

Investigating Long-Range Electron-Transfer Processes with Rigid, Covalently Linked Donor-(Norbornylogous Bridge)-Acceptor Systems

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Long-range electron transfer (ET) between two redox centers (chromophores) may be defined as those processes in which the electron transfer takes place over distances substantially larger than the sum of the van der Waals radii of the chromophores. In such circumstances, the direct, through-space overlap between the localized donor and acceptor wave functions is negligible; consequently any electronic coupling between the donor and acceptor groups resulting from this overlap should be unimportant. This type of cursory analysis might lead one to conclude, then, that all long-range ET processes are very slow, inefficient, and therefore of limited interest.

Nothing could be further removed from the truth! Many documented examples exist attesting to long-range ET processes taking place over large distances at lightning speeds and with high efficiencies, one of the most spectacular of which is to be found in the photosynthetic reaction centers of certain photosynthetic bacteria.¹ The primary photoinduced ET events in the center are observed to take place on a picosecond time scale, with near unit efficiency, over interchromophore separations exceeding 10 Å!² Moreover, not only can long-range ET be rapid, but it can also be associated with exquisitely controlled directionality. Again using the photosynthetic reaction center as an example, it is found that the primary ET cascade, emanating from the "special pair", and terminating at the quinone groups, takes place exclusively along the so-called L branch of chromophores, rather than along the M branch, even though both branches are apparently related by near perfect C_2 symmetry.^{1,2}

Of course, the reason why long-range ET can be so facile is that the chromophores are not generally separated from each other by a complete vacuum, but rather, the space between them is occupied by other molecules, or parts of molecules. These species may be solvent molecules, or a molecular bridge, if the chromophores happen to be distally connected to each other by such a device, or they may be components of a supramolecular assembly, such as the protein matrix which envelops the photosynthetic reaction center. This intervening medium facilitates ET by what is known as a superexchange mechanism,³ to put it crudely, the medium provides "orbitals" (π , π^* , σ , σ^* , etc.) which

the migrating electron can use to tunnel between the chromophores. In those situations where the medium is saturated and only σ and σ^* orbitals are available for coupling with the chromophores, the superexchange mechanism is then often referred to as a through-bond-coupling mechanism.⁴ Of course, the superexchange mechanism would also explain the directionality of certain long-range ET processes mentioned above since the orbitals of the intervening medium provide one or more pathways for the tunneling electron to follow.

Although the superexchange or through-bond mechanism has been known for some time, its characteristics have, until recently, remained somewhat obscure. By characteristics is primarily meant the distance and orientational dependence of the dynamics of long-range ET, and how this dependency is affected by the nature and composition of the intervening medium. It is this aspect of long-range ET processes that has captured the attention of a broad cross section of the chemical community since a deeper understanding of medium effects on long-range ET is essential to the successful design of molecular photovoltaic systems and other intriguing molecular electronic devices.⁵

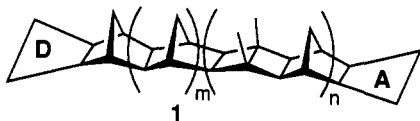
Experimental investigation of distance dependence of ET dynamics is best achieved using systems in which two chromophores are covalently linked to a bridge, thereby generating a donor-bridge-acceptor dyad (or D-B-A). It should be noted that the bridge serves the dual role of providing a molecular scaffolding to which the chromophores are affixed at well-defined separations and orientations, and of providing a medium which modulates the ET dynamics by the superexchange mechanism.

Many different types of bridges have been used, but the two main classes are suitably modified proteins and peptides, on one hand,⁶⁻⁹ and saturated hydrocarbon bridges on the other.¹⁰⁻¹⁷ Both types of bridge have

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Michael Paddon-Row was born in England in 1942 and received his B.Sc. in chemistry from King's College, University of London, in 1963 and a Ph.D. in medical chemistry from the Australian National University in 1967. He joined UNSW in 1985, where he is now a Professor of Chemistry. He has held visiting professorships at Louisiana State University, Carnegie-Mellon University, and the Universities of Pittsburgh and Amsterdam. Research interests span synthetic and computational chemistry and their application to problems in physical organic chemistry.

provided invaluable insights into the nature of long-range ET.^{6-8,11,18} The different types of saturated hydrocarbon bridges that have been employed include cyclohexanes, decalin, and steroid-based systems,¹⁰⁻¹³ oligobicyclo[2.2.2]octanes,¹⁴ triptycene,¹⁵ polyspirocyclobutanes,¹⁶ and norbornylogous bridges, comprising a mixture of linearly fused norbornyl and bicyclo[2.2.0]-hexyl groups, such as 1.¹⁷ In this Account, I focus on



the norbornylogous bridge system, 1. This bridge, on account of its complete rigidity, its symmetry, and the comparative synthetic ease by which its length and configuration can be altered, coupled with our ability to attach a wide range of different chromophores to its termini, has provided valuable insights into various aspects of long-range intramolecular ET processes.

