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Investigation of Through-Bond Coupling Dependence on Spacer Structure

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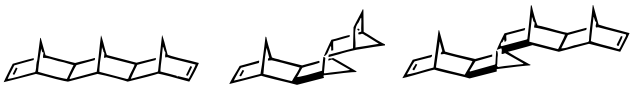
Abstract: Intramolecular electron transfer rate constants in solution are measured for radical anions and cations of molecules having biphenyl and naphthalene groups as donor and acceptor. The molecules have one or more five-bond hydrocarbon chains between the donor and acceptor groups in *trans*, *gauche*, and *cis* conformations. The rates suggest that one *trans* chain is as effective as two *gauche* chains or three *cis* chains, consistent with Hoffmann's prediction of more effective coupling through *trans* hydrocarbon chains. *Ab initio* calculations of the couplings are in reasonable agreement with the experiments. Calculations of electronic coupling pathways provide insight into the reason for the superiority of the *trans* conformation, which gives constructive interference between the two largest pathways. The calculations also show that "cross talk" can enhance couplings in cyclic spacers in contrast to its deleterious effect in norbornyl spacers. Comparisons of couplings through these spacers with simple hydrocarbon chains require that large nonbonded interactions be taken into account.

1. Introduction

The electronic coupling interaction between a donor and acceptor is one of the least understood aspects of charge transfer reactions. In intramolecular charge transfer reactions where the donor (D) and acceptor (A) are tethered by a rigid spacer (S) in the form DSA, the coupling between the donor and acceptor has been found to occur primarily through the bonds of the spacer. This is true even when the spacer is an insulator, such as a saturated hydrocarbon. Though there are many important aspects about this interaction, the focus of the present study is to determine how this through-bond (TB) interaction depends on the structure of the spacer.

In 1968, Hoffmann and co-workers[1,2] proposed that through-bond interactions were relatively large in magnitude and strongly dependent upon the orientation of the intervening bonds. Evidence leading to Hoffmann's study had been growing from a variety of areas, including structural effects on chemical properties[3] and UV spectra.[3−5] Hoffmann concluded that a fully extended, *all-trans* configuration of the bonds yielded the best through-bond interaction, and deviation from this configuration reduced the magnitude of this interaction. The first clear example came in the late 1970s from Pasman and co-workers[6,7] in a study of the UV spectra of dicyanovinyl thioether isomers. Further confirmation came from the elegant compounds of Paddon-Row and co-workers who measured and computed splittings in photoelectron spectra for several compounds, including those shown above, and measured electron transfer rates in related compounds having larger π groups.[8−13] The first compound pictured has *all-trans* chains between the two ethylenic π groups, whereas the other two include one and two cisoid linkages shown in bold. The cisoid linkages (dihedral angles = 46° from MM2 calculations[14]) were found to reduce the couplings substantially.[12] The reduction per cisoid link varied depending on the number of links, their relative positions, and whether the rates or photoelectron splittings were measured.[12] Many other experimental results demonstrate the importance of through-bond interactions.[15−31]



In the present study, the charge transfer rates of a new series of compounds are used to investigate the structural dependence

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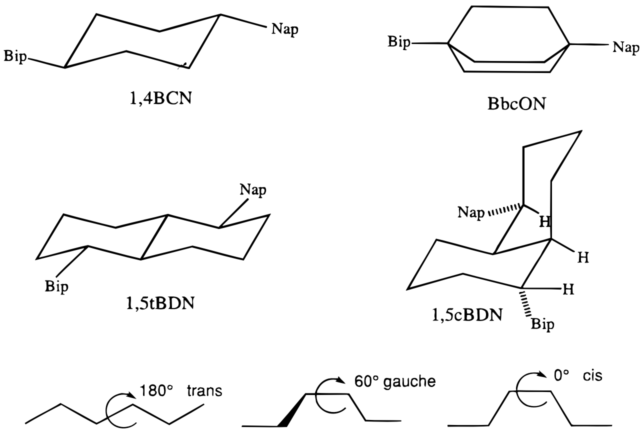

Figure 1. Compounds used for experimental investigation of the dependence of coupling on structure of the spacer. B = biphenyl, N = naphthyl; 1,4C = 1,4-cyclohexane, bcO = 1,4-bicyclo[2.2.2]octane, 1,5tD = 1,5-*trans*-decalin, and 1,5cD = 1,5-*cis*-decalin. At the bottom of the figure are five-bond hydrocarbon chains having the same conformations as those in the molecules.

of through-bond coupling (Figure 1). All the compounds have chains of four saturated carbon atoms (five saturated carbon−carbon bonds) separating the donor and acceptor. The dihedral angles about the central C−C bonds vary from 0° to 180°. For the two 1,5-decalin spacers, the dihedral angle in the central five-bond, four-carbon chain is nearly 180°, to give that central chain the ideal *trans* conformation favored by Hoffmann and shown in the lower left of Figure 1. The 1,4-substituted cyclohexane (1,4C) spacer has two identical five-bond chains connecting the donor and acceptor. In each of these chains the dihedral angle about the central C−C bond is ca. 60°. Thus, the 1,4C spacer can be viewed as containing two five-bond chains, each having a *gauche* conformation, as shown in the bottom center of Figure 1. Similarly, the 1,4-substituted bicyclooctane has three five-bond *cis* chains with central dihedral angles of 0° (lower right in Figure 1). In the 1,5-decalins, in addition to the central five-bond chain, two seven-bond chains are present to hold the five-bond chain in the desired conformation. The expectation that the seven-bond chains contribute little to the coupling is supported in section 4.C.2. The intramolecular electron transfer (ET) and hole transfer (HT) rates were measured for the radical anions and radical cations of these molecules. The experimental results are presented along with the calculated results on model systems using *ab initio* molecular theory.[32,33]

Invocation of the concept of localized or partly localized orbitals has enabled "dissection" the electronic couplings into the specific interactions that produce them.[1,2,6−8,13,15,17,21,34−40] These efforts evolved further to compute the "pathways" of interaction through the spacer to give an intuitive picture of what the important coupling interactions are.[13,41−47] The general conclusions are consistent with those from Hoffmann and others—longer range, vicinal interactions strongly affect the coupling. In this paper the term "chain" is used to refer to connected atoms or bonds and is distinguished from the terms "path" or "pathway", which refers to a series of electronic interactions between bonds in such a chain.

This paper presents measurements by pulse radiolysis of rates of electron transfer in anions and hole transfer in cations of the molecules shown in Figure 1. The results are compared with calculations of electronic couplings between simple CH_2 π donor/acceptor groups through the same spacers and through simple alkyl chains having *trans*, *gauche*, and *cis* conformations.

2. Experimental Methods

1,2-Dichloroethane (DCE) was purchased from Burdick and Jackson, distilled from P_2O_5 under an argon atmosphere, and then placed in an evacuated bulb over a mixture of 4 and 3 Å molecular sieves. Tetrahydrofuran (THF) was dried over sodium metal with benzophenone as a redox carrier and indicator, distilled under nitrogen, placed in a dry evacuated bulb with a sodium/potassium alloy, and sonicated for several minutes until the aqua blue color from solvated electrons appeared, indicating the solution was dry and oxygen-free. The samples were prepared by vacuum distilling the solvents into the silica cells containing the compounds. After the solvent was transferred to the sample cell, the solutions were cooled to temperatures just above the solvent freezing point and sealed while pumping at pressures of $<10^{-4}$ mbar.

The radical anions were generated by irradiating solutions of the DSA compounds in THF with 30 ps, 20 MeV electron pulses from the Argonne linac. Irradiation generates solvated electrons ($<2 \times 10^{-5}$ M) that attach to the donor and acceptor groups to form an equal distribution of D^-SA and DSA^-. In DCE the linac pulses produce two oxidizing species, $DCE^{\bullet+}$ and $CH_2{=}CHCl^{\bullet+}$. Electrons are dissociatively captured to produce Cl^- and radicals, neither of which reacts with the DSA molecules. Both cations react with the DSA compounds to form an equal distribution of D^+SA and DSA^+. The intramolecular charge transfer reactions were then observed photometrically as they proceeded to equilibrium. The HT reactions were monitored at 730 nm, and the ET reactions were monitored at 650 nm. Experimental methods for acquisition of transient absorption data and fitting of the data have been described elsewhere.[48]

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Synthesis of 1-((eq)-4-Biphenylyl)-5-((eq)-2-naphthyl)-*trans*-decalin and 1-((eq)-4-Biphenylyl)-5-((eq)-2-naphthyl)-*cis*-decalin. The following procedure is based on a synthetic methodology developed by Green,[49] who prepared similar compounds for electron transfer research.

