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Solvent-Mediated Electron Transfer: Correlation between Coupling Magnitude and Solvent Vertical Electron Affinity

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A wide variety of molecular structures promote the electronic interaction (coupling) required for long-distance electron transfer (ET) reactions.[1] The dependence of the coupling magnitude $|V|$ on the structural details of the "bridging unit" is a subject of current interest, particularly for ET reactions in proteins,[2] covalent donor-bridge-acceptor (DBA) molecules,[3] and across DNA.[4] In contrast to these types of structurally "frozen" bridges, little is known regarding the ability of *mobile fluids* to mediate coupling between D and A groups.[5] Information on solvent-mediated coupling can be obtained for fixed D/A separations by using rigid, C-clamp shaped molecules that (1) enable solvent to fill the cleft directly between the D and A and (2) contain bridges that are poor mediators of $|V|$.[6] We recently reported a pronounced solvent dependence of $|V|$ in a C-clamp shaped DBA for which bond-mediated coupling was symmetry forbidden.[6a] The internal cleft of that DBA (D/A separation of 7 Å) was wide enough for entry of a single, small solvent molecule. Calculations indicated that this solvent molecule was the primary mediator of D/A coupling.[7] Restricted rotation of the entrained solvent, a likely result of the narrow cleft, and the possible role of the solvent molecule as a "symmetry breaker", producing increased bond-mediated coupling, motivated this study of ET across a wider cleft in a symmetry-allowed DBA. The rate constants and $|V|$ for the linear and C-clamp molecules **1** and **2**, respectively, demonstrate the important role of solvent-mediated coupling in C-clamp molecules. The solvent-mediated $|V|$ for the C-clamp **2** increases with an increase in the solvent's vertical electron affinity.

The kinetics of intramolecular ET in DBA molecules **1** and **2**, starting from the lowest energy, singlet excited state (S_1) of the anthracene, were determined by time-resolved fluorescence spectroscopy. The D and A groups in **1** are separated by an *all-trans*, 7-bond bridge. The edge-to-edge D/A separation is 8.5 Å and the charge-transfer distance[7] is 12.2 Å. The D and A groups in **2** are separated by an 11-bond bridge containing one *s-cis* link. The two groups are roughly parallel, with edge-to-edge and charge-transfer distances both equal to 10.0 Å. In both **1** and **2**, the D and A LUMO's are symmetric with respect to the mirror plane symmetry element in the molecules. Thus, the $S_1 \leftrightarrow$ CT coupling is symmetry allowed.

The ET rate constants at 293 K for **1** (Table 1) increase with an increase in the solvent's refractive index, n_D.[8] Similar trends have been observed in charge separation reactions of other linear DBA molecules.[9] The ET rate constants for **2** at 293 K are smaller than the rate constants for **1** in the same solvent. The rate data from **2** do not exhibit a monotonic dependence on solvent n_D. In tetrahydrofuran and acetonitrile (MeCN), the ET rate constants are 100 times smaller for **2** than for **1**. In the aromatic solvents, benzylcyanide (BzCN), *o*-dichlorobenzene, and benzonitrile (PhCN), the ET rate constants are 38, 18, and 7 times smaller, respectively, for **2** than for **1** in the same solvent. The same D and A are present in both molecules and are separated by comparable distances. Thus, the activation barriers to ET should be comparable for **1** and **2** in the same solvent (vide infra).[10] The principal source of the smaller transfer rate constants for **2** must originate in a smaller $|V|$. The room-temperature kinetic results demonstrate that the reduction of $|V|$ from **1** to **2** varies dramatically with the solvent.

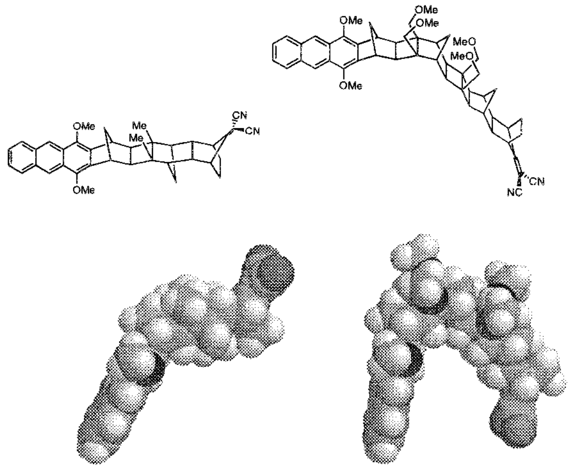

Figure 1. Structures and CPK models of DBA **1** (left) and **2** (right).