Herein, I present a short survey of how the norbornylogous dyads, 1, have been employed to explore the effects of distance, bridge configuration, through-bond coupling, and orbital symmetry on long-range ET processes. In addition, I present a brief account of how Koopmans' theorem calculations, together with a treatment based on natural bond orbitals, have provided a simple, yet useful theoretical model for analyzing electronic coupling through saturated bridges.

Basic Theoretical Background

Consider, for example, a charge separation ET process, schematized by eq 1.



The energy surface for this process, conveniently represented by a one-dimensional reaction coordinate which is supposed to describe changes in both geometry of the donor-acceptor system and solvent orientation, may be regarded in terms of two diabatic surfaces, one representing the electronic configuration of the reactant, D-A, and the other representing the electronic configuration of the product, ⁺D-A⁻ (Figure 1). In the region where the diabatic surfaces intersect, the two configurations mix, symmetry permitting, and this results in an avoided crossing. The magnitude of the avoided crossing is given by $2J$ (neglecting overlap

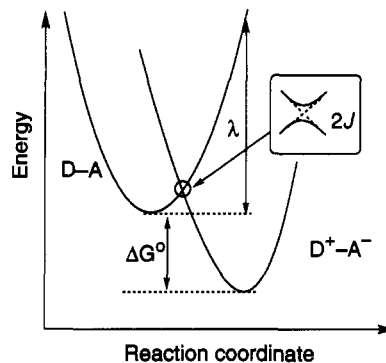


Figure 1. Schematic diabatic energy profiles for nonadiabatic electron transfer. The diabatic surfaces mix in the region where they intersect, resulting in a splitting of $2J$ (inset), where J is the electronic coupling term. λ is the reorganization energy.

between the two configurations), where J is the electronic coupling term. For the case of weak coupling, where $J < 100 \text{ cm}^{-1}$,^{19a} electron transfer may be considered to occur nonadiabatically, and application of Fermi's golden rule leads to the following expression for the ET rate, k_{et} :

$$k_{et} = \frac{4\pi^2}{h} J^2 (\text{FCWD}) \quad (2)$$

where FCWD is the Franck-Condon weighted density of states. In the high-temperature limit, FCWD may be represented classically as²⁰

$$\text{FCWD} = \frac{1}{(4\pi\lambda k_b T)^{1/2}} \exp\left(\frac{-(\Delta G^\circ + \lambda)^2}{4\lambda k_b T}\right) \quad (3)$$

where k_b and T are, respectively, Boltzmann's constant and the temperature, ΔG° is the standard free energy of reaction (negative of the driving force), and λ is the reorganization energy and contains contributions from solvent, as well as from molecular vibrations of the donor-acceptor system.

Distance Dependence of J : The Koopmans Connection

Although both the electronic coupling element, J , and the Franck-Condon factor, FCWD, of eq 2 influence the distance dependence of long-range ET dynamics, the former is generally dominant, and it is through this term that the superexchange mechanism is expressed.^{19b}

It is generally assumed that J and the associated ET rate constant, k_{et} , fall off approximately exponentially with increasing distance, r , viz.,

$$J \propto \exp(-\beta r) \quad (4)$$

$$k_{et} \propto \exp(-2\beta^\circ r) \quad (5)$$

where β and β° are attenuation coefficients. If the FCWD term in eq 2 is not distance dependent (which is rarely the case), then $\beta = \beta^\circ$.

(19) (a) Or, equivalently, $J < 1.2 \text{ kJ mol}^{-1}$ ($100 \text{ cm}^{-1} = 1.196 \text{ kJ mol}^{-1}$). (b) Even very small values of the electronic coupling, J , can have enormous effects on ET dynamics, as can be seen from the following example of ET occurring at 300 K in a system for which $\Delta G^\circ = 0$ (zero driving force) and $\lambda = 48 \text{ kJ mol}^{-1}$ (which is a typical value). Upon substituting these values into eqs 2 and 3, one finds that a value for J of only 0.1 kJ mol^{-1} leads to ET rates, k_{et} , in excess of 10^8 s^{-1} .

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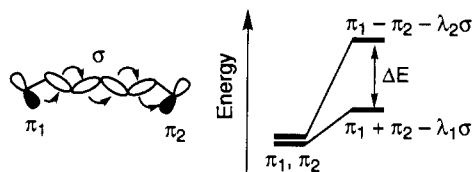
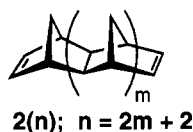


Figure 2. Interaction diagram representing through-bond coupling involving two degenerate π orbitals, π_1 and π_2 , interacting with the σ orbitals of a hydrocarbon bridge. The degeneracy of the π orbitals is lifted through mixing with the bridge orbitals of appropriate symmetry (λ_1 and λ_2 are mixing coefficients).