1,5-Decalindione. 1,5-Decalindiol was oxidized to 1,5-decalindione using a procedure by Johnson.[50] An oxidizing solution was prepared containing 35 g of sodium dichromate, 27 mL of acetic acid, and 47 mL of concentrated sulfuric acid in 155 mL of water. Twenty grams of the diol, suspended in 400 mL of benzene, was chilled in an ice bath. The oxidizing solution was slowly added to the benzene suspension over a 2 h period and vigorously stirred overnight with a mechanical stirrer. Additional water was added to the mixture, and the organic layer was separated. The aqueous layer was extracted with three 100 mL portions of benzene. The organic fractions were combined and washed with 200 mL of water, 200 mL of saturated sodium bicarbonate solution, and 200 mL of water. The benzene was evaporated, and the crude product was recrystallized from ethanol yielding 10.5 g of crystalline product. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.42 (1H, m), 2.34−2.40 (3H, m), 2.27 (2H, doublet of triplets, J = 6, 12 Hz), 2.08−2.16 (4H, m), 1.58−1.74 (4H, m).

1,5-Decalindione Monoethylene Ketal. The 1,5-decalindione monoethylene ketal was prepared by refluxing 10.5 g of 1,5-decalindione, 3.9 g (1 equiv) of ethylene glycol, and 0.1 g of *p*-toluenesulfonic acid in 150 mL of benzene overnight with a water separator. The mixture was washed with 40 mL of saturated aqueous sodium bicarbonate solution and 40 mL of water. The solvent was evaporated, and the crude product was purified by silica gel column chromatography. The 1,5-decalindione bis-ethylene ketal was eluted with pure hexane, and the monoketal was eluted with 10% methylene chloride/hexane. The crude 1,5-decalindione monoethylene ketal was recrystallized from hexane, yielding 5.2 g of pure product. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.80 (4H, m), 2.30 (2H, m), 2.05 (1H, s), 1.20−2.0 (11H, m).

5-(4-Biphenylyl)decalin-1-one. 4-Bromobiphenyl (5.0 g, 21 mmol) was dissolved in 100 mL of dry THF and cooled in a dry ice−acetone bath; 15.2 mL (24 mmol) of 1.6 M *n*-butyllithium was slowly added, and the mixture was stirred at low temperature for 0.5 h; 3 g (14 mmol) of 1,5-decalindione monoethylene ketal, dissolved in 40 mL of dry THF, was added, and the solution was stirred for an additional 45 min at low temperature. The solution was then allowed to warm to room temperature and stirred for an additional 2 h. Twenty milliliters of water was added to the solution, and the aqueous phase was extracted with three 40 mL portions of methylene chloride. The organic fractions were combined, washed with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was washed with pentane (to remove the excess biphenyl) and filtered, yielding 3.4 g of crude product. This was dissolved in 20 mL of THF and added to 1 pint of absolute ethanol with 4 mL of perchloric acid and 0.9 g of 10% Pd on carbon. The flask was evacuated, refilled with hydrogen gas, and stirred for 2 days. The catalyst was filtered off, and enough solvent was evaporated to allow the product to crystallize out. Yield: 0.86 g of 5-(4-biphenylyl)decalin-1-one. Mp: 216−7 °C. MS: m/z (M^+) 304. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60 (3H, m), 7.45 (2H, d), 7.40 (2H, m), 7.30 (2H, m), 2.65 (1H, doublet of triplets), 2.35 (2H, m), 2.05 (1H, d), 1.95 (1H, m), 1.20−1.90 (10H, m).

1-(4-Biphenylyl)-5-(2-naphthyl)decalin. 2-Bromonaphthalene (1.2 g, 5.6 mmol) dissolved in 40 mL of dry THF was cooled in a dry ice−acetone bath, and 3.9 mL (1.1 equiv) of 1.6 M *n*-butyllithium was slowly added. This mixture was stirred at low temperature for 1 h before 0.86 g (2.8 mmol) of 5-(4-biphenylyl)decalin-1-one, dissolved in 20 mL of dry THF, was added. This was stirred for 2 h at low temperature, allowed to warm to room temperature, and stirred for an additional 1 h; 20 mL of water was added to the solution, and the aqueous phase was extracted with three 40 mL portions of methylene chloride. The organic fractions were combined, washed with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was washed with pentane and filtered, yielding 0.73 g of crude product. The product was then dissolved in 15 mL of acetic anhydride and 1 mL of acetyl chloride and refluxed for 45 min. The acetyl chloride was distilled off under reduced pressure, and the residue was dissolved in methylene chloride so the acetic acid could be washed out with water extractions. The product was purified by column chromatography with silica gel, and the products were eluted with 5% methylene chloride/hexane; 0.39 g of mixed olefins was recovered. The proton NMR and TLC indicated that more than one olefin was present.

The mixture of olefins was hydrogenated by dissolving the mixture in 20 mL of THF and 150 mL of absolute ethanol with 0.1 g of 10% Pd on carbon. The atmosphere was replaced with hydrogen gas, and the mixture was stirred for 2 days. The catalyst was filtered off and the solvent evaporated. The proton NMR of the product indicated that there were several isomers present. The isomers were epimerized by the procedure used by Green[49] for similar compounds. The mixture was dissolved in 7 mL of DMSO (dried over 4 Å sieves) with 0.22 g of potassium *tert*-butoxide. The solution was stirred overnight at 80 °C, the reaction quenched with water, and the mixture acidified with several drops of dilute hydrochloric acid. The product was extracted with three 100 mL portions of methylene chloride; the methylene chloride extracts were combined, washed with water and brine, dried over anhydrous magnesium sulfate, and evaporated. The proton NMR indicated that product consisted mostly of two isomers.

The isomers were cleanly separated using normal phase column chromatography. The crude mixture was dissolved in a 10% methylene chloride/hexane solution and put onto a 30 cm long, 3 cm diameter column of neutral alumina (activity 1). The product was eluted with 10% methylene chloride in hexane solution, collected in 20 mL fractions. Each fraction was analyzed with reverse phase HPLC, using a 10 cm Alltech C18 econosphere column, eluted with 100% acetonitrile at 1.0 mL/min. The two products were recrystallized with absolute ethanol.

1-((eq)-4-Biphenylyl)-5-((eq)-2-naphthyl)-*trans*-decalin. Mp: 225−7 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 (t, 3H, J = 7.5 Hz), 7.60 (d, 3H, J = 8.8 Hz), 7.54 (d, 3H, J = 7.5 Hz), 7.40 (m, 4H), 7.35 (m, 3H), 2.48 (1H, doublet of triplets, J = 3, 11 Hz), 2.35 (1H, doublet of triplets, J = 3, 11 Hz), 1.88 (t, 2H, J = 11 Hz), 1.7−1.2 (m).

1-((eq)-4-Biphenylyl)-5-((eq)-2-naphthyl)-*cis*-decalin. Mp: 200−1 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.90 (t, 3H, J = 7 Hz), 7.60 (d, 3H, J = 8 Hz), 7.54 (d, 2H, J = 7 Hz), 7.44−7.38 (m, 6H), 7.35 (t, 1H, J = 7 Hz), 7.26 (d, 2H, J = 7 Hz), 3.0 (d, 1H, J = 13 Hz), 2.9 (d, 1H, J = 13 Hz), 2.2 (2H, doublet of triplets, J = 2, 14 Hz), 2.0 (1H, doublet of quartet, J = 3, 13 Hz), 1.9 (2H, doublet of triplets, J = 2, 13 Hz), 1.85 (d, 2H, J = 13 Hz), 1.75 (d, 2H, J = 13 Hz), 1.65 (d, 2H, J = 13 Hz), 1.6−1.2 (m), 1.15 (d, 1H, J = 11 Hz), 1.0 (d, 1H, J = 11 Hz).

