**, *14*, 363.

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

(11) Onuchic, J. N.; Beratan, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6771.

(12) (a) Naleway, C. A.; Curtiss, L. A.; Miller, J. R. *J. Phys. Chem.* **1991**, *95*, 8434. (b) Curtiss, L. A.; Naleway, C. A.; Miller, J. R. *J. Phys. Chem.* **1993**, *97*, 4050.

(13) Paddon-Row, M. N.; Jordan, K. D. In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenburg, A., Eds.; VCH Publishers: New York, 1988; p 115.

(14) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(15) (a) Paddon-Row, M. N.; Wong, S. S. *Chem. Phys. Lett.* **1990**, *167*, 432. (b) Jordan, K. D.; Paddon-Row, M. N. *J. Phys. Chem.* **1992**, *96*, 1188. (c) Jordan, K. D.; Paddon-Row, M. N. *Chem. Rev.* **1992**, *92*, 395. (d) Paddon-Row, M. N.; Jordan, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 2952.

(16) (a) Paddon-Row, M. N.; Shephard, M. J.; Jordan, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 3312. (b) Paddon-Row, M. N.; Shephard, M. J.; Jordan, K. D. *J. Phys. Chem.* **1993**, *97*, 1743.

0002-7863/94/1516-5328$04.50/0

Table 1. HF/3-21G π_+,π_- Splitting Energies, ΔE (eV), and $\beta_h(n,n+2)$ Values (per bond) Determined from the Splittings for Adjacent Members in the Divinyl Alkane **2(*n*)** and Polynorbornyl Diene **3(*n*)** Series

no. of bonds (n)	**2(*n*)**[a]		**3(*n*)**[b]	
	ΔE	$\beta_h(n,n+2)$	ΔE	$\beta_h(n,n+2)$
4	0.577	0.35	1.017	0.54
6	0.288	0.29	0.344	0.41
8	0.160	0.27	0.151	0.33
10	0.0936	0.27	0.0781	0.34
12	0.0550	0.26	0.0396	0.34
14	0.0324	0.26	0.0200	0.34
16	0.0191		0.0102	

[a] Using the HF/3-21G optimized geometries. [b] Using the HF/STO-3G optimized geometries.

using the Koopmans' theorem (KT) approach,[17] in which the π_+,π_- and π_+^*,π_-^* splitting energies are taken as measures of the electronic coupling for HT and ET, respectively.[10,13] It should be noted that the KT derived π_+,π_- couplings calculated in this study are more relevant for the process of thermal HT in the radical cations than for photoassisted ET in the neutral molecules. This is because the energy gaps between the relevant chromophore and bridge levels are different in the two types of experiment. Table 1 summarizes the calculated π_+,π_- splittings and the β_h-$(n,n+2)$ values (per bond) for successive pairs of molecules of the **2(*n*)** and **3(*n*)** series, for $n = 4$ to 16 (even values of n), using the 3–21G basis set.[18] (The subscript in β_h signifies that the β value refers to hole transfer processes.) It is immediately apparent from these results that the β_h values are markedly larger for the polynorbornyl dienes than for the divinyl alkanes, by as much as 35% for the shorter members, and leveling off to ≈20% for the longer members.

These results indicate that simple *n*-alkyl bridges are more effective mediators of TB coupling (in the hole manifold) over long distances than the polynorbornyl bridges, even though the double bonds in the latter are connected by two "alkyl" relays, as shown in Figure 1A, rather than one, as is the case for the divinyl alkanes. The differences in the β_h values for the **2(*n*)** and **3(*n*)** series imply that there is destructive interference occurring between various coupling pathways in the polynorbornyl bridge. The role of destructive interference in polynorbornyl bridges has been previously examined by Onuchic and Beratan.[11] Whereas these authors focused on interference effects due to pathways involving the C–H bonds and the C–C cross-link bonds connecting the two "alkyl" relays in polynorbornyl bridges (highlighted bonds in Figure 1B), we consider also the role of direct, through-space coupling between the two main relays. In this work we use ab initio calculations in conjunction with the natural bond orbital (NBO)[19] method in an effort to obtain a more detailed understanding of the destructive interference effects that occur in **2(*n*)** and **3(*n*)**. The NBO treatment has been demonstrated to provide quantitatively useful dissections of H_{el}.[12,15c,20–22]