An important issue is the size of β . In 1961, McConnell used a simple Hückel-type, tight binding Hamiltonian based superexchange model for calculating the distance dependence of electronic coupling in a series of α,ω -diphenylalkanes.³ This model predicted fairly large values for β of ca. 2.5 \AA^{-1} which, if correct, would indicate that electronic coupling through saturated hydrocarbon media is strongly attenuated with increasing distance, to the extent that ET would occur slowly ($>$ millisecond time scale) for interchromophore separations exceeding 7 \AA .

In 1968 Hoffmann *et al.* published their classic extended Hückel (EH) MO studies on through-bond orbital interactions.^{4a,b} Such interactions arise through mutual hyperconjugative mixing of π -type, or non-bonding orbitals of two chromophores with the σ and σ^* orbitals of the connecting saturated bridge.⁴ This is shown schematically in Figure 2 for the case of two initially degenerate π orbitals mixing with the underlying bridge σ orbitals. Through-bond coupling results in lifting of the π orbital degeneracy by an amount ΔE , called the splitting energy. The distance dependence of ΔE for a series of α,ω -polyenediyl systems was found to follow a weak exponential distance decay, with a β value of only 0.37 \AA^{-1} ,^{4a,b} which is 6 times smaller than that predicted by the McConnell model.³

Hoffmann's results were sufficiently tantalizing for us to launch, in the early 1980s, a combined computational and experimental investigation of the distance dependence of through-bond coupling in the polynorbornyl dienes, **2(n)**, where n refers to the number of C-C bonds in each of the two relays connecting the double bonds.^{4c,21,22} Experimental values for the π,π and



π^*,π^* splitting energies for **2(4)** and **2(6)** were obtained, respectively, from the difference between the two vertical π ionization potentials (ΔIP), using photoelectron spectroscopy, and from the difference between the two vertical π^* electron affinities (ΔEA), using electron transmission spectroscopy.^{4c,21,22} The experimental splitting energies for **2(4)** and **2(6)** (Table 1) show that through-bond coupling in these systems not only is strong but also displays a weak distance decay depen-

Table 1. ΔIP and ΔEA Splitting Energies (eV) and Corresponding Koopmans' Theorem STO-3G splitting energies, ΔE_π and ΔE_{π^*} , for dienes **2(n)**

diene	ΔIP^a	ΔE_π^b	ΔEA^a	$\Delta E_{\pi^*}^b$
2(4)	0.87	0.99	0.80	0.85
2(6)	0.32	0.35	0.25	0.23
2(8)		0.14		0.066
2(10)		0.065		0.019
2(12)		0.0294		0.0057

^a ΔIP and ΔEA data from refs 21 and 22. ^b From ref 25.

Scheme 1



dence, with β values (per bond²³) of 0.50 (for ΔIP) and 0.58 (for ΔEA).

Importantly, it was found that simple *ab initio* SCF Koopmans' theorem²⁴ calculations on **2(4)** and **2(6)**, using the STO-3G basis set, gave π,π and π^*,π^* splitting energies, ΔE_π and ΔE_{π^*} , respectively, that are in acceptable agreement with the experimental values (Table 1). This enabled calculation of the splitting energies for higher members of the **2(n)** series to be carried out with confidence, and thereby a more comprehensive distance dependence profile for ΔE_π and ΔE_{π^*} could be obtained.²⁵ The calculated splittings for **2(4)**–**2(12)** gave limiting β values (per bond) of 0.40 for ΔE_π and 0.60 for ΔE_{π^*} , which are fairly close to the Hoffmann EH value of 0.42 (per bond), for a series of α,ω -polyenediyls.⁴

The nexus between these studies and ET processes is that the ΔE_π and ΔE_{π^*} splittings for **2(n)** are proportional, respectively, to the electronic coupling for hole transfer, J_{ht} , in the cation radicals (Scheme 1; $(*) = +$) and to electron transfer, J_{et} , in the anion radicals (Scheme 1; $(*) = -$) of these dienes,^{21b,22} *i.e.*,

$$\Delta E_\pi \propto J_{\text{ht}} \propto \exp(-0.40n) \quad (6)$$

$$\Delta E_{\pi^*} \propto J_{\text{et}} \propto \exp(-0.60n) \quad (7)$$

Within this context, the Koopmans' theorem results for **2(n)** suggest that not only should through-bond-mediated ET processes in the cation radicals and anion radicals of these molecules display a fairly weak exponential distance decay dependence, but they might also take place extremely rapidly ($>10^{12} \text{ s}^{-1}$) over distances greater than 12 \AA .²² Pioneering studies by Verhoeven¹² and by Closs and Miller¹⁰ had provided supportive evidence for efficient through-bond-mediated ET across steroid bridges. However, a more systematic study was called for, one which used a D-B-A dyad, whose bridge length and configuration could be systematically varied, thereby enabling distance dependence and other characteristics of ET to be investigated.