3. Theoretical Methods

A. Coupling Calculation. The method used to calculate the coupling interactions is based on previous studies.[41,42,45−47,51,52] The method replaces the donor and acceptor chromophores with methylene groups. The rational for this substitution is that the greatest interaction between the donor and acceptor with the spacer occurs at their point of contact with the spacer. This minimizes the number of atoms involved in the calculation. In this model, the methylenes are initially a pair of degenerate p orbitals (related by symmetry). The coupling interaction between the two orbitals results in a mixing that splits them into symmetric and antisymmetric combinations. Koopmans' theorem[53] (KT) provides an approximate way to calculate the splitting parameter, Δ, from the differences in the eigenvalues, ϵ, of the molecular orbitals corresponding to the symmetric (ϕ^+) and antisymmetric (ϕ^-) combinations of the p orbitals on the

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CH_2 donor and acceptor groups:[54]

$$\Delta = \epsilon(\phi^-) - \epsilon(\phi^+) \tag{1}$$

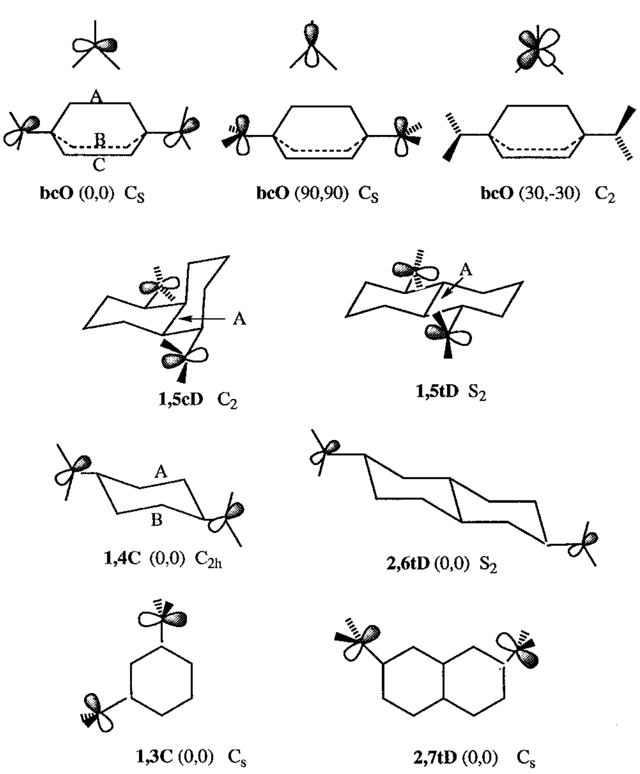
The Δ is associated with the electronic coupling V_{DA} by[54]

$$V = \frac{\Delta}{2} \tag{2}$$

The validity of the various KT values depends, in part, on the importance of electronic relaxation. The sign convention used for the KT couplings is similar to that used by Newton.[54] The interaction is defined as positive when energy of the symmetric orbital ϕ^+ from the many electron wave function is lower than the energy of the antisymmetric orbital ϕ^-. The ΔSCF (self-consistent field) method was also used to calculate couplings. This method uses the unrestricted Hartree−Fock (UHF) energies of the ground (E_g) and first excited (E_e) states, $V = \pm(E_g - E_e)/2$. The ΔSCF method includes electronic relaxation effects of the excitation that are not included in the KT method and thus might be expected to be more realistic, although Kim[55] found long-distance KT couplings through polynorbornyl spacers to be in better agreement with ΔMP2 couplings, which include correlation effects, than with ΔSCF couplings. The same sign convention is used for the ΔSCF couplings as was used for the KT couplings. The KT calculations were carried out on the neutral triplet radicals, whereas the ΔSCF calculations were done on doublet cations and anions.

Ab initio molecular orbital theory[32,33] was used to obtain couplings for comparison with experiment. All *ab initio* calculations were done at the HF/3-21G level. The 3-21G basis has been found to give reasonable agreement with couplings calculated using larger basis sets.[45,52] The semiempirical molecular orbital method AM1 was also used to calculate couplings to assess its reliability for larger systems. The UHF method was used in calculations on open-shell systems (cation, anion, neutral triplet). The resulting wave functions had delocalized donor/acceptor orbitals, that is, an equal electron distribution on the -CH_2 groups for structures with symmetrical donor/acceptor groups.

B. Structures Used in the Calculations. Optimized structures of the neutral triplet radicals were used in the calculations. The structures were initially obtained from molecular mechanics (MM2 optimization)[56−58] and then refined at the semiempirical AM1[59] molecular orbital level. The angles of the methylene groups are constrained to be those preferred by the aromatic chromophores (based on molecular mechanics calculations and NMR experiments). The structures of *trans*-1,4-dimethylenecyclohexane (1,4C), 1,4-dimethylenebicyclooctane (bcO), 1,5-dimethylene-*trans*-decalin (1,5tD), and 1,5-dimethylene-*cis*-decalin (1,5cD) are illustrated in Figure 2. Molecules having CH_2 donor and acceptor groups will be abbreviated using only the name of the spacer (e.g., 1,4C will be used for 1,4-dimethylenecyclohexane). The orientations of the donor/acceptor orbitals, which mimic those of the aromatic donor and acceptor groups, are also shown in the figure. The five-bond backbone chains in 1,5cD and 1,5tD have *all-trans* configurations (dihedral angle of 180°). The methylene groups in 1,5cD have a (0,0) conformation as illustrated in Figure 3 for the five-bond backbone chain. The methylene groups in 1,5tD are twisted by 30° in opposite directions about the C−C bond. The five-bond chains in bcO and 1,4C have dihedral angles of 0° and about 60°, respectively. In addition to these molecules, we also considered systems with three-, four-, and seven-bond chains as the shortest link between the donor and acceptor, including *cis*-1,3-dimethylenecyclohexane (1,3C), 2,7-dimethylene-*trans*-decalin (2,7tD), and 2,6-dimethylene-*trans*-decalin (2,6tD). The structures and orientations of the methylenes are illustrated in Figure 2. These three donor/acceptor systems were studied previously[47] using slightly different structures. Experimental measurements have also been reported previously for compounds containing the 1,3C, 2,7D, and 2,6tD spacers.[48,60] The results are presented here for comparison with the five-bond compounds. All of the methylene-substituted donor/acceptor systems have symmetry and are listed in Figure 2.



bcO (0,0) C_S **bcO** (90,90) C_S **bcO** (30,-30) C_2

1,5cD C_2 **1,5tD** S_2

1,4C (0,0) C_{2h} **2,6tD** (0,0) S_2

1,3C (0,0) C_s **2,7tD** (0,0) C_s

Figure 2. Illustrations of conformers of bcO, 1,5cD, 1,5tD, and 1,4C with CH_2 donor/acceptor groups and five-bond chains. Also illustrated are 1,3C, 2,6tD, and 2,7tD.

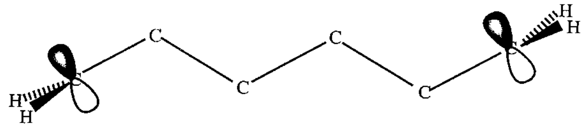


Figure 3. Illustration of five bond-chain of 1,5cD.

C. Superexchange Analysis. We use the superexchange pathways method to provide information about how electronic coupling is transmitted through the bonds of the spacer. The pathways method is based on the idea of superexchange[61−64] (SE), the indirect coupling of donor (D) to acceptor (A) wave functions through a chain (path) of high-energy intermediate

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Table 1. Intramolecular Charge Transfer Rates, Bond Coupling Ratios, and Center-to-Center Distances

		electron transfer		hole transfer	
compd[a]	$R_{\text{B-N}}$[b] (Å)	k_{ET}[c] (s^{-1})	coupling per chain[d]	k_{HT}[c] (s^{-1})	coupling per chain[d]
1,5tBDN	12.0	$3.0 \times 10^9 \pm 20\%$	1.2	0.99×10^9	1.0
1,5cBDN	12.0	2.1×10^9	1.0	0.97×10^9	1.0
1,4BCN	11.7	2.0×10^9	0.49	$1.0 \times 10^{9\,e}$	0.50
BbcON	11.6	2.0×10^9	0.33	5.6×10^9	0.25

[a] Abbreviations: BbcON, 1-(4-biphenyl)-4-(2-naphthyl)bicyclo[2.2.2]-octane; 1,4-BCN, 1-(4-biphenyl)-4-(2-naphthyl)cyclohexane; 1,5tBDN, 1-(4-biphenyl)-5-(2-naphthyl)-*trans*-decalin; 1,5cBDN, 1-(4-biphenyl)-5-(2-naphthyl)-*cis*-decalin. Stereochemistry of aromatics on six-member rings is equatorial. [b] The biphenyl to naphthalene center-to-center separation was calculated by MM2 molecular mechanics using PCMODEL.[57] [c] Estimated uncertainties are ±15% unless otherwise stated. [d] Relative to 1,5cD. Calculated by $|V/\text{chain}| = (k_{\text{et}})^{1/2}/(\text{no. of equivalent chains})$. [e] Rate constant from ref 60.