Computational Methodology

The geometries of **2(*n*)** and **3(*n*)** were optimized[23] at the Hartree–Fock (HF) level of theory using the 3-21G and the STO-3G basis sets, respectively.[18] Symmetry constraints used for the optimizations were C_2 and C_{2v} for **2(*n*)** and **3(*n*)**, respectively. With the divinyl alkane systems, the dihedral angle between the plane of each double bond and its respective allylic C–C bridge bond was fixed at 90° in order to maximize the σ–π overlap. This arrangement is clarified by (A) in Chart 1.

The NBO technique for analyzing TB coupling has been described elsewhere[22] and only a brief summary is given here. The diagonal elements of the Fock NBO matrix correspond to the self energies of the NBOs, and the off-diagonal elements correspond to the interaction energies between pairs of NBOs. By progressively adding appropriate off-diagonal elements to a "blank" Fock NBO matrix (i.e., one that contains only the diagonal elements), followed by diagonalization of the resulting matrices, one obtains a quantitative dissection of the TB coupling in terms of interactions between various NBOs. In this study, the NBO analysis is applied to Fock matrices generated from HF calculations using the 3-21G basis set. As a check of the sensitivity of the results to the localization scheme, calculations using the Foster–Boys localization procedure[24] have also been carried out.

Our choice of the 3-21G basis set over more flexible ones is justified by the results of an earlier study on the dienes **3(*n*)**, in which we demonstrated that the π_+,π_- splittings obtained with the 3-21G basis set are nearly the same as those obtained with more flexible basis sets.[15b] Consequently, increased flexibility beyond that in the 3-21G basis set appears to be unimportant for describing the net coupling in the π manifold of the polynorbornyl dienes.

Two other aspects of the calculations—the use of the KT approximation, and the use of the optimized geometries of the neutral molecules—warrant further discussion. The KT approximation neglects the contributions made by orbital relaxation and correlation effects toward the ionization potentials (IPs). We have recently shown that, although both the relaxation and correlation corrections to the IP values are sizable, these two corrections act in opposite directions, with the result that the KT and second-order Møller–Plesset[25] (MP2) IP values are in fairly good agreement.[26] Moreover, the rate of falloff of the IP values with increasing bridge length is nearly the same in the KT and MP2 calculations. These results provide a justification for the use of the KT procedure for analyzing the electronic couplings in the π manifold of the polynorbornyl dienes.

The KT calculations were carried out using the HF/3-21G optimized geometries of the neutral molecules. The resulting IP values are thus particularly relevant for comparing with the results of photoelectron spectroscopic studies. However, for the purpose of obtaining couplings relevant for thermal hole transfer in the radical cations, it would be more appropriate to apply the KT approach to the neutral dienes using the optimized geometries calculated for the cation radical transition structures, at which the diabatic potentials for the radical cations cross. In order to determine whether the use of the geometries of the neutral molecules rather than the transition structures introduced significant errors in the π_+,π_- splittings, the geometries of the ground state radical cations of the first five members of the polynorbornyl series **3(*n*)** were optimized using the spin-unrestricted Hartree–Fock (UHF) method under the constraint of C_{2v} symmetry. KT calculations were then carried out on the neutral dienes at the optimized geometries of their corresponding cation radicals. The results are presented in Table 2. It is apparent from these results that, compared with those given for **3(*n*)** in Table 1, comparable π_+,π_- splittings and β_h values are obtained for both sets of geometries. Consequently, little error is introduced by using the optimized geometries of the neutral dienes.

Results and Discussion

In order to verify that destructive interference between the relays is the major factor causing the TB coupling in the polynorbornyl dienes to be less effective than that in divinyl alkanes, an NBO analysis was conducted on a modified **3(*n*)** series. In this analysis, only interactions occurring through *one* of the two relays connecting the double bonds were retained. This single relay series is denoted by **3s(*n*)** (Chart 1). The following series of NBO models were applied to **3s(4)**–**3s(12)**.

