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Communications to the Editor

A Simple Procedure for Investigating the Influence of a Chromophore's Orbital Energies on Electronic Coupling through Saturated Hydrocarbon Bridges

Michael N. Paddon-Row,[*,†] Michael J. Shephard,[†] and
Kenneth D. Jordan[*,‡]

School of Chemistry, University of New South Wales
P.O. Box 1, Kensington, NSW, Australia 2033
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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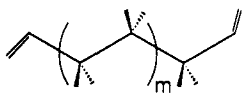
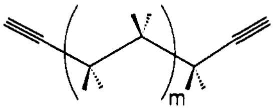
Long-range intramolecular electron transfer (ET) in donor–{saturated hydrocarbon bridge}–acceptor molecules continues to generate considerable experimental[1-3] and theoretical activity,[4-6] and substantial progress has been made in determining how the electronic coupling responsible for ET depends on such factors as the length and configuration of the bridge and on the orientation and characteristics of the chromophores. However, to what extent does the energy of each relevant chromophore orbital affect the distance dependence of the electronic coupling? In this communication we present a useful yet simple approach for addressing this important question.

The importance of this issue became apparent through our recent HF/3-21G calculations of the π_+,π_- and π_+^*,π_-^* orbital energy splittings for the divinyl alkanes **1**(*n*), *n* = 4–20, and diethynyl alkanes **2**(*n*), *n* = 4–24, for even values of *n*, where *n* is the number of C–C bonds spanning the chromophores. In both series, the alkane bridges have the all-trans conformation.[5f] Using



1(n) n=2m+2



2(n) n=2m+2

Koopmans' theorem (KT),[7] the π_+,π_- and π_+^*,π_-^* splitting energies are taken as measures of the electronic couplings relevant for hole and electron transfer, respectively.[8]

The π_+,π_- splittings for the divinyl molecules follow approximately an exponential decay with increasing number (*n*) of C–C bonds: $\Delta E(\pi) = A\exp(-\beta_h n)$, with $\beta_h \approx 0.26$ per bond. In marked contrast, the β_h values determined from the π_+,π_- splittings of successive members in the diethynyl series steadily diminish with increasing chain length, down to a limiting value of only 0.11 per bond. The different behavior of the π_+,π_- splittings in the two classes of molecules can be traced to the fact that the π/C–C σ energy gap in **2**(*n*) is smaller than that in **1**(*n*)[9] and that it may be sufficiently small to invalidate that McConnell equation,[10] which forms the basis of the predicted exponential distance dependence for the electronic coupling.[11]

The importance of this "energy gap" effect an be elegantly gauged through application of the natural bond orbital[12] (NBO) analysis that has successfully been used for exploring aspects of electronic coupling in hydrocarbon bridges.[5d-f,6a-d] The procedure is as follows. The self-energy of the vinyl π NBO (–10.1 eV) is simply replaced with that of the ethynyl π NBO (–11.0 eV) in the Fock NBO matrix for each member of the **1**(*n*) series, and the resulting matrices are diagonalized to get the "modified" π_+,π_- splittings. If energy gap differences alone are responsible for the different trends in the β_h values for the two series, then the β_h values obtained from this procedure should be the same as those calculated from the π canonical MOs for the **2**(*n*) series.

The HF/3-21G results are presented in Table I.[13-15] Importantly, both π_+,π_- splittings and β_h values determined from the modified NBO Fock matrices are in close agreement with those calculated for the actual diethynyl systems **2**(*n*). Reversal of the procedure, namely replacing the in-plane π NBO self-energies for the ethynyl groups in the Fock NBO matrices for **2**(*n*) with the π NBO self-energies of the vinyl groups, gave π_+,π_- splittings and β_h values in good agreement with those calculated for the actual divinyl systems **1**(*n*). We therefore conclude that the energy gap effect is indeed largely responsible for the differences

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[†] University of New South Wales.

[‡] University of Pittsburgh.

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(8) The Koopmans's theorem approach has been shown to be quite successful at predicting couplings through saturated bridges.[5,6g]

(9) For example, at the HF/3-21G level of theory, the π orbital of acetylene is 0.7 eV more stable than that of ethylene.

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(14) Geometries of **1**(*n*) were optimized under C_2 symmetry using the HF/3-21g method, and those of **2**(*n*) were optimized under C_{2v} symmetry using the HF/STO-3G method. For **1**(*n*), the dihedral angle between each double bond and the C–C bridge bond was fixed at 90° in order to maximize the σ–π overlap.