The Molecules

Our observation of large through-bond couplings in the **2(n)** series suggested that we retain the polynor-

(23) Note that henceforth the distance dependence will be expressed in terms of the number of bonds separating the chromophores, rather than in terms of distance in angstroms.

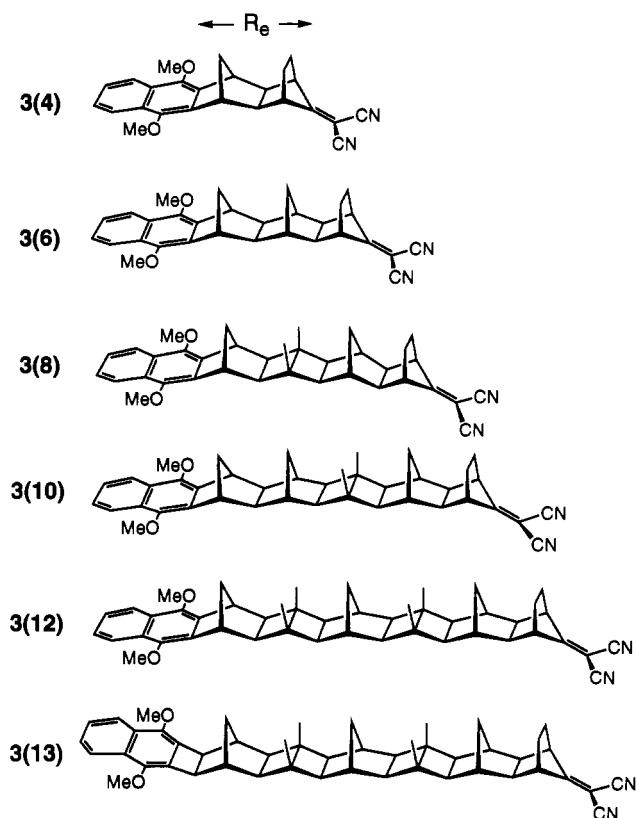
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Scheme 2



bornyl type bridge but that more appropriate redox centers than double bonds be used. This led to the design and synthesis^{17,26} of the series 3(n), shown in Scheme 2, in which dimethoxynaphthalene (DMN) donor and dicyanovinyl (DCV) acceptor groups are fused to a norbornylogous bridge, ranging in length from four to 13 bonds.

Thermal Intramolecular ET in Anion Radicals of 3(n)

Thermal charge shift intramolecular ET in the anion radicals of 3(4)–3(12), shown by eq 8, were investigated using pulse radiolysis, in collaboration with the Miller group.



The electron-transfer rates were found to be $>10^9 \text{ s}^{-1}$ (the time resolution of the equipment) for all molecules.²⁷ Although direct measurements of the ET rate constants could not be obtained, optical electron transfer bands were observed in the visible–near-infrared absorption spectra of the anion radicals of 3(4)–3(8). Analysis of these bands led to estimates of the magnitude of the electronic coupling J_{et} , for the charge shift process of eq 8, of 0.16, 0.06, and 0.03 eV for 3(4), 3(6), and 3(8), respectively. These limited data give a β value of *ca.* 0.35–0.49 (per bond) for the distance dependence of J_{et} , which is even smaller than that predicted from Koopmans' theorem calculations (*i.e.*, eqs 6 and 7). These large values of J_{et} imply ET rates in excess of 10^{11} s^{-1} , even for the anion radical of 3(12),

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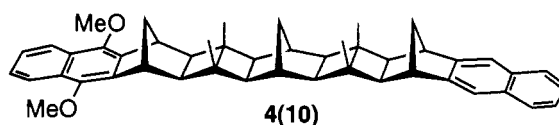
Table 2. Rates of Photoinduced Electron Transfer (k_{et}) for 3(n), 5(6), and 5(8) at 24 °C in a Series of Solvents^a

compd	k_{et} (10^8 s^{-1}) (MeCN)	k_{et} (10^8 s^{-1}) (EtOAc)	k_{et} (10^8 s^{-1}) (THF)
3(6)	≈ 2500	≥ 2900	≥ 3300
3(8)	300	450	670
3(10)	24	85	120
3(12)	1.6	6.3	13
3(13)	≤ 0.15	0.79	1.5
5(6)	360	770	
5(8)	22	89	165

^a Data from refs 29, 31, and 33.

in which the edge-to-edge interchromophores separation (R_e) is 13.5 Å!