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

(18) Hehre, W. J.; Radom, L.; Schleyer, P.v.R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons; 1986; also references cited therein.

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

(20) Liang, C.; Newton, M. D. *J. Phys. Chem.* **1992**, *96*, 2855.

(21) McKinley, A. J.; Ibrahim, P. N.; Balaji, V.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 10631.

(22) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Am. Chem. Soc.* **1990**, *112*, 1710.

(23) *Gaussian 92*; Revision A, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foreman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavacchari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian Inc.: Pittsburg, PA, 1992.

(24) (a) Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296. (b) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300.

(25) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(26) Kim, K.; Jordan, K. D.; Paddon-Row, M. N. *J. Phys. Chem.* Submitted for publication.

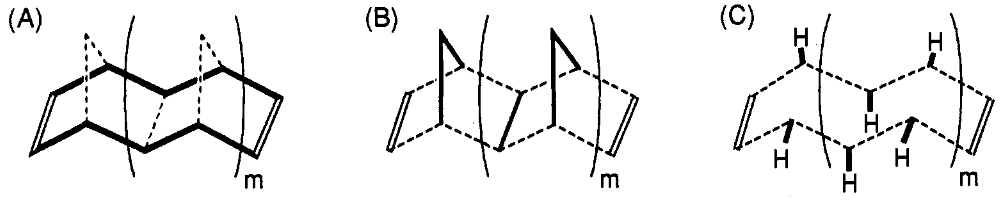
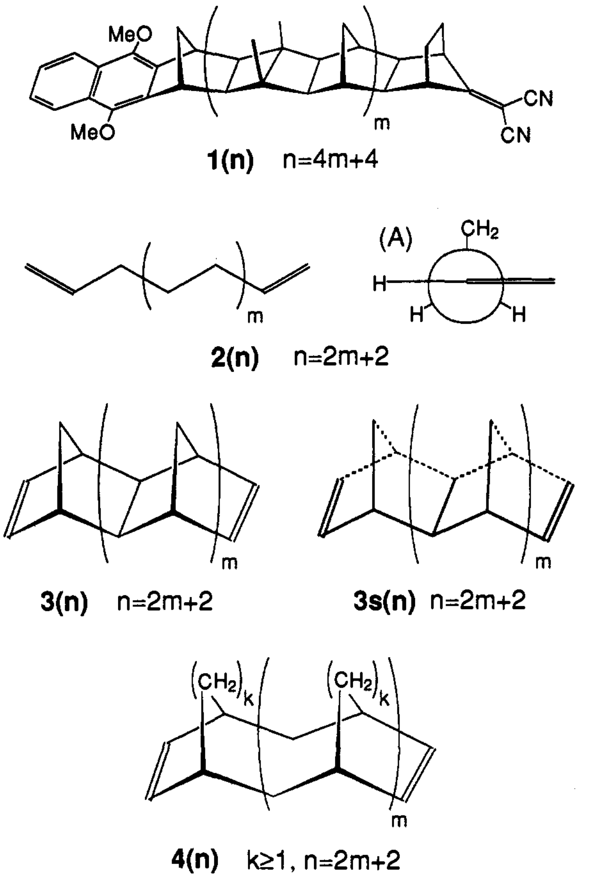


Figure 1. The three major components that affect the electronic coupling in **3(*n*)** are the following: (A) the two alkyl relays connecting the two chromophores (highlighted bonds); (B) the cross-links connecting the two alkyl relays (highlighted bonds); (C) the C–H bonds adjoining the two alkyl relays (highlighted bonds).

Chart 1[a]



[a] The label *n* refers to the number of C–C σ bonds connecting the chromophores along a single relay of the bridge.

Table 2. HF/3-21G π_+,π_- Splitting Energies, ΔE (eV), and $\beta_h(n,n+2)$ Values (per bond) Determined from the Splittings for Adjacent Members of the Neutral Polynorbornyl Diene **3(*n*)** Series at the Geometries of the Corresponding Radical Cation Transition Structures for Hole Transfer[a]

molecule **3(*n*)**	ΔE	$\beta_h(n,n+2)$
3(4)	1.278	0.59
3(6)	0.394	0.45
3(8)	0.160	0.38
3(10)	0.0752	0.39
3(12)	0.0348	

[a] Using the UHF/STO-3G optimized geometries of the corresponding ground state, C_{2v} symmetry, cation radical polynorbornyl diene.