states. From perturbation theory,[64,65] the coupling of the donor and acceptor by one such chain (the *k*th) is given by

$$V_k = -\prod_{n+1}(-\beta_{ij})/\prod_{n}(B_i) \qquad (3)$$

The β_{ij} are the couplings between the *i*th and *j*th states. The B_i is the energy difference between the *i*th state and states D and A. In a molecular electron transfer reaction, there will be many such chains. The total coupling is the algebraic sum over all chains

$$V = \Sigma_k V_k \qquad (4)$$

This superexchange picture can be effectively implemented if the ratio β_{ij}/B_i of the coupling elements to the energy denominators is small. Unfortunately, β_{ij}/B_i is large if the representation is made up of atomic orbitals. A more useful representation is one in which the intermediate states of the saturated hydrocarbon are localized σ and σ^* bond orbitals. We have used Fock matrix elements from Weinhold's natural bond orbitals (NBOs),[66,67] which are localized orbitals. These localized orbitals are obtained by transforming the canonical (i.e., delocalized) SCF molecular orbitals (MOs) into a set of orthonormal bond orbitals. The NBOs can be divided into "occupied" and "unoccupied" orbitals. The former include core orbitals, lone pairs, and σ or π bonds, and the latter include σ^* or π^* antibonds and extra-valence-shell orbitals (Rydbergs). These NBOs are used in the calculation of the electronic coupling interactions in eq 3. The coupling elements, β_{ij}, and the energy denominators, B_i, used in eq 3 are obtained from off-diagonal and diagonal elements of the Fock matrix in the NBO representation of the UHF wave function. Paths involving hops (forward or backward) between occupied orbitals, unoccupied orbitals, and both occupied and unoccupied orbitals (referred to as mixed paths) are included in the SE results. In this study the SE pathways analysis of coupling was carried out using the β orbitals of the neutral triplet biradical to estimate couplings for the anion. The signs for the SE couplings are taken from the KT couplings.

4. Results and Discussion

A. Comparison of Experimental Couplings for Different Spacers. Electron transfer and hole transfer rate data are presented in Table 1. Because the donor−acceptor separations are roughly constant throughout these compounds (for donor−acceptor separations of five bonds), their Franck−Condon factors are expected to differ little. With this simplification, the relative coupling between the spacers can be directly deduced from the charge transfer rates by the relation $|V| \propto (k_{\text{et}})^{1/2}$.

Table 2. Comparison of Experimental Hole Transfer Coupling Elements to *ab initio* Calculations

		experimental		UHF/3-21G[d]			
compd[a]	$R_{\text{D-A}}$ (Å)[b]	k_{HT} (s^{-1})	approximate coupling ratio[c]	KT (mH)	ratio[e]	ΔSCF (mH)	ratio[e]
1,5cBDN	12.0	0.99×10^9	1	−13.78	1	−13.3	1
1,5tBDN	12.0	0.97×10^9	1.0	−13.57	0.98	−12.0	0.91
1,4BCN	11.7	$1.0 \times 10^{9\,f}$	1.0	−3.70	0.27	−6.27	0.47
BbcON	11.6	5.6×10^8	0.75	−1.65	0.12	−0.51	0.04
1,3BCN	10.0	$3.5 \times 10^{9\,f}$	1.9	10.87	0.79	14.2	1.1
2,7tBDN	12.5	$2.9 \times 10^{8\,f}$	0.78	8.78	0.64	8.14	0.61
2,6tBDN	14.0	$5.0 \times 10^{7\,f}$	0.24	−1.46	0.11	−2.14	0.16

[a] Abbreviations: B, biphenyl; N, naphthalene; cD, *cis*-decalin; tD, *trans*-decalin; C, cyclohexane. The numbers preceding the abbreviated spacer indicate donor/acceptor attachment position. Stereochemistry is equatorial in all cases. [b] The biphenyl to naphthalene center-to-center separation was calculated by MM2 molecular mechanics using PCMODEL.[57] [c] Determined from the square root of the ratio of the HT rate of the compound relative to the rate of 1,5cD. [d] Calculations were performed on molecules in which the biphenyl and naphthalene groups are replaced by CH_2 groups (see Figure 2). AM1-minimized structures of the triplet biradical were used in the calculations. [e] Ratio of the HT coupling of the molecule relative to the coupling of 1,5cD. [f] Rate constant from ref 60.

Though the spacers vary substantially in structure, the charge transfer rates do not. With the assumption that each symmetrically identical path of carbon−carbon bonds connecting the donor and acceptor will contribute equally to the total electronic coupling, it is possible to infer the coupling efficiency as a function of the conformation of the hydrocarbon chains in the bridges. The column entitled "coupling per chain" is the coupling efficiency for each five-bond chain relative to 1,5cD which has the *trans* planar geometry that is expected to yield the largest through-bond coupling. The results for this set of donor/acceptor compounds indicate that the *cis* five-bond chain (in bcO) has a coupling of about one-fourth to one-third that of the *trans* chain (in 1,5cD and 1,5tD), whereas the *gauche* chain (dihedral of 57° in 1,4C) has a coupling of about one-half that of the *trans* chain. Remarkably this relationship is the same for electron transfer in anions and hole transfer in cations.

These conclusions are in accord with Hoffmann's predictions[1,2] about coupling through hydrocarbon chains. These conclusions rely on the assumptions that direct interactions are unimportant and that the two chains in cyclohexane and the three in bcO contribute approximately additively to the total coupling. These assumptions can be examined, and the nature of the coupling can be elucidated by comparison of the experimental results with calculations of the electronic coupling.

B. Comparison of Experimental and Theoretical Couplings. The measured HT and ET couplings are compared with the 3-21G KT and ΔSCF couplings in Tables 2 and 3. The AM1 couplings are given in Table 4. The couplings normalized to that of 1,5cD are included to simplify the comparison of the experimentally determined values with the calculated couplings. For the HT data, the actual couplings are unknown, so it is especially useful to normalize the data. Differences in the donor−acceptor separation can also alter the Franck−Condon factors because a shorter donor−acceptor separation will reduce the solvent reorganization energy. In the compounds where the donor and acceptor are separated by five bonds, the distances are nearly constant (Table 1), so no correction has been made.

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Table 3. Comparison of Experimental Electron Transfer Coupling Elements with *ab initio* Calculations

	experimental[a]		couplings, UHF/3-21G[b]			
compd[c]	V (cm^{-1})	ratio[d]	Koopmans (mH)	ratio[d]	ΔSCF (mH)	ratio[d]
1,5cBDN	140	1	−9.17	1	−10.1	1
1,5tBDN	170	1.2	−9.41	1.0	−9.54	0.95
1,4BCN	140	1.0	−12.43	1.4	−11.4	1.1
BbcON	140	1.0	−5.77	0.63	−5.25	0.52
1,3BCN	160	1.1	13.66	1.5	14.5	1.4
2,7tBDN	58	0.41	5.61	0.61	5.65	0.56
2,6tBDN	27	0.19	−2.49	0.27	−2.26	0.22

[a] Electronic couplings were obtained from the ET rates by reference to the known coupling for a steroid spacer[72] and correcting[73] for distance dependence of solvent reorganization energy by use of an approximate dielectric continuum model. [b] Calculations were performed on molecules in which the biphenyl and naphthalene groups were replaced by CH_2 groups. AM1-minimized structures of the triplet biradical were used in the calculations. [c] For abbreviations, see Table 2. [d] Ratio of the ET rate of the compound relative to the rate of 1,5cD.