Pulse radiolysis studies revealed an extremely rapid hole-transfer rate ($>10^9 \text{ s}^{-1}$) in the cation radical of 4(10), from DMN donor to naphthalene cation radical acceptor, thereby demonstrating that both hole transfer and ET charge shift processes are extremely facile in the norbornylogous systems.^{28a} Rapid hole-transfer rates have also been observed in other systems.^{28b}



Photoinduced Intramolecular ET (Charge Separation) in 3(n)

Electronic excitation of the DMN chromophore into its first excited singlet state (*DMN) provides sufficient driving force for the following charge separation ET process for 3(n) to occur in several solvents:



Representative rates of photoinduced intramolecular charge separation ET for these systems, obtained by Oevering, are given in Table 2.^{17,29} These rates are very large, although not as large as those deduced for the thermal charge shift processes in the anion radicals of 3(n), mentioned above; this is probably due to the fact that the charge separation process involves Coulombic interactions that are absent in the charge shift processes. The efficiency of charge separation is near unity for 3(4)–3(10) and falls off to 89% for 3(12) and 45% for 3(13) (both in THF solvent).

Confirmation that the charge separation process shown by eq 9 is indeed occurring, following flash photolysis of 3(n), was unambiguously demonstrated by Warman using the technique of time-resolved microwave conductivity (TRMC).³⁰ This technique provides a convenient method for estimating changes in the dipole moment of a species following electronic excitation. The TRMC-determined dipole moments, p^* , of the charge-separated states for 3(n), resulting from photoinduced electron transfer, are given in Table 3, together with the corresponding calculated values, p_{cc} , expected for complete charge separation. The

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(29) (a) Oevering, H.; Paddon-Row, M. N.; Heppener, H.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* 1987, 109, 3258. (b) Paddon-Row, M. N.; Verhoeven, J. W. *New J. Chem.* 1991, 15, 107.

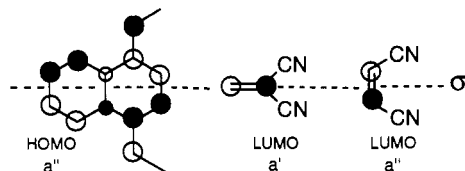
(30) de Haas, M. P.; Warman, J. M. *Chem. Phys.* 1982, 73, 35.

Table 3. Rates of Photoinduced Electron Transfer (k_{et}), Lifetimes (τ_{cr}), and Dipole Moments (p_{cc} and p^*) of the Charge-Separated States of 3(4)–3(12)^{31a} and 3(13)^{31b} in Benzene Solution at 24 °C

compound	k_{et} (s ⁻¹)	τ_{cr} (ns)	p^* (D) ^a	p_{cc} (D) ^b
3(4)	>10 ¹¹	≈1	26 ^c	34
3(6)	>10 ¹¹	6 (0.5 ^d)	37	43
3(8)	5.2 × 10 ¹⁰	32 (2.5 ^d)	55	56
3(10)	7.2 × 10 ⁹	360 (43 ^d)	68	64
3(12)	7.3 × 10 ⁸	740 (297 ^d)	77	71
3(13)		550 (1500 ^d)		75

^a Experimental value calculated assuming unit efficiency for electron transfer. ^b Calculated dipole moment expected for complete center-to-center charge separation. ^c Value determined in cyclohexane. ^d Value determined in *p*-dioxane.

Scheme 3



excellent agreement found between the calculated and the experimentally determined sets of dipole moments confirms that essentially complete charge separation occurs in these systems, following flash photolysis.³¹ The enormous dipole moment of 77 D observed for the giant charge-separated state of 3(12) is particularly noteworthy.

The distance dependence of the rates of photoinduced ET for 3(*n*) follows an approximately exponential decay, generalized by eq 5, that is solvent dependent. The β° values (per bond) are 0.46 (THF), 0.50 (EtOAc), and 0.61 (MeCN). These values are not corrected for distance dependence of the FCWD term of eq 2, and consequently, they represent upper values of β for the distance dependence of the electronic coupling term, J .³² Nevertheless, they are comparable in magnitude to the Koopmans' theorem values, given in eqs 6 and 7.

Clearly, these results demonstrate that the norbornylogous bridge dramatically accelerates long-range ET processes, both charge shift and charge separation types, in 3(*n*), by a through-bond-coupling mechanism.

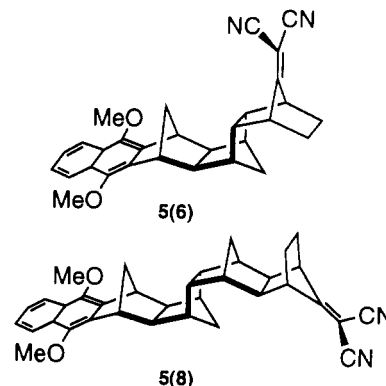
Bridge Configuration, the All-Trans Rule, and ET

A well-known consequence of the through-bond-coupling mechanism is the *all-trans* rule, which simply states that the coupling through a bridge is maximized for an *all-trans* (antiperiplanar) configuration of bridge bonds.⁴ If such a coupling mechanism were mediating the ET processes observed for 3(*n*), then the rates of

(31) (a) Paddon-Row, M. N.; Oliver, A. M.; Warman, J. M.; Smit, K. J.; de Haas, M. P.; Oevering, H.; Verhoeven, J. W. *J. Phys. Chem.* 1988, 92, 6958. (b) Warman, J. M.; de Haas, M. P.; Smit, K. J.; Paddon-Row, M. N.; van der Pol, J. F. *Mol. Cryst. Liq. Cryst.* 1990, 183, 375.

