Electronic Coupling in C-Clamp-Shaped Molecules: Solvent-Mediated Superexchange Pathways

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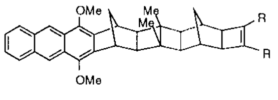
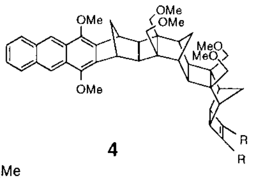
Electron transfer (eT) rate constants are determined, in part, by the magnitude of donor (D)/acceptor (A) electronic coupling, $|V|$. When the D and A are separated beyond van der Waals contact, the intervening medium may mediate $|V|$. D/A coupling across rigid media, such as covalent spacers,[1] proteins,[2] and frozen glasses,[3] has been extensively investigated. The formation and recombination reactions of solvent-separated ion pairs have demonstrated that liquid solvents may also mediate $|V|$.[4] The geometries at which the latter reactions occur are not well characterized. Herein, we report (1) electronic coupling mediated by *fluid* solvent in C-clamp-shaped D−S(pacer)−A molecules possessing well-defined D/A separations and orientations[5] and (2) the dependence of $|V|$ on solvent electronic structure.

Superexchange models are frequently used to interpret the dependence of $|V|$ on the intervening medium's structure.[3,5,6] According to these models, the D/A coupling and its distance dependence, β, are determined, in part, by the difference between the mediating and tunneling state energies, Δ.[7] D/A environments possessing mediating state energies proximate to the tunneling energy should produce larger $|V|$.[8] In an effort to probe solvent mediation of D/A coupling, C-clamp-shaped DSAs **2**−**4** were prepared[9] and their fluorescence dynamics investigated. In these molecules, a direct line from D to A crosses a cavity large enough to accommodate one or more solvent molecules. Furthermore, bond-mediated coupling between the D's lowest excited singlet state and A is "symmetry forbidden";[6b] i.e., the eT active LUMOs on the D and A transform as a′ and a″ representations, respectively, within the C_s point group of **1**−**4**. The "forbidden" topology present in **1**[9] previously was shown[10] to reduce $|V|$ more than an order of magnitude relative to "allowed" DSA topologies.[11] The D/A spatial and bond separations are listed in Table 1.

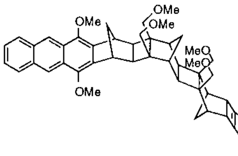


1



4

R = CO_2Me



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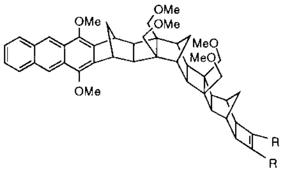

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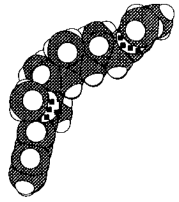
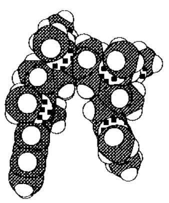


1 [CPK]



4 [CPK]

$|V|$'s for the photoinduced electron transfer reactions (D* → A) of **1**−**4** in CH_3CN, C_6H_5CN, and $(CH_3)_2NCOCH_3$ (DMA) were determined (Table 1) from the temperature dependence[12] of eT rate constants. Semiclassical models express the eT rate constant as a product of $|V|^2$ and a Franck−Condon weighted density of states.[13] A priori calculations of the latter are difficult, thus the need for temperature dependent measurements to extract $|V|$. The solvent dependence of $|V|$ in **1** serves to check the validity of extracting $|V|$ from temperature dependence data. For **1**, which is nearly linear, solvent inclusive superexchange pathways are longer than through-bond pathways and should contribute little to the coupling. As the $|V|$'s determined for **1** in all three solvents are very similar, the approach appears to be reliable.

The most striking results in Table 1 are the *large* and *solvent dependent* $|V|$'s found for **4**. Three sources of coupling may be advanced to explain these results: (1) through-bond coupling "paths" unique to the spacer in **4**, (2) through-space D/A coupling, and (3) solvent-mediated D/A coupling. Unique coupling paths might arise from the proximity of three sets of C−H bonds which line the interior cavity of **4**.[14] Although such paths might produce larger coupling than found across the shorter spacer in **1**, they do not account for the observed solvent dependence. Furthermore, calculations find small, in vacuo D/A couplings (<0.5 cm^{-1}) in **4**.[15] Direct, through-space coupling

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(7) The tunneling energy is the eT transition state energy. For electron-mediated superexchange, the mediating state energy is that of a vertically formed D^+S^-A, where S is solvent or spacer.