Model I: Only those interactions involving the π NBOs and the C–C σ and σ^* NBOs that comprise the single relay are included, as shown by the highlighted bonds in Figure 2A. The C–C σ and σ^* NBOs of the ethylenic groups are not included.

Model II: In addition to the interactions present in model I, those involving the non-vinyl C–H σ and σ^* NBOs adjoining the relay are included. The NBOs used in this model are shown (highlighted) in Figure 2B.

Model III: In addition to those interactions present in model II, those involving the C–C σ and σ^* NBOs of the cross-links are included. The NBOs used in this model are shown (highlighted) in Figure 2C.

The π_+,π_- splittings and the associated β_h values (per bond) for **3s(*n*)** obtained from application of these models are summarized in Table 3. Included for comparison are the π_+,π_- splittings and β_h values for the divinyl alkane species obtained from the application of models I and II to **2(*n*)**.

Comparison of the NBO results for **3s(*n*)** (Table 3) with the full HF calculations on **3(*n*)** (Table 1) shows that the decay of the coupling with increasing bridge length is much slower for the former. The magnitude of the π_+,π_- splittings for the shorter members of the **3s(*n*)** series, for all three models, is about one-half of the HF values. On the other hand, the splittings for the longer members of the **3s(*n*)** series are larger than the corresponding HF values.

It is gratifying to note that both the π_+,π_- splittings and the β_h values for all three NBO models applied to **3s(*n*)** are close to the respective values for the NBO models applied to **2(*n*)** and to the full HF results for **2(*n*)**. For example, the limiting β_h values for **3s(*n*)** obtained using models I, II, and III are 0.23, 0.26, and 0.27, respectively, while the corresponding limiting β_h values for **2(*n*)** are 0.22 for model I, 0.24 for model II, and 0.26 for the HF calculations. These results indicate that the TB coupling through a single relay of the polynorbornyl dienes closely approximates that through the alkyl bridge in the divinyl alkanes. Thus, the geometrical differences existing between **3s(*n*)** and **2(*n*)** have negligible effect on the β_h values.

Given the similarity in the TB coupling between the **3s(*n*)** and **2(*n*)** systems, one might expect, from consideration of simple perturbation theory, that the π_+,π_- splittings in **3(*n*)** should be twice as large as the respective splittings for **2(*n*)**, and that the β_h values should be similar for both series. As the data in Table 1 clearly show, this is not the case; consequently, some form of destructive interference in the TB coupling of **3(*n*)** must be occurring.

There are two possible mechanisms for this destructive interference. Firstly, the two relays could interfere via a direct, through-space mechanism resulting from inter-bridge orbital overlap ("cross-talk" mechanism). Examples of possible "cross-talk" interactions are shown in Figure 3. Alternatively, the interference may be caused by the cross-link bonds, which interfere with the TB coupling occurring in a relay, and also allow destructive interactions to pass from one relay to the other, as originally suggested by Onuchic and Beratan[11] ("cross-links" mechanism). The relative importance of these two mechanisms can be assessed through application of the following NBO models to **3(4)**–**3(12)**.

Model IV: Only the interactions involving the π NBOs and the C–C σ and σ^* NBOs of both relays are included. The C–C σ and σ^* NBOs associated with the ethylenic groups are not included. The NBOs used in this model are shown in Figure 1A.

Model IV′: Identical to model IV, with the exception that all σ–σ and σ^*–σ^* inter-relay interactions are deleted.

Model V: In addition to those interactions included in model IV, the non-vinyl C–H σ and σ^* NBOs of the two relays are included. The C–H NBOs used are shown in Figure 1C.

Model V′: Identical to model V, with the exception that all σ–σ and σ^*–σ^* inter-relay interactions are deleted.