(15) It has been demonstrated that KT/3-21G calculations satisfactorily reproduce experimental π_+,π splittings in a variety of compounds.[5]

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Table I. HF/3-21G π_{+},π_{-} Splitting Energies and Associated $\beta_h(n, n + 2)$ values (per bond) Determined from the Splittings for Adjacent Members in the **1**(n) and **2**(n) Series for Different Choices of the π NBO Self-Energies

	π self-energies (eV)					π self-energies (eV)	
molecule	-9.25	-10.1 divinyl[a]	-11.0 "diethynyl"[b]	-11.7	molecule	-10.1 "divinyl"[c]	-11.0 diethynyl[a]
1(4)	0.528	0.577	0.640	0.682	**2**(4)	0.454	0.500
1(6)	0.223	0.288	0.397	0.533	**2**(6)	0.219	0.291
1(8)	0.108	0.160	0.261	0.429	**2**(8)	0.119	0.187
1(10)	0.0549	0.0936	0.183	0.363	**2**(10)	0.0693	0.132
1(12)	0.0277	0.0550	0.130	0.314	**2**(12)	0.0413	0.0971
1(14)	0.0140	0.0324	0.0943	0.275	**2**(14)	0.0248	0.0732
1(16)	0.0071	0.0191	0.0690	0.245	**2**(16)	0.0150	0.0566
$\beta_h(4,6)$	0.43	0.35	0.24	0.12	$\beta_h(4,6)$	0.36	0.27
$\beta_h(6,8)$	0.36	0.29	0.21	0.11	$\beta_h(6,8)$	0.31	0.22
$\beta_h(8,10)$	0.34	0.27	0.18	0.08	$\beta_h(8,10)$	0.27	0.17
$\beta_h(10,12)$	0.34	0.27	0.17	0.07	$\beta_h(10,12)$	0.26	0.15
$\beta_h(12,14)$	0.34	0.26	0.16	0.06	$\beta_h(12,14)$	0.26	0.14
$\beta_h(14,16)$	0.34	0.26	0.16	0.06	$\beta_h(14,16)$	0.25	0.13

[a] This column refers to the results for the unperturbed system. [b] This column refers to the results using the diethynyl, **2**(n), self-energies. [c] This column refers to the results using the divinyl, **1**(n), self-energies.

in the β_h values in the series **1**(n) and **2**(n).[16] The strong sensitivity of the π_{+},π_{-} splittings on the π NBO self-energy is caused by the mixing between the σ NBO being so strong that, for the longer alkane bridges, the top of the energy band of the resulting precanonical σ MOs comes very close to the energies of the π NBOs, particularly in the case of the diethynyl systems.

We have also carried out calculations with the "vinyl" π NBO energies set equal to -9.25 and -11.7 eV. Increasing the self-energy of the "vinyl" π NBO to -9.25 eV has the effect of increasing β_h and making it constant (0.34 per bond) for all but the first two members of the series. On the other hand, decreasing it to -11.7 eV leads to very small β_h values which fall off rapidly with increasing bridge length. These results lead us to an important generalization, namely that the distance dependence for the rate of hole transfer in α,ω-bichromophoric alkanes will depend sensitively on the ionization potentials of the chromophores. For example, we predict that changing the chromophore ionization potential from 9.25 to 11.7 eV not only would bring about a dramatic acceleration in the rate of hole transfer (by more than 3 orders of magnitude for alkane bridges having >16 C–C bonds) but also would cause a pronounced change in the distance dependence of the electronic coupling (and the hole-transfer rate) from near exponential to markedly nonexponential behavior.[17]

Although it is well known that one of the advantages of NBOs is that they are transferable, this has not previously been exploited in examining the role of the self-energy in determining the electronic coupling through bridges. The approach described above is capable of powerful generalization. For example, by varying appropriate matrix elements in the Fock NBO matrices, one should be able to probe the consequences of modifying the bridge orbital energies and couplings on the π_{+},π_{-} and π_{+}^{*},π_{-}^{*} splittings and the associated β values.[18] Such information would be invaluable in the design of bridges for mediating long-range electron-, hole-, and energy-transfer processes.

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(16) Although we have presented results for the even-membered series of **1**(n) and **2**(n), (n = even), preliminary calculations show similar results for the corresponding odd-membered series.

(17) In a different context, see ref 2e for experimental work on orbital energy tuning in probing superexchange mechanisms in ET processes.

(18) The extension of the approach described herein to the π^{*} manifold is complicated by the presence of low-energy virtual orbitals representing approximations to continuum functions.[5c,5d] This vexing problem is under active investigation.