(8) The correlation between $|V|$ and $|\Delta|^{-1}$ fails for small $|\Delta|$.[6e]

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(11) DSAs **2**−**4** have the same symmetry, D, and A as **1**. The symmetry constraint on spacer-mediated coupling is comparable in **1**−**4**.[15]

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Table 1. Geometric Parameters, D*/A Electronic Coupling (|*V*|) and Low-Frequency Reorganization Energy (λ_S) at 295 K in **1**−**4**

	1	**2**	**3**	**4**[e]
R_{DA},[a] Å	11.5	10.2	10.6	7.1
bonds in spacer[b]	7	9	10	9
|*V*|. cm^{-1}				
CH_3CN	15.1 ± 1.4[c,d]		3.1 ± 1.5[c]	21.0 ± 2.6[e]
$(CH_3)_2NCOCH_3$	14.2 ± 1.7[c]			14.9 ± 2.9[e]
C_6H_5CN	12.5 ± 1.4[c]	6.8 ± 0.8[c]	8.9 ± 1.0[c]	63.7 ± 8.6[e]
λ_S, eV				
CH_3CN	1.52 ± 0.26[c]		1.50 ± 0.26[c]	1.47 ± 0.50[e]
$(CH_3)_2NCOCH_3$	1.36 ± 0.24[c]			1.15 ± 0.44[e]
C_6H_5CN	1.14 ± 0.24[c]	1.09 ± 0.24[c]	1.16 ± 0.25[c]	1.40 ± 0.50[e]

[a] Center to center distance obtained from the calculated CT state dipole moment.[15] [b] Minimum number of bonds in spacer separating D and A. [c] Uncertainty represents 2 standard deviations. $\Delta G°$(295) range −0.5 to −0.7 eV (MeCN, $(CH_3)_2NCOCH_3$) or −0.4 to −0.6 eV (PhCN).[12] [d] Previously reported as 5.4 cm^{-1}, with $\Delta G°$ and λ_S treated as temperature independent.[10] [e] Uncertainty represents two standard deviations. $\Delta G°$ range −0.5 to −1.0 eV.[12]

within **4** could be significant in conformations with small D/A separation. Molecular mechanics calculations[14b] indicate that fewer than 0.01% of DSA molecules access conformations with D/A separations of 5.5 Å or less at 300 K. The magnitude of through-space |*V*| at this separation is calculated to be less than 8 cm^{-1}.[15,16] Additionally, Closs *et al.* concluded that through-space coupling is not significant in a 2,7-diaxially substituted trans-decalin with an *equilibrium* D/A separation of 6.2 Å.[17] Thus, a strong case for through-space coupling in DSA **4** can not be made.[18]

The |*V*|'s determined for **4** are consistent with models of (solvent-mediated) superexchange. First, Molecular Mechanics calculations confirm that solvent molecules readily access unsymmetrical positions within the cavity, with respect to the DSA symmetry plane. Properly placed solvent orbitals may interact simultaneously with both symmetric and antisymmetric orbitals of the DSA, thus generating non-"symmetry forbidden" pathways for the D/A interaction. Second, AM1 gas phase calculations place the LUMO of PhCN 1 eV lower in energy than the LUMOs of MeCN and DMA.[19] The perturbation expression for a single step, superexchange coupling,[3b,6a] is $|V| = (H_{ss})^2/\Delta$, where H_{ss} is the exchange interaction between adjacent molecules. Approximating $\Delta(\text{MeCN}) - \Delta(\text{PhCN}) = 1$ eV[19] and $H_{ss}(\text{MeCN}) = H_{ss}(\text{PhCN})$, the |*V*|'s for DSA **4** (Table 1) yield $\Delta(\text{PhCN}) = 0.48$ eV and $H_{ss} = 500$ cm^{-1}. The latter value is comparable to H_{ss} found in contact ion pairs.[20] Transfer of an electron from D* to PhCN is nearly thermoneutral in CH_3CN.[21,22] Thus, it is reasonable that the $D^+(PhCN^-)A$ mediating state for **4**, with PhCN within the cavity, lies ~0.5 eV above the eT transition state.[23]

The energy gap, Δ, may be altered through variation of either the mediating or tunneling state energy. Studies of charge shift kinetics from Miller's laboratory have demonstrated that β depends on the tunneling electron energy.[24] The present results demonstrate the dependence of |*V*| on the mediating state energy.[15] Additionally, this study demonstrates that solvent-mediated pathways can dominate D/A coupling in covalently linked systems.[25] Disorder and rapid fluctuations within the solvent pathways may reduce the magnitude[26] and distance over which solvent-mediated coupling can be effective.