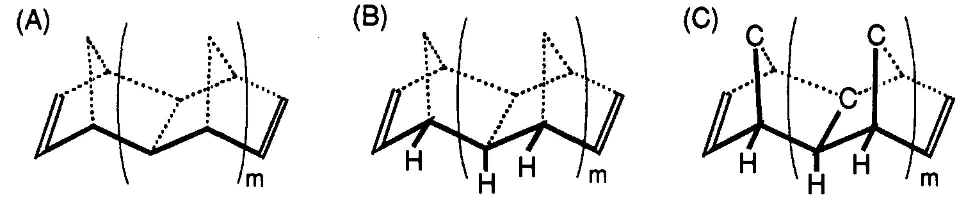


Figure 2. The three NBO models used for analyzing TB coupling interactions in a single relay of **3(*n*)**—the highlighted bonds indicate the NBOs included in each model: (A) a single relay comprised of only the C–C σ and σ^* NBOs (model I); (B) the NBOs included in model I and the C–H σ and σ^* NBOs adjoining the single relay (model II); (C) the NBOs included in model II and C–C cross-link σ and σ^* NBOs (model III).

Table 3. HF/3-21G π_+,π_- Splitting Energies (eV) and $\beta_h(n,n+2)$ Values (per bond) Determined from the Splittings for Adjacent Members in a Single Relay of the Polynorbornyl Dienes **3s(*n*)** and Divinyl Alkanes **2(*n*)** for NBO Analysis Models I, II, and III

no. of	3s(*n*)			2(*n*)	
bonds (*n*)	I	II	III	I	II
4	0.537	0.600	0.680	0.581	0.674
6	0.351	0.365	0.384	0.328	0.353
8	0.214	0.219	0.213	0.205	0.206
10	0.132	0.135	0.118	0.130	0.125
12	0.0827	0.0811	0.0692	0.0836	0.0769
$\beta_h(4,6)$	0.21	0.25	0.29	0.29	0.32
$\beta_h(6,8)$	0.25	0.26	0.30	0.23	0.27
$\beta_h(8,10)$	0.24	0.24	0.30	0.23	0.25
$\beta_h(10,12)$	0.23	0.26	0.27	0.22	0.24

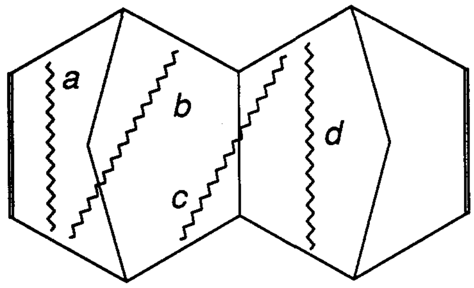


Figure 3. Four examples of "cross-talk" interactions, *a*-*d*, between the two relays of **3(*n*)**. The largest interactions (about 1.2 eV in magnitude) are those between directly opposite pairs of NBOs, denoted by *a* and *d*. The next largest interaction (*c*) is ca. 0.35 eV in magnitude. All other "cross-talk" interactions, such as *b*, are less than 0.04 eV.

Table 4. HF/3-21G π_+,π_- Splitting Energies, ΔE (eV), and $\beta_h(n,n+2)$ Values (per bond) Determined from the Splittings for Adjacent Members in the Polynorbornyl Dienes **3(*n*)** for NBO Analysis Models IV, V, and VI

molecule	IV		V		VI	
3(*n*)	ΔE	$\beta_h(n,n+2)$	ΔE	$\beta_h(n,n+2)$	ΔE	$\beta_h(n,n+2)$
3(4)	0.893	0.36	0.922	0.37	0.977	0.43
3(6)	0.435	0.36	0.441	0.35	0.413	0.41
3(8)	0.212	0.36	0.218	0.36	0.180	0.42
3(10)	0.102	0.36	0.106	0.36	0.0783	0.42
3(12)	0.0493		0.0514		0.0339	

Model VI: In addition to those interactions included in model V, the C–C σ and σ^* NBOs of the cross-links connecting the two relays are included. The cross-links are shown in bold in Figure 1B.

Model VI′: Identical to model VI, with the exception that all σ–σ and σ^*–σ^* inter-relay interactions are deleted.