(32) In general, the FCWD term decays with increasing distance between the chromophores. This is because the magnitudes of both ΔG° and λ (particularly the solvent component of λ) increase with increasing distance (see eq 3). ΔG° increases because more work must be expended in separating the charges as the distance between the chromophores is increased. The solvent component of λ increases because the number of solvent molecules between the chromophores that undergo reorganization accompanying charge separation increases with increasing distance. Consequently, the measured β° values for the charge separation process are larger than the corresponding β values for the distance dependence of the electronic coupling term, J .

these processes should be modulated by changes in the configuration of the norbornylogous bridge, in accordance with the dictates of the *all-trans* rule. This was tested using the "kinked" systems 5(6) and 5(8), which possess, respectively, one and two *cisoid* configurations of bridge bonds (highlighted in the structures). Koop-



mans' theorem calculations on model dienes^{25a} predicted that through-bond coupling should, indeed, be weaker in the "kinked" systems 5(6) and 5(8), compared to through-bond coupling in the respective *all-trans* molecules, 3(6) and 3(8). In agreement with prediction, the photoinduced-ET rates in the *all-trans* systems were found to be faster than those in the "kinked" molecules by as much as an order of magnitude (see Table 2).³³

This study, together with a subsequent one,^{15b} nicely confirms the operation of through-bond-mediated ET in the norbornylogous-bridged and other bridged systems.

Orbital Symmetry and ET

Orbital symmetry can influence ET dynamics through the electronic coupling term, J . For example, if the two diabatic surfaces of Figure 1 have opposite symmetries, then J will be 0 and therefore, the associated ET rate will also be 0, by eq 2. Orbital symmetry effects on ET processes in cyclophanes have been noted and discussed previously,³⁴ but the rigidity and symmetry of the norbornylogous systems 3(*n*) provide an excellent opportunity for a more thorough investigation, illustrative of which is the following recent example.

If one ignores conformational mobility of the methoxy groups, then the ground states of 3(*n*) belong to the totally symmetric A' representation of the C_s point group. However, the charge-separated states of these species, resulting from photoinduced ET, belong to the antisymmetric, A'' representation, because, as illustrated in Scheme 3, the singly occupied MOs of the DMN cation radical and the DCV anion radical moieties are antisymmetric (a'') and symmetric (a'), respectively (the product of which, of course, is a'').

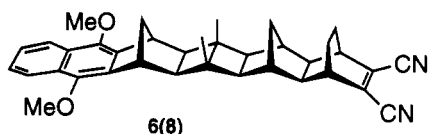
Consequently, the charge recombination process, from the charge-separated state to the ground state, as shown by eq 10, is symmetry "forbidden" and should proceed more slowly than symmetry "allowed" charge recombination in a structurally similar system.

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This effect of orbital symmetry was addressed through comparison of the rate of charge recombination from the charge-separated state of **3(8)** with that of **6(8)**, in which the acceptor group is a maleonitrile moiety, instead of a DCV group. Now the symmetry of



the charge-separated state in **6(8)** is A' , since the singly occupied MO of the maleonitrile anion radical is a'' (Scheme 3). Consequently, charge recombination in this system is symmetry "allowed".

It was found that charge recombination from the charge-separated states of both **3(8)** and **6(8)** was accompanied by charge-transfer fluorescence, the analysis of which enabled the electronic couplings, J_{cr} , for charge recombination to be calculated for these systems. The J_{cr} values for **3(8)** and **6(8)** were found to be 36 and 129 cm^{-1} , respectively (in benzene).^{36a} This result means that orbital symmetry effects on electronic coupling in norbornylidene systems are rather weak, amounting to a factor of only 3.6.^{36a} From eq 2, this translates into a factor of 13 for orbital symmetry effects on the rates of charge recombination.^{36b}

A Bridge for All Chromophores!