Fluctuation in D/A coupling associated with solvent motion[15] amounts to a breakdown in the Condon approximation and may alter the proper theoretical description of electron transfer rate constants.[6m,26] The conventional assumption that |*V*| is temperature independent may not be appropriate. The fitting results for λ_S (295 K) in Table 1 may contain evidence of these effects. Whereas the magnitudes and solvent dependences of λ_S for DSAs **1**−**3** are consistent with conventional models of λ_S,[27] the values for **4** are larger than predicted, particularly in C_6H_5CN. As solvent-mediated coupling for **4** in C_6H_5CN is large and sensitive to solvent position within the C-clamp cavity,[15] the barrier to eT may contain additional terms derived from accessing solvent configurations with favorable |*V*|. It will be interesting to pursue this issue using more complete theoretical models of through-solvent coupling.

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(12) (a) The *k*(*T*) data (determined by time-resolved fluorescence,[10,] 80−100 K range) were fitted to the semiclassical expression for eT rate constants.[13] $\lambda_V = 0.39$ eV and $\hbar\omega = 1410$ cm^{-1} were used.[10] $\Delta G°(T)$ and $\lambda_S(T)$, the low frequency (solvent) reorganization energy, were calculated as $\Delta G°(T) = \Delta G°(295\text{ K}) + \Delta\Delta G°(T - 295\text{ K})$ and $\lambda_S(T) = \lambda_S(295\text{ K}) + \Delta\lambda_S(T - 295\text{ K})$. $\Delta\Delta G°(T - 295\text{K})$ and $\Delta\lambda_S(T - 295\text{K})$ were calculated using standard continuum models,[5c] 4.5 Å for the D and A radii, R_{CC} given in Table 1, and literature values for d*n*/d*T* and $d(\epsilon_s)/dT$.[12b] As $\Delta G°$(295 K) are not known, a range of values (see notes *c* and *e* in Table 1) for this parameter were used. Nonlinear regression analyses of the eT data provided |*V*| and λ_S(295 K) as a function of $\Delta G°$(295K). The average (and 2σ) of the |*V*|'s and λ_S(295 K) are listed in Table 1. (b) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Techniques of Chemistry*, 4th ed.; Weissberger, A., ed.; Wiley Interscience: New York, 1986; Vol. II.

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(14) (a) The H atoms directed toward the clamp interior on C2, C5, and C8 of the bridge (anthracenonorbornene bridgehead is C1) are separated by 1.95 and 2.03 Å, pairwise respectively. (b) Distances, energies, and geometry optimizations performed using the MM2 force field implemented in CAChe Mechanics, Version 3.6, CAChe Scientific, 1994.

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(16) The magnitudes of the experimental and theoretical[15] |*V*|'s are not scaled. The corresponding "experimental" |*V*| at this geometry is not known.

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(18) The solvent dependence of |*V*| in DSA **4** might originate from through-space coupling if MeCN and DMA are more effective than PhCN at entering the cavity and preventing the approach of D and A. Molecular mechanics calculations for DSA **4** with solvent do not support this explanation.[14b]

(19) (a) The AM1[19b] LUMO energies are 0.66, 1.67, and 1.66 eV for PhCN, MeCN, and DMA, respectively (MOPAC Version 94.1 in CAChe, Version 3.6, CAChe Scientific, 1994). (b) Dewar, M. J. S.; *et al. J. Am. Chem. Soc.* **1985**, *107*, 3902.

(20) Reported values: 600−900 cm^{-1}. (a) Li, B.; Peters, K. S. *J. Phys. Chem.* **1993**, *97*, 13145. (b) Gould, I. R.; *et al. J. Am. Chem. Soc.* **1994**, *116*, 8188.

(21) In MeCN (vs SCE), E_{ox} (donor) = 0.83 V,[10] E_{00} (Donor) = 3.0 eV,[10] E_{red} (PhCN) = −2.17 V: Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317.

(22) The fluorescence lifetimes, emission maxima, and line shapes of D*S molecules in butyronitrile, PhCN, and propionitrile ($20 < \epsilon < 27$) are nearly identical. This indicates that the D* state in PhCN does not possess significant exciplex character [D^+ ($PhCN^-$)].

(23) (a) λ_V and λ_S for related dicyanoanthracene/methylated benzene contact ion pairs in MeCN are 0.2−0.3 eV and 0.55 eV, respectively.[4b,23b] Thus, a vertical $D^+(PhCN^-)$ mediating state in MeCN lies <0.85 eV above the corresponding adiabatic state and D*SA. The $D^+(PhCN^-)A$ mediating state energy for **4** in the higher refractive index solvent, PhCN, will be lower. The eT activation energy for **4** in PhCN is 0.06 eV. (b) Gould, I. R.; *et al. J. Am. Chem. Soc.* **1993**, *115*, 3830.

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