The π_+,π_- splittings and the associated β_h values (per bond) obtained from application of models IV, V, and VI to **3(*n*)** are summarized in Table 4. In going from model IV to model V, which includes the interactions involving the relay C–H NBOs, there are only slight changes in the π splittings, and thus the two sets of β_h values are nearly the same. However, in going from model V to model VI, which includes the interactions involving the cross-link NBOs, the β_h values increase by 0.06.

Table 5. HF/3-21G π_+,π_- Splitting Energies, ΔE (eV), and $\beta_h(n,n+2)$ Values (per bond) Determined from the Splittings for Adjacent Members in the Polynorbornyl Dienes **3(*n*)** for the NBO Analysis Models IV′, V′, and VI′ Where "Cross-Talk" Is Excluded

molecule	IV′		V′		VI′	
3(*n*)	ΔE	$\beta_h(n,n+2)$	ΔE	$\beta_h(n,n+2)$	ΔE	$\beta_h(n,n+2)$
3(4)	1.028	0.27	1.068	0.28	1.106	0.35
3(6)	0.601	0.27	0.605	0.27	0.554	0.33
3(8)	0.351	0.27	0.352	0.27	0.284	0.33
3(10)	0.206	0.26	0.204	0.27	0.147	0.33
3(12)	0.122		0.120		0.0761	

Table 6. Average Percentage Increase in the β_h Value Resulting from the Inclusion of Different NBO Interactions in the NBO Analyses

NBO	molecule					
interaction	2(4)	2(12)	3s(4)	3s(12)	3(4)	3(12)
C–H NBOs	10	9	19	13	3	2
cross-links			16	4	19	19
cross-talk					32	35

NBO models IV′, V′, and VI′ are used to examine the importance of the "cross-talk" mechanism. The primed models differ from the respective unprimed ones only in that all σ–σ and σ^*–σ^* inter-relay interactions are deleted from the former set, i.e., "cross-talk" is excluded.[27] The results of applying models IV′–VI′ to **3(*n*)** are presented in Table 5.

In comparing the results for the primed models with those for the unprimed models (Table 4), it is immediately apparent that there is a consistent decrease of 0.08 to 0.10 in the β_h values for all models of the former. This result indicates that the inclusion of the "cross-talk" interactions causes the electronic coupling element to drop off much more rapidly with increasing bridge length.

The "cross-talk" interactions between opposing pairs of NBOs, such as those denoted by *a* and *d* in Figure 3, are ≈1.2 eV in magnitude, while interactions between displaced pairs of NBOs across a ring fusion, such as *c*, are about 0.35 eV. All the other "cross-talk" interactions, such as *b*, are less than 0.04 eV.

To examine the contributions made by the "direct" interactions, *a* and *d*, to the TB coupling, the analysis of **3(*n*)** using models IV–VI was repeated, but omitting only the σ–σ and σ^*–σ^* interactions of the *a* and *d* types. From this analysis, it is found that the *a* and *d* type interactions are responsible for >90% of the interference caused by the "cross-talk" mechanism.

Table 6 summarizes average percentage increases in the β_h values for **2(*n*)**, **3s(*n*)**, and **3(*n*)** upon inclusion of interactions involving the C–H NBOs, the cross-link NBOs, and inter-relay "cross-talk" interactions. Inclusion of interactions involving the C–H NBOs causes the β_h values to increase by about 10–19% for **2(*n*)** and **3s(*n*)**, but by only about 3% for **3(*n*)**. Onuchic and Beratan predicted that coupling pathways that involve the CH bonds would cause significant destructive interference in the TB coupling through both alkyl and polynorbornyl bridges. Our

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[27] The σ–σ^* inter-relay interactions are not deleted in models IV′, V′, and VI′, as additional calculations showed that they have only a small effect on the coupling.