So far, most of our attention has been focused on bridges bearing the DMN and DCV chromophores. However, the synthetic versatility of the norbornylidene bridge enables one to fuse a wide variety of chromophores to it,^{28,29,36,37} four examples of which are **7(6)**,^{36b} **8(6)**,^{36a} **9(6)**,^{36a} and **10(10)**.^{36c} This wonderful menagerie of dyads is providing us with valuable insights into how the ET dynamics *through a given bridge* are affected by changes in the chromophores, *without changing chromophore orientation and separation*. Photoinduced ET studies on **7(6)** and the *N*-methylpyridinium derivative of **8(6)** have revealed rates of ET in excess of 10^9 s^{-1} in these systems.³⁸ Ball-and-chain molecules, such as **10(10)**, and others, bearing an *N,N*-dimethylaniline group in place of the dimethoxybenzene group,^{36d} are particularly intriguing, and their ET characteristics are being explored.

Bridge Structure and Electronic Coupling

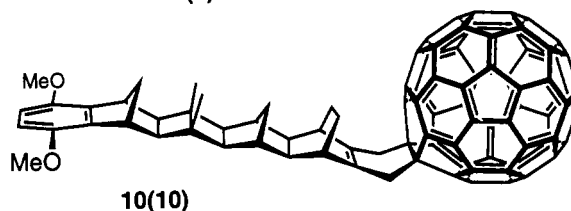
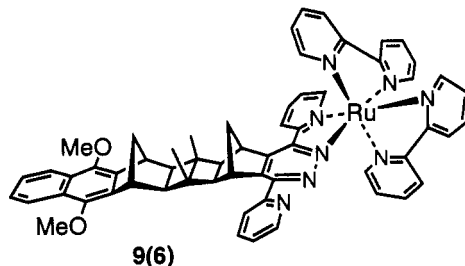
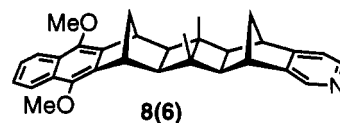
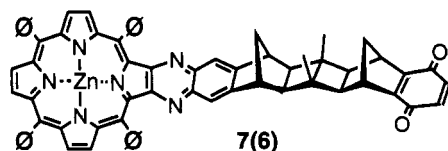
The generality of through-bond-mediated ET has now been amply demonstrated using a number of different

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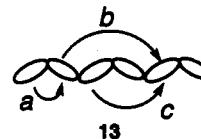
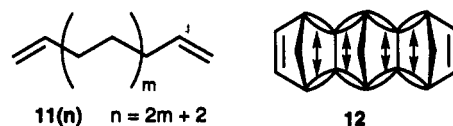
(37) Warrenner, R. N.; Pitt, I. G.; Butler, D. N. *J. Chem. Soc., Chem. Commun.* **1983**, 1340.

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bridges.^{6-18,28,29,33} An important question is how the distance dependence behavior of the electronic coupling depends on bridge composition. This issue is being addressed theoretically using several approaches,³⁹ one of which⁴⁰ uses Koopmans' theorem calculations in conjunction with natural bond orbital (NBO⁴¹) analyses.

An example of this approach is the comparison of the distance dependence of electronic coupling through the norbornylidene bridge, compared to that through a simple *n*-alkyl chain. Koopmans' theorem calculations (using the 3-21G basis set) on the polynorbornyl dienes **2(n)** and the *all-trans*-divinylalkanes **11(n)** gave β values (per bond) of 0.34 and 0.26, respectively, suggesting, perhaps surprisingly, that the *n*-alkyl chain, possessing an *all-trans* conformation of C-C bonds, is superior to the norbornylidene bridge in relaying electronic coupling.^{40b} Intriguingly, the prediction that simple *n*-alkyl chains are efficient mediators of through-bond coupling is consistent with various experimental electron-transfer studies on monolayer assemblies.⁴²



An NBO analysis of **2(n)** and **11(n)** provided a reason for this outcome. Briefly, the analysis entails⁴³ trans-

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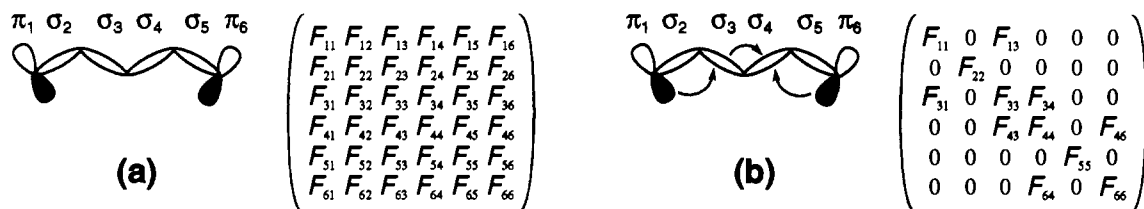


Figure 3. A schematic of an NBO analysis of a six-orbital system comprising two π NBOs linked to a chain of four σ NBOs. (a) This Fock matrix in the basis of the NBOs includes all interactions (the indexes of the matrix elements indicate the orbital identities; e.g., $F_{1,3}$ represents the interaction between NBOs π_1 and σ_3). (b) This Fock matrix includes only those interactions between NBOs indicated by curved arrows in the structure.