Table 4. Comparison of AM1-Calculated Coupling Elements with Experiment[a]

	electron transfer			hole transfer		
		AM1[b]			AM1[b]	
compd	experimental[a] coupling ratio	KT (mH)	relative ratio	experimental[a] coupling ratio	KT (mH)	relative ratio[c]
1,5cD	1.0	3.79	1.0	1.0	5.68	1.0
1,5tD	1.2	2.96	0.78	1.0	5.17	0.91
1,4C	1.0	1.54	0.41	1.0	0.09	0.02
bcO	1.0	0.64	0.17	0.75	2.40	0.42
1,3C	1.1	5.23	1.4	1.9	4.02	0.71
2,7tD	0.41	1.79	0.47	0.78	2.93	0.52
2,6tD	0.19	0.30	0.080	0.24	0.12	0.02

[a] See previous tables for a description of experimental couplings and abbreviations. [b] Electronic couplings were calculated with the AM1 semiempirical Hamiltonian[59] for molecules having CH_2 donor and acceptor groups. Koopmans' theorem was used on the neutral triplet biradical. [c] Ratio to coupling calculated with the 1,5cD spacer.

The Koopmans' theorem approach gives results that are usually within 20% of the ΔSCF method (Tables 2 and 3) but are occasionally off by up to a factor of 2, consistent with the findings of previous studies.[42,52]

The agreement between the experimental ratios and theory (ΔSCF) is often within 20%, but there are important exceptions, particularly the calculated ET coupling for bcO and the HT couplings for 1,4C, 1,3C, and bcO. In these worst cases the discrepancy in the calculated coupling ratios is less than a factor of 2, except for the spectacular failure to calculate HT couplings for bcO. The differences of a factor of 2 between experiment and theory are probably due to uncertainty of the theoretical couplings because of dependence on the choice of geometry, level of theory, and use of the CH_2 groups in place of the larger chromophores. In the case of bcO, the HT coupling is especially sensitive to the geometry. The use of the optimized structure of the cation instead of the neutral triplet structure gives a coupling that is in reasonable agreement with experiment. The dependence of coupling on the choice of structure used in the calculation will be presented in a future publication. In this paper we have used AM1-optimized structures for the neutral triplet radical in all coupling calculations. When the semiempirical AM1 method is used to calculate couplings, the results are in greater disagreement with the experimental results (see Table 4).

C. Calculations on Isolated Chains and SE Pathways Analysis. We now discuss the dependence of the calculated couplings on geometry using HF/3-21G calculations on molecules having only one chain of carbon atoms and SE pathways analysis of the chains and complete spacer molecules. In the first part of this section, we present calculations of the couplings through isolated *trans*, *gauche*, and *cis* five-bond fragments of the full spacer. These fragments are created by removing the other carbon atoms and associated hydrogens and tying off the dangling bonds with hydrogens. We refer to them as fragments because they contain only one chain, although they are complete donor−spacer−acceptor molecules. In the second part, the couplings in the five-bond fragments are compared to those from the five-bond chains within the full spacers, and in the third part, additivity of the couplings is examined. This study is done for anion coupling because it is less sensitive to the molecular structure, but the conclusions are expected to be similar for the cations.

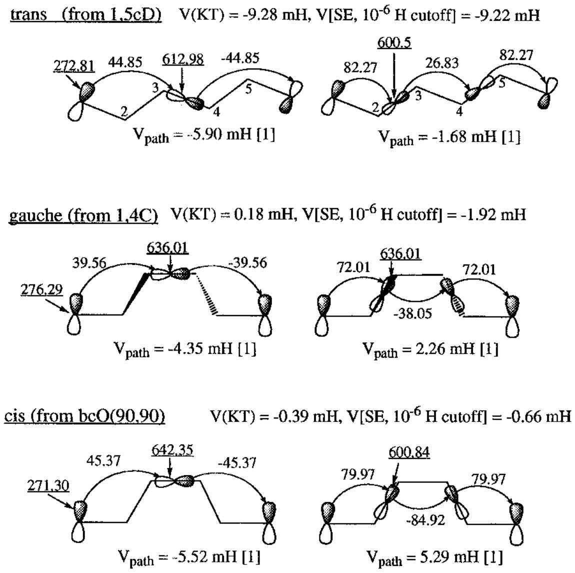
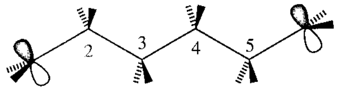


Figure 4. Most important paths of the *trans*, *gauche*, and *cis* five-bond fragments from 1,5cD, 1,4C, and bcO (90,90), respectively, based on neutral triplet β orbitals. The symmetries of the fragments are C_{2h}, C_2, and C_{2v}, respectively. The total couplings from KT [V(KT)] and SE analysis [V(SE), convergence to 10^{-6} hartree] are also given. The structure of the fragment has the AM1-optimized geometry of the spacer from which it is derived. (Use of bond lengths and angles from the *trans* conformer in a calculation on the *cis* conformer changes the KT value from −0.39 to 0.11 mH.) All results are from 3-21G calculations. Underlined numbers are diagonal matrix elements; other numbers are off-diagonal matrix elements.

1. Five-Bond Fragments. The effect of rotation about the C_3-C_4 bond in the *trans* alkyl C_6H_{12} is investigated in conformers having $C_2-C_3-C_4-C_5$ dihedral angles of 180° (*trans*), 57° (*gauche*), and 0° (*cis*). The molecular structures (bond lengths and bond angles) of these three conformers are taken from the five-bond (C_6) chains of the AM1-optimized structures of 1,5cD, 1,4C, and bcO, respectively. The cut C−C bonds are *replaced* with hydrogens (i.e., C−H bonds), whereas the orientation of the terminal (D and A) CH_2 groups are the same as in the full systems. The *trans* form is about 9 kcal/mol more stable than the *cis* form at the 3-21G level. The five-bond fragments are illustrated in Figure 4.



trans

At the HF/3-21G level (KT results), the magnitude (absolute value) of the coupling in the five-bond anion fragment is reduced

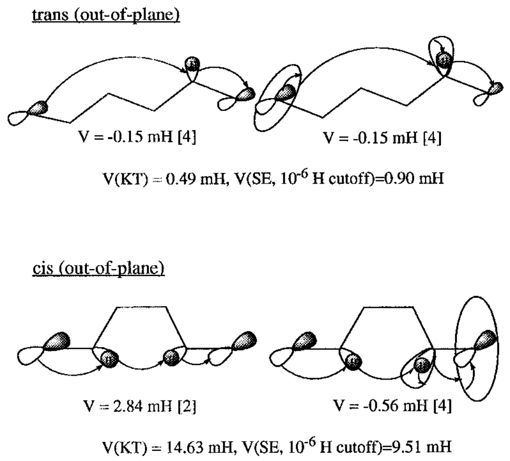


Figure 5. Effect of CH$_2$ rotation on the most important paths and total coupling of *trans* and *cis* five-bond fragments (geometry is the same as in Figure 4). Most important pathways are shown. The donor/acceptor p orbitals are out of the plane containing the carbon atoms of the bridge. The pathway calculations are based on neutral triplet β orbitals with convergence to 10^{-6} hartrees. All results are from 3-21G calculations.

from 9.28 mH in the *trans* structure to 0.39 mH in the *cis* structure and 0.18 mH in the *gauche* structure. Similar results have been reported by Liang and Newton,[42,46] and Broo and Larsson[68] for C$_6$H$_{12}$. Seeing that these calculations are in accord with the predictions of Hoffmann,[1,2] we now apply the pathway method to seek insight into the superior coupling through *trans* chains. Figure 4 shows the two most important pathways for anion coupling from SE analysis in the *cis*, *gauche*, and *trans* structures. The contribution from the first and most important pathway, which passes through only the central C−C antibond, remains almost constant in the *trans*, *gauche*, and *cis* conformers. But the NBO Fock matrix elements listed in Figure 4 indicate that the matrix element between the C2−C3* and C4−C5* antibonds is very sensitive to rotation. Even though the magnitude of this matrix element increases in the *cis* and *gauche* structures, the change in sign causes the contributions from the first and second paths to reinforce in the *trans* but to cancel in the *cis* and *gauche* conformers (see Figure 4). Thus the pathway method identifies the angle dependence of the interactions between the next-to-central antibonds as a principal origin of Hoffman's *trans* rule. The picture developed here has features in common with early, qualitative pictures of Hoffman[1,2] and Paddon-Row.[8,13]

A dramatic change also occurs in the coupling with 90° rotation of the terminal CH$_2$ groups. The results are shown in Figure 5. The CH$_2$ groups are oriented to place the donor/acceptor p orbitals out of the plane containing the carbon atoms of the bridge. Rotation from in-plane (Figure 4) to out-of-plane (Figure 5) orientation reduces the magnitude (absolute value) of the coupling (KT) from 9.28 to 0.49 mH for the *trans* structure and increases the coupling from 0.38 to 14.63 mH for the *cis* structure. When the donor/acceptor p orbitals are out-of-plane, they do not interact with the C−C bonds or antibonds of the spacer, thus eliminating the principal pathways. However in the out-of-plane orientation, pathways through C−H bonds of the spacer become important, although their magnitudes are smaller. In this case the coupling in the *cis* form is much larger than the *trans* form because of better interaction between the CHs (see Figure 5) and the contribution of many paths. This illustrates how important C−H bonds can be in determining the coupling. The energy for rotation of the terminal CH$_2$ groups for both the *cis* and *trans* forms is small (<1 kcal/mol). This type of effect has also been noted by Liang and Newton[35] for C$_6$H$_{12}$ and Paddon-Row and Jordan[69] for dienes, where they refer to it as laticyclic hyperconjugation.