Table 7. HF/3-21G π_+,π_- Splitting Energies, ΔE (eV), and $\beta_h(4,6)$ Values (per bond) Determined from the Splittings for the Polynorbornyl Dienes **3(4)** and **6(4)** for NBO Models IV–VI and IV′–VI′, Using Foster–Boys Localized Orbitals (Values in Parentheses Are Those Obtained Using NBOs)

	IV		V		VI	
molecule **3(*n*)**	ΔE	$\beta_h(n,n+2)$	ΔE	$\beta_h(n,n+2)$	ΔE	$\beta_h(n,n+2)$
3(4)	1.021 (0.893)	0.40 (0.36)	0.975 (0.922)	0.42 (0.37)	1.052 (0.977)	0.49 (0.43)
3(6)	0.455 (0.435)		0.424 (0.441)		0.394 (0.413)	

	IV′		V′		VI′	
molecule **3(*n*)**	ΔE	$\beta_h(n,n+2)$	ΔE	$\beta_h(n,n+2)$	ΔE	$\beta_h(n,n+2)$
3(4)	1.203 (1.028)	0.33 (0.27)	1.159 (1.068)	0.35 (0.28)	1.214 (1.106)	0.42 (0.35)
3(6)	0.617 (0.601)		0.574 (0.605)		0.525 (0.554)	

results show that this is not the case for the polynorbornyl bridges. However, it should be noted that our analysis includes interactions with both C–H σ and C–H σ^* orbitals, whereas that of Onuchic and Beratan included explicitly interactions with the CH σ orbitals only. (Some influence of the C–H σ^* orbitals may have been included implicitly through the parametrization of the model Hamiltonian used by these authors). We believe that the inclusion of pathways involving the CH σ^* orbitals is responsible for the decreased importance of of the C–H bonds found in our study.

Inclusion of the cross-link NBOs causes a 19% increase in the β_h values for **3(*n*)**, indicating that the "cross-links" mechanism leads to diminished TB coupling. However, it is the "cross-talk" mechanism which causes an increase of the β_h values by about 33%, that is the major destructive interference occurring in the electronic coupling of **3(*n*)**.

The C–H NBOs of the methylene (CH_2) carbons also have a significant influence on the distance decay dependence of the electronic coupling in **3(*n*)**. The changes in the respective β_h values in going from NBO model VI (Table 4) to the full HF calculations (Table 1) are almost entirely due to inclusion of these methylene C–H NBOs. As can be seen, rather than changing all of the β_h values in the same direction, the methylene C–H interactions cause an increase in the $\beta_h(4,6)$ value, almost no change in the $\beta_h(6,8)$ value, and decreases in the β_h values for the longer members. The interactions involving the methylene C–H NBOs are largely responsible for the deviation from exponential distance decay dependence of the electronic coupling occurring in **3(*n*)**. The TB coupling involving the methylene groups has been referred to as laticyclic hyperconjugation.[28]

Analyses Using Foster–Boys Localized Orbitals

For our conclusions to be meaningful, the decomposition of the splittings for the bridged dienes into various component interactions should be largely independent of the orbital localization scheme employed. This appears to be the case for cyclohexa-1,4-diene in which three different orbital localization schemes, namely the Weinhold NBO,[19] the Weinhold NLMO,[19] and the Foster–Boys (FB)[24] schemes, gave similar decompositions for the π_+,π_- splitting.[29]

In order to verify that this similarity is also obtained in the present case, we have repeated the decomposition scheme for the first two members of the polynorbornyl dienes, **3(4)** and **3(6)**, using FB localized orbitals.[30] The π_+,π_- splittings and the associated β_h value, obtained from application of models IV–VI and models IV′–VI′ to **3(4)** and **3(6)** using the FB localized orbitals, are summarized in Table 7. For ease of comparison, relevant splittings and β_h values obtained using NBOs are presented in parentheses. The data using the FB analysis show that both the "cross-talk" and "cross-links" interference mechanisms are still important causes of destructive interference. More importantly, the magnitude of the interference caused by both the cross-talk and cross-links mechanisms is little changed from those values obtained with the NBO method, as indicated by the similar increases in β_h value, due to either interference mechanism. In the case of the NBO analysis, the increase in β_h value ranges from 0.06 to 0.09, while in the case of the FB analysis the increase is 0.07.