Table 1. Solvent Dielectric Properties, 293 K Electron Transfer Rate Constants, ET Activation, and Reaction Free Energy for **1** and **2**

			k(ET)		E_A		$\Delta G°$(295 K), eV	
solvent	$n_D(295)^{24}$	$\epsilon_S{}^{24}$	**1**[25]	**2**[25]	**1**[a]	**2**[a]	**1**	**2**
MeCN	1.342	37	$7.2 \times 10^7\ s^{-1}$	$\leq 7 \times 10^5\ s^{-1}$	5.4[26]	[b]	−0.26	−0.27
THF	1.405	7.6	$3.3 \times 10^8\ s^{-1}$	$< 3 \times 10^6\ s^{-1}$	3.4[26]	[b]	−0.09	−0.12
BzCN	1.521	19	$4.2 \times 10^8\ s^{-1}$	$1.1 \times 10^7\ s^{-1}$	4.3	4.9	−0.18	−0.19
PhCN	1.526	25	$4.9 \times 10^8\ s^{-1}$	$7.3 \times 10^7\ s^{-1}$	4.1	4.5	−0.21	−0.22
o-diClB	1.549	9.9	$5.9 \times 10^8\ s^{-1}$	$3.2 \times 10^7\ s^{-1}$	3.6	4.0	−0.11	−0.14

[a] Activation energy in kcal/mol. [b] ET rate constant too small to determine activation energy.

Values of $|V|$ (Table 2) were extracted from the variable-temperature rate constant data by using a single quantized mode, semiclassical model for the rate constant[11] and Matyushov's[12] description of the solvent reorganization energy, λ_S. This model of λ_S includes contributions from both solvent dipole reorientation

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(10) λ_V and the single mode frequency ω should be the same in **1** and **2**. $\Delta G°$ and λ_S should be very similar. Thus the Franck−Condon factors (FCWDS) for charge separation in both molecules should be comparable.

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and translation upon ET. This combination of measurements and analyses generates reasonable and self-consistent values of $|V|$ and λ_S in highly polar solvents,[13] but significantly overestimates both quantities in weakly polar solvents. Thus, $|V|$ for **1** and **2** were only determined in solvents with ϵ_S greater than 15.

The D/A electronic coupling for **1** is approximately 40 cm^{-1} in both high and low refractive index, polar solvents. Solvent-mediated coupling may be present, but its contribution to $|V|$ is small and/or weakly solvent dependent. The *all-trans* bridge connecting the D and A appears to provide the dominant coupling pathway.[14] By contrast, the electronic coupling in the C-clamp molecule **2** is distinctly solvent dependent. $|V|$ in PhCN is 1.6 times larger than $|V|$ in BzCN and ~7 times larger than $|V|$ in MeCN. As the ET rate constant is proportional to $|V|^2$, electronic coupling produces a 2.6-fold and 49-fold rate enhancement in PhCN compared to BzCN and MeCN. The remainder of the rate enhancement for PhCN arises from the smaller activation barrier.

What is the origin of the solvent-dependent coupling in **2**? It is unlikely that solvent modulation of bond-mediated coupling is responsible. The DBA topology is symmetry allowed.[9c] Distortions of the molecule or solvent environment from C_s symmetry should not enhance bond-mediated coupling. The different solvents should not significantly alter the bridge shape or D/A separation. Previous experiments have shown that $|V|$ decreases ~40% with each additional σ-bond in an *all-trans* spacer[15] and that the presence of an *s-cis* link reduces the coupling another factor of 3.[16] With these factors and a $|V|$ of 40 cm^{-1} across the 7-bond spacer in **1**, the bond-mediated contribution to $|V|$ in **2** is estimated to be <2 cm^{-1}. The generalized Mulliken-Hush method[14b] finds $|V| = 1.3$ cm^{-1} for **2** in the absence of solvent.[17] These two "bond-mediated" estimates of $|V|$ are small compared to the values determined in the aromatic solvents but are similar to the value estimated in MeCN. The $|V|$ for **2** in MeCN may include a significant contribution from the bridge. However, the aromatic solvents clearly provide an additional coupling pathway that is more effective than the bridge in **2**.

Electronic couplings between D and A connected to covalent bridges[1] or randomly distributed in glasses[18] are commonly analyzed by using superexchange models. Superexchange-mediated coupling is effected by a set of exchange interactions between orbitals spanning the space between the D and A. A simplified perturbation theory expression for the coupling magnitude[19] is given by