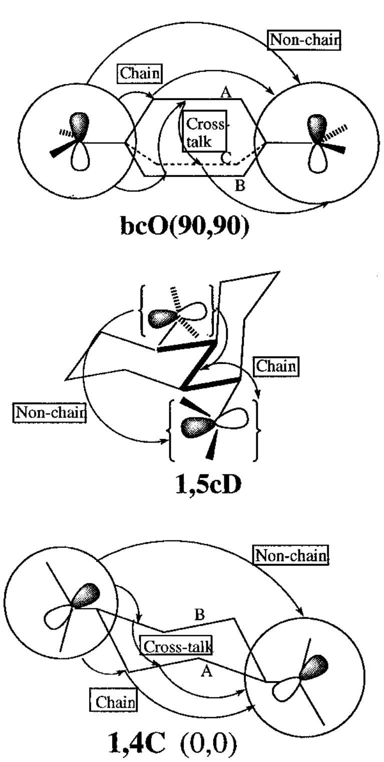


Figure 6. Illustration of decomposition of coupling in full spacers into three types: (1) chain, (2) nonchain, and (3) cross talk.

2. Comparison of Couplings for Five-Bond Fragments and Full Spacers. The couplings (KT) in the *cis* and *gauche* fragments are much less (−0.39 and 0.18 mH, respectively, compared to −9.28 mH for the *trans* fragment) than expected on the basis of the experimental results for the full spacers, which suggest *cis* $\cong$ $^{1}/_{2}$*gauche* $\cong$ $^{1}/_{4}$*trans*. In order to investigate the reason for this difference and to compare with couplings through the five-bond chains of the full spacers, the couplings for the full spacers and fragments have been separated into three parts as illustrated in Figures 6 and 7. For the full spacers, the three parts are (1) "nonchain", (2) "chain", and (3) "cross talk." The nonchain part includes contributions from direct interactions between the lone pairs, Rydbergs located on the donor/acceptor carbons, and any other paths that do not pass through the central three-bond part of the five-bond chain as illustrated in Figure 6. Cross talk[70,71] includes paths that hop between the chains in 1,4C or bcO spacers. The chain part includes all other paths that pass through the central three-bond portion as illustrated in Figure 6. (The Rydbergs on the bridgehead carbons are considered to be nonchain.) The decomposition is similar for the five-bond fragments, except that cross talk is absent and instead there is a contribution from paths through CHs used to tie off the dangling bonds. This part is denoted "CH". The nonchain and chain parts for the fragment are defined in the same way as for the full spacer and are illustrated in Figure 7.

The separation is computed using two methods: (1) SE and (2) Koopmans' theorem via diagonalization (DIAG) of the Fock matrix with selected off-diagonal matrix elements deleted. In

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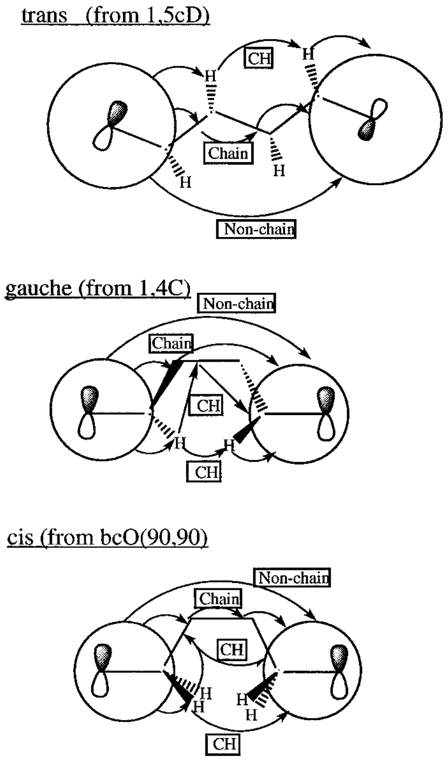


Figure 7. Illustration of decomposition of coupling in five-bond chain fragments into three types: (1) chain, (2) nonchain, and (3) CH.

both methods the neutral triplet β Fock matrix was used to compute couplings for anions. In the SE method, paths of different types (1, 2, or 3) at 10^{-4} hartree convergence were computed and added together. This is straightforward in the pathway method because all paths are assumed to be additive. In the diagonalization method, some explanation is required. We first discuss the procedure for the full spacer. To obtain the nonchain coupling, V_{nonchain}, all off-diagonal matrix elements associated with the central three-bond chain NBOs (C−C bonds and antibonds, C Rydbergs, C−H bonds and antibonds, H Rydbergs) were set to zero and the Fock matrix was diagonalized. The cross talk part, $V_{\mathrm{cross\ talk}}$ is obtained by deleting (setting to zero) all elements connecting the NBOs of one chain to those of the second (and third in the case of bcO) and subtracting the resulting coupling from the total coupling. The chain coupling was then computed as $V_{\mathrm{chain}} = V_{\mathrm{total}} - V_{\mathrm{nonchain}} - V_{\mathrm{cross\ talk}}$. The total coupling is $V_{\mathrm{total}} = V_{\mathrm{nonchain}} + V_{\mathrm{cross\ talk}} + V_{\mathrm{chain}}$. This is approximately true in the KT method.

The decomposition by diagonalization for the case of the five-bond fragments proceeds as follows: The contribution, V_{CH}, from the C−H bonds used to tie off the dangling C−C bonds is calculated by deleting the off-diagonal NBO elements of these CH groups and subtracting the resulting coupling from the total coupling. The nonchain part, V_{nonchain}, is calculated by deleting the chain NBOs and the CH NBOs and diagonalizing the Fock matrix. Finally, the chain coupling was computed as $V_{\mathrm{chain}} = V_{\mathrm{total}} - V_{\mathrm{nonchain}} - V_{\mathrm{CH}}$.

Table 5. Contributions (in mH) to Anion Coupling between CH_2 D/A Groups in Five-Bond Chain Fragments (with Geometries from Full Spacers)[a]

contribution	type of analysis	1,5cD	1,4C	bcO
CH[b]	SE	−0.15	5.05	2.12
	diag	0.14	4.95	2.09
nonchain[c]	SE	1.02	−0.08	0.99
	diag	0.57	0.30	1.46
chain (three-bond)[d]	SE	−12.06	−5.58	−2.63
	diag	−9.99	−5.07	−3.94
total[e]	SE	−11.26	−0.60	0.38
	diag	−9.28	0.18	−0.39

[a] 3-21G calculations based on SE analysis (10^{-4} hartree convergence) and diagonalization (Koopmans' theorem) with deleted matrix elements. The column labels (e.g., 1,4C) indicate the spacer from which the five-bond fragment was obtained. [b] Contributions from paths passing through C−H bonds used to tie off dangling C−C bonds. See Figure 7 for illustration of these paths. [c] Includes direct interactions and contributions from paths not passing through the three-bond part of the chain as illustrated in Figure 7 or from paths passing through C−H bonds used to tie off dangling C−C bonds. [d] Contribution from paths passing through central three-bond chain as illustrated in Figure 7. (Does not include paths passing through C−H bonds used to tie off dangling C−C bonds.) For SE analysis, *gauche* = 0.45*trans* and *cis* = 0.22*trans*. For diagonalization, *gauche* = 0.58*trans* and *cis* = 0.44*trans*. [e] Total coupling ≅ nonchain + CH + chain.