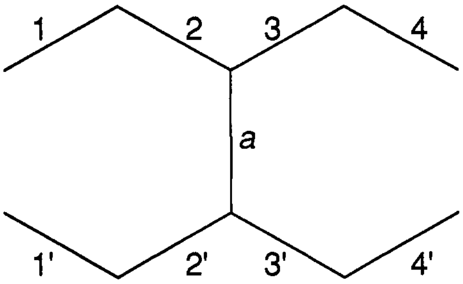

Figure 4. A bridge segment, consisting of two parallel strands, both comprised of four C–C bonds labeled 1, 2, 3, and 4 in one strand and 1′, 2′, 3′, and 4′ in the other. The two strands are connected by a cross-link bond, *a*. See the conclusion section for its application to the parity rule.

Conclusion

The results of the NBO analyses reveal that the TB coupling behavior through a *single* relay of **3(*n*)** closely approximates that through the alkyl chain in the **2(*n*)** series. Consequently, one might have expected that the β_h values for the full polynorbornyl diene system, **3(*n*)**, and the divinyl alkane system, **2(*n*)**, would be similar. In fact, the β_h values for **3(*n*)** are markedly larger than those for **2(*n*)**, and this is attributable to the operation of destructive interference effects in the former series.

Three possible destructive interference mechanisms operating in **3(*n*)** were examined using NBO analyses: (1) interference caused by the C–H bonds associated with the two relays; (2) the "cross-links" mechanism, in which the destructive interference is caused by the cross-link bonds joining the two relays; and (3) the "cross-talk" mechanism, in which the interference occurs by way of direct, through-space interactions between the two relays.

The NBO analyses reveal that interactions involving the C–H bonds of the relays are relatively unimportant for the π_+,π_- splittings in **3(*n*)**, although these C–H bonds proved to be important for **2(*n*)** (causing a ≈10% increase in β_h values in this series). While the "cross-links" mechanism makes a sizable contribution to the destructive interference, increasing the β_h values for **3(*n*)** by ≈19%, the "cross-talk" mechanism is even more important, increasing the β_h values for **3(*n*)** by ≈33%.

The origin of the destructive interference due to the "cross-links" and "cross-talk" mechanisms is most clearly seen by considering the generalized McConnell-type nearest-neighbour models, illustrated in Figure 4. This figure considers the case of two parallel bridges, each consisting of four C–C bonds and one cross-link. In one strand, the bonds are labeled 1, 2, 3, and 4, and in the other they are labeled 1′, 2′, 3′, and 4′. The cross-link between the two strands is labeled *a*.

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

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

(30) The Foster–Boys localized orbitals were obtained using the Gaussian 92 program.

In the McConnell perturbative analysis[31] the coupling, ΔE, along a pathway involving a single strand is given by

$$\Delta E = \frac{(t_{12})(t_{23})(t_{34})}{(\Delta)^3} \tag{4}$$

or by

$$\Delta E = \frac{(t_{1'2'})(t_{2'3'})(t_{3'4'})}{(\Delta)^3} \tag{5}$$

where the *t*s represent the Hamiltonian matrix elements between adjacent NBOs, and Δ is the energy gap between the chromophore orbitals and the C–C σ NBOs of the bridge. (All C–C σ NBOs are assumed to have the same self energy.) An example of the coupling for a pathway involving the cross-link bond is given by

$$\Delta E = \frac{(t_{12})(t_{2a})(t_{a3'})(t_{3'4'})}{(\Delta)^4} \tag{6}$$

and a corresponding example for the coupling for a pathway involving cross-talk between the two bridges is

$$\Delta E = \frac{(t_{12})(t_{22'})(t_{2'3'})(t_{3'4'})}{(\Delta)^4} \tag{7}$$

The *t* matrix elements are negative in sign, and as a result, the couplings for the former two pathways (eqs 4 and 5) and the latter two (eqs 6 and 7) have opposite signs. Given this difference in sign, the cross-link and the cross-talk couplings destructively interfere with the couplings involving only a single chain. This is an example of the parity rule.[7b,d] Consequently, because of this parity rule, coupling pathways that differ by an odd number of bonds destructively interfere.

Further investigations on the "cross-links" and "cross-talk" mechanisms are being conducted, especially with regard to finding ways of minimizing the "cross-talk" interactions. This may be done by moving the two relays further apart by, say, removing the ring fusions and by replacing the CH_2 bridges by longer ones, as shown by **4(*n*)**.

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[31] McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508.