forming the (fully delocalized) canonical MOs (CMOs) of a molecule into localized two-center and one-center NBOs (σ , π , σ^* , π^* , rydbergs, core). The Fock matrix in the basis of these NBOs is then constructed. The off-diagonal elements of this matrix are a measure of the interactions between pairs of NBOs. The contributions made by particular NBOs to the overall electronic coupling can be assessed simply by diagonalizing the Fock matrix containing only those off-diagonal elements involving the particular NBOs (all other off-diagonal elements being set equal to 0). This procedure is illustrated in Figure 3 for a six-orbital case, where two π NBOs are connected by a chain comprising four σ NBOs. In Figure 3a, the full Fock matrix in the basis of the NBOs is presented. Diagonalization of this matrix, which includes all interactions, gives the CMO energies. The matrix in Figure 3b includes only those interactions between NBOs indicated by curved arrows. Diagonalization of this matrix provides a measure of the contribution made by this particular mode of orbital coupling to the overall π, π splitting energy.

Using the NBO method, we found that the principal cause for the stronger distance dependence of electronic coupling through the norbornylogous bridge, compared to a simple n -alkyl chain, is the presence of destructive interference^{39b} between the two parallel relays in the former.^{40e} This interference occurs largely *via* direct, through-space interactions between pairs of NBOs located on different relays, as shown by the double-headed arrows in the polynorbornyl diene structure, 12.

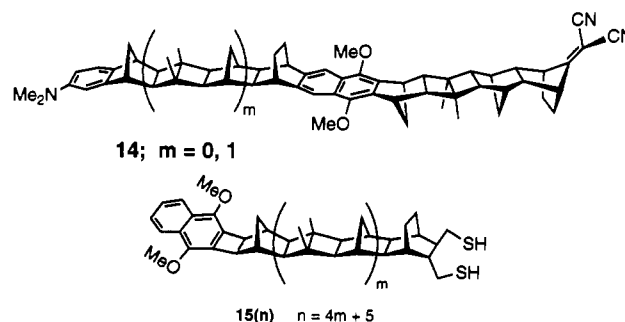
Finally, NBO analyses have also demonstrated that correct distance dependence behavior of electronic coupling through a saturated bridge, 13, can only be realized if long-range interactions between NBOs, such as b and c, are included, in addition to nearest neighbor interactions, a.^{40a,c,d} This explains why the McConnell model, which considers only nearest neighbor interactions, gives grossly exaggerated distance dependence behavior for electronic coupling. It is also important to note that non nearest neighbor interactions, such as b and c, are also responsible for the dependence of the strength of through-bond coupling on bridge configuration, as expressed by the *all-trans* rule.^{4c,22,40a,44}

Concluding Remarks

The main purpose of this Account is to demonstrate that a combination of synthesis, photophysics, and

simple theory can provide valuable insight into the fascinating world of long-range ET. Efforts along these lines by several research groups⁶⁻¹⁸ have demonstrated the pivotal role played by through-bond coupling in determining the character of long-range ET processes. Knowledge gained from such studies will have applications in the rational design of molecular electronic devices in the sense that bridges connecting chromophores may be regarded as "molecular wires" that control the direction and dynamics of ET by through-bond-coupling effects.

Our research goals now include the synthesis of rigid polychromophoric systems and thiols, such as 14⁴⁵ and 15(n),⁴⁶ respectively. An important requirement for the



successful design of molecular photovoltaic and photosynthetic mimicking devices is longevity of the charge-separated state following photoinduced ET. The lifetime of the charge-separated state generally increases with increasing separation between the redox centers, as testified by the lifetimes of charge recombination, τ_{cr} , for the charge-separated states of 3(n), shown in Table 3. However, the efficiency of formation of the charge-separated state diminishes rapidly with increasing interchromophore distance.

The problem of combining efficient formation of the charge-separated state with longevity of that state may be solved using triads, D_2-D_1-A , such as 14, which constitute a gradient of redox centers arranged within a spatially well-defined array. This configuration enables the photoinduced ET process to take place in a sequence of short, rapid "hops" between adjacent chromophores, the final result being efficient formation of a long-lived, giant charge-separated state, $^+D_2-D_1-A^-$. Remarkable progress has recently been made in this area.^{18c,47} Our successful synthesis of norbornylogous triads, 14,⁴⁵ has opened new opportunities for studying systematically the factors responsible for

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controlling the efficiency of formation and longevity of giant charge-separated states.

Totally rigid thiols, **15(n)**, provide an excellent opportunity for forming conformationally unambiguous self-assembled monolayers on electrode surfaces. Consequently, using **15(n)**, in place of conformationally mobile *n*-alkyl systems, will enable exploration of

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heterogeneous ET⁴⁸ to be carried out with less structural ambiguity than has previously been achieved. Preliminary studies on **15(5)** are encouraging.⁴⁶

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