$$|V| = t_{0,1} \prod_{m=1}^{N-1} \frac{t_{m,m+1}}{\Delta_m}$$

where $\mathbf{t}_{m,m+1}$ is the exchange integral between sites m and $m + 1$, and Δ_m is the vertical energy gap between the transition state for ET and the superexchange state formed by transfer of an electron from the donor (site 0) to site m.[20] Site N is the acceptor. There is no simple way to evaluate the effective t for a pathway involving randomly positioned solvent molecules.[21] Δ may be estimated on the basis of the vertical ionization potential of the donor and the vertical electron affinity of the solvent (Table 2). Δ amounts to ~1.3 eV in PhCN, 4.3 eV in MeCN, and 2.3 eV in BzCN.[22] If t is solvent independent, and a single solvent molecule comprises the coupling pathway ($N = 2$), the energy gap (denominator) generates a $|V|$ in BzCN that is 56% as large as $|V|$ in PhCN: a result that is in good agreement with the experimental couplings. The energy denominator generates a $|V|$ in MeCN that is 29% as large as the $|V|$ in PhCN. This ratio is twice as large as the experimental result. MeCN is smaller than the aromatic solvents and a single solvent molecule in the cleft cannot easily contact both the D and A. In this case, t will be smaller for MeCN in the cleft than for the aromatic solvents. Alternatively, more than one MeCN molecule may be needed to span the cleft ($N > 2$). This will also generate a smaller $|V|$.[19]

Table 2. Solvent Vertical Electron Affinity and Regression Estimates of $|V|$ and λ_S(295 K) for **1** and **2** in Polar Solvents

solvent	EA_V[a]	$|V|$(**1**)[b,d]	$|V|$(**2**)[b,d]	$\lambda_S(1)$[c,d]	$\lambda_S(2)$[c,d]
PhCN	0.2	41	14	0.89	0.88
BzCN	−0.8[e]	44	8.7	0.88	0.94
MeCN	−2.8	40	≤2 [f]	1.17	1.17[f]

[a] Vertical electron affinity[27] in eV. [b] Coupling in cm^{-1}. [c] Low-frequency reorganization energy in eV. [d] Determined as one of two regression parameters in analysis of temperature-dependent rate constant data.[13] [e] Estimated from the EA_V of toluene (−1.1 eV) and the inductive effect of the 2nd nitrile group on the EA in malonitrile.[27] [f] $|V|$ in MeCN determined from the room-temperature ET rate constant assuming $\lambda_S(2)$ in MeCN equals $\lambda_S(1)$ in the same solvent.

The solvent dependence of $|V|$ in **2** is similar to that observed in the previous study of "symmetry-forbidden" C-clamp molecules. Clearly, symmetry breaking and/or restricted solvent mobility are not prerequisites for solvent-mediated coupling. We conclude that solvent-mediated D/A coupling contributes significantly in systems where (1) through bond coupling magnitudes are small, (2) the molecular topology requires a small number of nearest neighbor solvent molecules to span the gap from D to A, and (3) the solvent provides superexchange states that are considerably lower in energy than those provided by the covalent bridge. Fluid, aromatic solvents effectively mediate D/A couplings across distances greater than 1 nm.[23] The effect of solvent mobility on the coupling magnitude will be the subject of future investigations.

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[20] In systems where the D is electronically excited, Δ is much smaller if the antibonding orbitals (as opposed to bonding orbitals) of the solvent propagate the "transferred" electron.

[21] (a) In solvent-mediated coupling, the position and orientation of the solvent molecules between the D and A influences the magnitude of $|V|$,[7,21b] presumably through alteration of t. The appropriate means to evaluate and average t over solvent configuration is not obvious. Furthermore, the proper form of the rate equation in cases of fluctuating $|V|$ has not been experimentally verified.[21c] (b) M. Newton, personal communication. (c) Daizadeh, I.; Medvedev, E. S.; Stuchebrukhov, A. A. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 3703−3708.

[22] Δ is calculated as $\text{IP}_D - \text{EA}_V - \text{E}_{00} - (e^2/R_{DS}) - [(eR_{\text{dip}})^2/a^3][(n^2 - 1)/(2n^2 + 1)]$ where IP_D is the anthracene, vertical ionization potential (7.4 eV), EA_V is the solvent vertical electron affinity (Table 2), E_{00} is the anthracene singlet state energy (3.0 eV), R_{DS} is the mean separation of charge for calculation of the Coulomb energy of the D^+S^- pair (5.5 Å to account for delocalization of charges), R_{dip} is the dipole moment of the D^+S^- pair (taken to be $^1/_2$ the D/A separation, 5 Å), a is the radius of the solvent cavity surrounding the DBA (6.5 Å), and n is the solvent refractive index (Table 1).

[23] This statement applies to electron transfers initiated from an electronically excited donor.

[24] Marcus, Y. *Ion Solvation*; John Wiley & Sons: Chichester, 1985; p 136.

[25] ET rate constant determined as $k_f(\text{DBA}) - k_f(\text{DB})$, where k_f is the S_1 state decay rate constant for the DBA molecule or for a donor-bridge (DB) analogue. At 293 K, $k_f(\text{DB})/10^7$ s^{-1} = 2.4 (MeCN), 3.3 (THF), 3.1 (BzCN), 3.3 (PhCN), and 4.1 (*o*-diClB).

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