Table 6. Contributions (in mH) to Total Coupling in D/A Full Spacer Anion Systems with Five-Bond Chains from SE Analysis (10^{-4} Hartree Convergence) and Diagonalization with Deletion of Matrix Elements (3-21G Basis)

contribution	type of analysis	1,5cD	1,5tD	1,4C	bcO	
					(90,90)	(0,0)
direct (LP)	SE	−0.23	−0.11	−0.45	−0.37	−0.40
direct (LP Rydberg)[a]	SE	0.22	0.42	1.11	1.68	1.40
nonchain[b]	SE	−3.48	−2.18	0.59	1.19	1.00
	diag	−1.38		0.42	0.68	0.62
cross talk (xt)[c]	SE			−4.30	−2.65	−5.23
	diag			−2.64	−2.98	−2.97
chain[d] A	SE	−9.93	−9.15	−6.01	−5.10	0.24
B	SE			−6.01	−0.73	−3.54
C	SE				−0.73	−3.54
chain total (no xt)[e]	SE	−9.93	−9.15	−12.02	−6.56	−6.84
	diag	−7.78		−10.20	−3.39	−3.48
chain av (no xt)[f]	SE	−9.93	−9.15	−6.01	−2.18	−2.84
	diag	−7.78		−5.40	−1.13	−1.16
total[g]	SE	−13.41	−11.33	−15.73	−8.02	−11.07
	diag	−9.16		−12.42	−5.69	−5.77

[a] Includes interactions through Rydberg orbitals on the donor/acceptor (LP) carbons. [b] Includes direct interactions and other contributions from other paths not passing through the three-bond part of the chain as illustrated in Figure 6. [c] Includes contributions from paths that involve jumps from one chain to another as illustrated in Figure 7. This quantity is not determined for 1,5cD and 1,5tD as they have only one three-bond chain. [d] Contributions from paths passing through individual chains as illustrated in Figure 6. [e] Total contribution from paths passing through all three-bond chains. [f] Average contribution per chain in full spacer. For SE analysis, *gauche* = 0.60*trans* and *cis* = 0.22(or 0.28)*trans*. For diagonalization, *gauche* = 0.69*trans* and *cis* = 0.15*trans*. [g] Total coupling ≅ nonchain + cross talk + chain.

The decomposition results for the fragments are given in Table 5. They indicate that for the *trans* conformer the chain contribution is dominant [SE: −12.06 mH (chain) vs 1.02 (nonchain)], whereas in the *cis* and *gauche* fragments the chain contributions are nearly canceled by those from nonchain and CH parts, which are of opposite sign from the chain part. This cancellation results in the surprisingly small couplings reported in Table 5. This cancellation in the *cis* and *gauche* fragments is largely due to the importance (positive contribution) of paths between the C−H bonds added when the second chain (or chains in bcO) was removed. The SE analysis shows that on the basis of the chain contributions in the C_6H_{12} fragments, the *gauche* fragment yields about one-half and the *cis* fragment about one-third of the coupling from the *trans* fragment. The results from the fragments are consistent with the conclusions drawn from the experimental results for the full spacers in section 4. A. While experimental results are similar for hole transfer, a similar analysis was not done there because the calculations do not agree well with experiment for the *cis* (bcO) case.

In Table 6, the couplings for anions of 1,5cD, 1,4cD, 1,4C, bcO (90,90), and bcO (0,0) are separated into chain, nonchain, and cross talk contributions as illustrated in Figure 6. In addition, the chain part is further separated into contributions from the individual three-bond chains, for example, A, B, and C in bcO (see Figure 6), by the SE analysis. The cross talk makes significant contributions (2−5 mH) to the coupling, as has been found in calculations by Onuchic and Beratan[70] for edge-fused cyclobutanes and by Shephard and co-workers in norbornyl systems.[71] Both Onuchic and Shephard found that cross talk reduced the coupling through two parallel chains with cross connections relative to separate chains. An interesting aspect is that, by contrast, for both 1,4C and bcO, cross talk *increases* the coupling. This opposite effect of cross talk may be the reason that couplings through cyclohexane-based spacers have almost the same distance dependence as that through norbornyl spacers, despite the significant *all-trans* advantage of the norbornyl systems. The norbornyl systems do give much larger couplings, but this may be attributed mainly to distance-independent factors, larger coefficients, and double attachments of the donor and acceptor groups.[22] Although cross talk is significant, the major contributions come from the five-bond chains. The coupling from the five-bond *gauche* chain of 1,4C (−6.0 mH) is ca. one-half that of the five-bond chain of 1,5cD (−9.9 mH). This is similar to the results on the fragments and is consistent with the deduction from experiment that *gauche* $\cong$ ${}^1/_2$*trans*. The results for 1,5tD in Table 6 are also consistent with this conclusion.

In 1,5cD and 1,5tD the contributions from paths passing through the peripheral seven-bond chains are included in the nonchain entry in Table 6. They can be estimated to be about −3 mH for 1,5cD and −2 mH for 1,5tD by subtraction of the direct and LP Rydberg contributions (rows 1−2) from the nonchain total. Thus, as expected, the contributions from those two longer chains are much smaller than those from the central, *trans* five-bond chains.

The results in Table 6 indicate that for bcO the three *cis* five-bond chains do not contribute equally to the coupling because of dependence on orientation. For bcO (90,90), the upper chain (A) contributes −5.54 mH, whereas the lower chains (B and C) each contribute −0.75 mH. For the bcO (0,0) conformer, the two lower bridges (B and C in Figure 7) make contributions of −3.54 mH each (see Table 5), whereas the upper bridge contribution is near zero (0.24 mH) because of symmetry. The 3.54 mH coupling for each lower bridge in bcO (0,0) is consistent with the bcO (90,90) result on the basis of a cosine relation, that is, (5.10 mH) × $[\cos(30°)]^2 = 3.82$ mH. The average of the contributions from the paths through the three *cis* five-bond chains in bcO (90,90) and bcO (0,0) is 2.50 mH based on SE analysis. Thus, *cis* $\cong$ ${}^1/_4$*trans*, consistent with the experimental conclusions. From diagonalization, the average contribution is smaller, −1.14 mH, but may be a reflection of the smaller KT coupling compared to the SE coupling. Also, note that the KT coupling in bcO is about one-half of the coupling in 1,4C.

The most important pathways between the donor and acceptor in bcO, 1,5tD, 1,5cD, and 1,4C are shown for anion coupling in Figure 8. In the case of bcO, results for three orientations of the CH_2 groups are shown: (0,0), (90,90), and (30,−30). The coupling contributions shown in Figure 8 for the first two paths in 1,5cD are similar to those of the *trans* C_6H_{12} fragment in Figure 4 derived from it, in that they are large and of the same sign as well as being through the *trans* chain. The coupling contributions for the first two paths in 1,4C are also similar to those of the *gauche* C_6H_{12} fragment derived from it in that they are large and of opposite signs as well as being through a single *gauche* five-bond chain. The most important paths in bcO (90,90) are through the top bridge (A in Figure 8). This is expected because of the favorable interaction with the D/A orbitals. The contributions for the first two paths in the A branch of bcO (90,90) are similar to those of the *cis* C_6H_{12} fragment derived from it, although they are larger (absolute value) and the ordering is reversed, that is, the most important path is the two-step path instead of the one-step path. The NBO matrix elements in Figures 4 and 8 indicate that this is due to larger off-diagonal interaction elements as well as smaller denominators (B_i, i.e., the difference in diagonal elements).

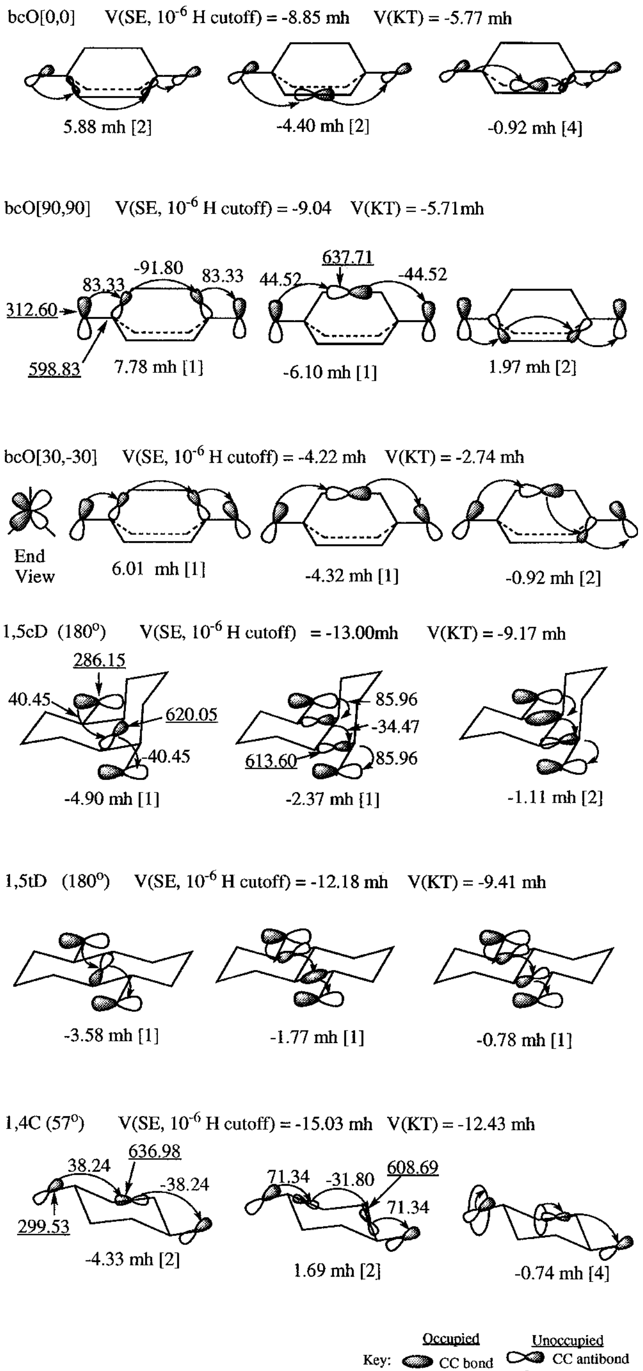
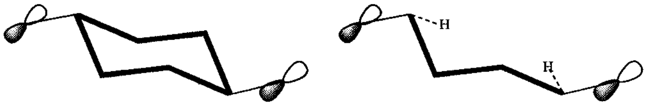


Figure 8. Most important paths and total coupling for electron transfer in species having five-bond paths from SE calculation using neutral triplet β orbitals with convergence to 10^{-6} hartrees. All results are from 3-21G calculations. Underlined numbers are diagonal matrix elements; other numbers are off-diagonal matrix elements.

3. Additivity of Couplings. The 1,4-cyclohexane spacer can be viewed as two partly overlapping five-bond chains, each of which contributes a through-bond coupling. Can such a spacer be considered as the additive sum of two hydrocarbon



	Δ/2, mh
paths thru two three-bond chains	2 x -6.01
non-chain	0.59
cross-talk	-4.30
total coupling	-15.73

	Δ/2, mh
paths through three-bond chain	-5.58
non-chain	-0.08
CH (shown dashed) paths	5.05
total coupling	-0.60

Figure 9. Decomposition of coupling in 1,4C and the *gauche* five-bond fragment from the SE calculation using 3-21G, neutral triplet β orbitals with SE analysis convergence to 10^{-4} hartrees. See text for a description of the nonchain, chain, cross talk, and CH contributions.

chains? The coupling between two CH_2 groups attached at angles (0,0) to 1,4C is −15.73 mH as calculated by the SE pathway method (or −12.42 mH from Koopmans' theorem) using neutral triplet β orbitals and 3-21G basis (see Table 5). If a "one-armed" cyclohexane is created by removal of two carbons (Figure 9) so the two CH_2 groups are attached to a four-carbon chain having the same conformation as in cyclohexane, the coupling is −0.60 mH (0.18 from KT). Given the known dominance of through-bond interactions, we might expect that 1,4C with two chains might produce twice as much coupling as the single $(CH_2)_4$ chain, but instead the 1,4C produces 26 times (−69 times from KT) as much! This result indicates that the coupling through two $(CH_2)_4$ chains is not twice that through one. Such nonadditivity can also be seen in calculations of Liang and Newton.[42] Why? The pathway method will be employed to delineate the reasons for this apparent failure of additivity and to show that the concept of additivity is valid, but that TB couplings can behave in unexpected ways due to important effects of nonbonded interactions.

The decomposition of the coupling for 1,4C by the *ab initio* pathways method is illustrated in Figure 9. The SE pathways analysis on the complete structure (Table 5) indicates that the paths through each bridge contribute −6.0 mH (−12.0 mH total) to the total coupling of −15.73 mH. Pathways that include hops between the two bridges of the ring (cross talk) add another −4.3 mH to the coupling. The coupling through a five-bond *gauche* chain fragment is only −0.6 mH, but the SE analysis shows that it is that small because of a 5.0 mH contribution from the C−H bonds introduced when the dangling bonds were capped by the hydrogens illustrated on the right in Figure 9. The coupling through the *gauche* chain without those C−H bonds, which are not present in the full 1,4C spacer, is −5.0 mH. Once those C−H bonds are accounted for, it is seen that the two *gauche* chains contribute a coupling of about 11.2 mH, which differs from the total for 1,4C by approximately the −4.3 mH cross talk between the two chains and the 0.6 mH direct interaction. Those two contributions, particularly the substantial contribution from cross talk, mean that the total is not just the sum of contributions from the two *gauche* chains. Both the large contributions from the capping C−H bonds and the cross talk are predominantly nonbonded interactions. These findings contribute further to the picture developed earlier when the pathway method showed[41,45] that most through-bond interactions arise from paths that skip bonds. The message is similar here: Through-bond couplings are ironically developed largely through nonbonded interactions.

5. Conclusions

The following conclusions can be drawn from this study of electron transfer in these compounds containing five-bond chains with dihedral angles ranging from 0° to 180°.

The measured electron and hole transfer rates of the four compounds with five-bond chains are all approximately the same despite the different conformations of the chain. Because bcO has three five-bond chains, 1,4C has two, and 1,5tD and 1,5cD have one, the results follow the approximate additive relationship: 1 *trans* chain ≅ 2 *gauche* chains ≅ 3 (or 4) *cis* chains, that is, *gauche* ≅ $^1/_2$*trans*, *cis* ≅ $^1/_3$(or $^1/_4$)*trans*. This relationship holds for both electron transfer in anions and hole transfer in cations. Thus, these compounds appear to obey the *trans* rule set forth by Hoffmann and are qualitatively consistent with observations and calculations of Paddon-Row and co-workers.[12]

The superiority of *trans* chains in transmission of electronic coupling is due to constructive (in *trans*) and destructive (in *cis* and *gauche*) interference between two principal pathways, one of which has little angle dependence and one of which has strong angle dependence. This picture is from *ab initio* pathway calculations on anions of five-bond hydrocarbon chains.

Theoretical calculations of the hole and electron transfer couplings in model molecules having CH_2 donor/acceptor groups are in fair agreement with the trends found from experimentally measured rates. They agree to within a factor of 2, with the exception of hole transfer in bcO. In this case, theory and experiment are in sharp disagreement. The reason may be due to the sensitivity of the calculations to the structure.

The SE analysis of the five-bond (*cis*, *gauche*, and *trans*) fragments and the full spacers reveals that the theoretical couplings for 1,5cD, 1,4C, and bcO are approximately consistent with the relationship, *gauche* ≅ $^1/_2$*trans*, *cis* ≅ $^1/_4$*trans*, found experimentally. Cross talk between chains and direct interactions are found to be more important in the case of bcO and 1,4C spacers, so that the total coupling is not just the sum of contributions from the separate chains in these cases.

Cross talk between the *gauche* chains of 1,4C and the *cis* chains of bcO *enhances* the coupling between the π donor and acceptor in contrast to its deleterious effect in the case of cyclobutyl[70] and norbornyl-based[71] spacers. This opposite effect of cross talk may account for the fact that the distance dependence of electronic couplings through cyclohexyl-based spacers is only slightly steeper than that through *all-trans* norbornyl spacers, despite the substantial superiority of *all-trans* conformation.

Trans alkyl chains, $(CH_2)_n$, have couplings similar to rigid molecules (*cis* and *trans* 1,5D) containing *trans* chains with the same conformation. This is not true for *gauche* and *cis* alkyls in which the couplings are strongly influenced by interactions through the C−H bonds used to tie off dangling bonds left when other chains were removed from 1,4C or bcO. When coupling through a carbon chain is poor, as in the *cis* chain from bcO or the *gauche* chain from 1,4C, the nonbonded interactions of CHs make an important contribution to the total coupling.

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