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Theoretical Study of Solvent Effects on the Electronic Coupling Matrix Element in Rigidly Linked Donor−Acceptor Systems

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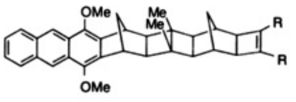
The recently developed generalized Mulliken−Hush approach for the calculation of the electronic coupling matrix element for electron-transfer processes is applied to two rigidly linked donor−bridge−acceptor systems having dimethoxyanthracene as the donor and a dicarbomethoxycyclobutene unit as the acceptor. The dependence of the electronic coupling matrix element as a function of bridge type is examined with and without solvent molecules present. For clamp-shaped bridge structures solvent can have a dramatic effect on the electronic coupling matrix element. The behavior with variation of solvent is in good agreement with that observed experimentally for these systems.

Introduction

In weakly interacting systems the electronic coupling matrix element (H_{ab}) is primarily responsible for the distance and orientation dependence of electron-transfer (et) rates.[1,2] For most rigidly linked systems, through-bond (tb) interactions appear to be the primary means for coupling donor−acceptor pairs.[1] However, for linkers which position the donor and acceptor in reasonably close proximity, it has been suggested that solvent-mediated superexchange interactions may contribute to the electronic coupling.[3−8] In this letter, H_{ab} in a pair of rigidly linked donor−bridge−acceptor (D−B−A) systems,[3] **1** and **4**, is evaluated using the recently developed generalized Mulliken−Hush (GMH) approach[8,9] in conjunction with wave functions obtained using the semiempirical INDO Hamiltonian.[10−12] The nature of the electronic coupling in these two systems is quite distinct. When a solvent molecule (S) is added to the isolated system **4**, the calculations yield a dramatic enhancement of H_{ab} that has a pronounced dependence on the type, position, and orientation of S and appears to arise from specific solvent-mediated superexchange coupling involving DSA pathways. In contrast, for the case of **1**, the solvent molecule appears to cause a relatively modest perturbation of superexchange which remains dominated by pathways involving the DBA framework.

DBAs **1** and **4** both possess dimethoxyanthracene as the electron donor (D) and dicarbomethoxycyclobutene as the electron acceptor (A). System **1** has a straight-chain bridge (i.e., where the shortest covalent sequences are all trans-staggered) containing seven bonds; **4**, a so-called C-clamp structure (with two cis linkages in the shortest covalent sequences), contains nine bonds in the bridge. Experimentally,[3] electron transfer in **1** and **4** is observed in solution following excitation to the lowest electronically excited singlet state (D*) of D and yields D^+ and A^- in their ground electronic states. We denote this forward et as "charge separation" (CS) and the corresponding matrix element as H_{CS}. The "charge recombination" (CR) rate to re-form ground state D and A was not measured experimentally, but we calculate H_{CR} here as well, including the three states of interest (DBA, D*BA, D^+BA^-) in the GMH analysis.[10,13]



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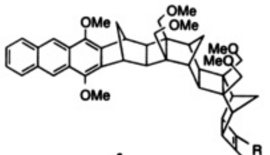

4

R = CO_2Me

1[CPK]

4[CPK]

Structures of Solvated Species

Energetically accessible[14] structures of the DBA-S complexes were sampled by assuming an initial distribution of solvent molecules at various positions and orientations on the "under-side" of DBA (where enhancement of coupling is likely to be most effective) and in each case finding the nearest local minimum energy configuration (including optimization of intra-as well as intermolecular coordinates[15]) using the MM2 force field[16] (see Table 1 for details). Three different solvent molecules were employed for the studies: *n*-pentane, acetonitrile (MeCN), and benzonitrile (PhCN). For the case of the C-clamp structure **4**, solvent placed on the concave side of the molecule between the donor and acceptor is denoted below as "in cavity". As a control, we also obtained optimized structures for S on the outer surface or below the cavity ("out of cavity" solvent), geometries which are not expected to create effective pathways for H_{ab}.

The low-energy structures involve a number of multiple minima associated with conformations of the methoxy (MeO)

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TABLE 1: Calculated Values of H_{CS} and H_{CR} (cm^{-1})

				H_{CS}[b]		H_{CR}[b]	
DBA	solvent	structure type[a]	sample size	rms	range	rms	range
1	solvent removed		8	4.1	2.4−7.6	68.4	66.6−73.3
	n-pentane	in[c]	2	3.8	3.1−4.4	69.8	69.7−69.9
	MeCN	in[d]	3	6.3 (15)[e]	1.1−23.0	62.3	56.0−63.4
	PhCN	in[f]	3	19.3 (12)[e]	10.6−22.6	71.5	65.7−81.8
4	solvent removed		14	0.08	0.004−0.2	3.1	2.5−3.8
	n-pentane	in[g]	3	16.3	8.3−24.1	59.7	9.7−99.4
		out[h]	2	0.6	0.003−0.9	2.5	1.9−3.0
	MeCN	in[i]	2	7.1 (21)[e]	6.2−7.9	16.0	14.3−17.5
	PhCN	in[j]	5	45.9 (65)[e]	13.6−74.4	231.1	80.9−337
		out[k]	2	6.0	0.05−8.4	4.5	2.2−5.5

[a] Structures with one solvent molecule are classified as "in" (solvent in the cavity of **4** or on the underside of **1**) or "out" (solvent outside the cavity of **4**, or partially outside). A set of energetically accessible structures (in the number indicated) was sampled by assuming an initial distribution of solvent molecule locations (i.e., position and orientation relative to the DBA system) and in each case determining the local minimum-energy structure using the MM2 force field[16] as implemented by the CAChe system, version 3.6 (Tektronix, Beaverton, OR). The structures so obtained are described in footnotes *c*, *d*, and *f*−*k*, making reference to the CPK structures for **1** and **4**, with the three rings of the anthracene donor (D) denoted as R1, R2, and R3 (proceeding outward from the bridge (B)), and their junctions as R1/R2, etc. [b] The Boltzmann-weighted rms values and the range of magnitudes for H_{CS} and H_{CR} are displayed for each solvent/structure type. The range obtained with solvent removed are based on the entire set of DBA structures for which local minima were obtained with solvent present. [c] (i) The C5 backbone is in the quasi-C_s plane of DBA, aligned along the long axis of **1** below D and B. (ii) Rotated ~30° out of the C_s plane and lying beneath B. [d] Approximately in the quasi-C_s plane: (i) below D (centered about R1/R2); (ii) below B; (iii) parallel to but displaced from the C_s plane, along one of the basal "rails" of B, extending under A. [e] Experimental estimates based on analysis of solution-phase rate constants.[3] [f] See cases i−iii defined in text. In case i the PhCN was moved 0.3 Å from the HH2 minimum to yield D−S interactions comparable to those obtained in the other cases examined. [g] (i) The C5 backbone is perpendicular to the C_s plane, passing between R2 and double bond of A; (ii) similar to case i, but passing between R2/R3 and outer portion of A; (iii) rotated ~20° out of the C_s plane, extending from near R3 toward the middle of the cavity. [h] Perpendicular to the inner face of R3, extending below A; (ii) perpendicular to the C_s plane, adjacent to outer the face of R3. [i] Both structures have MeCN roughly perpendicular to the C_s plane, with either the Me or CN moiety inside the cavity, and the other moiety extending outside. [j] All five structures have the PhCN plane roughly adjacent to the inner D surface, spanning a wide range of CN orientations relative to the C_s plane. [k] (i) adjacent to the outer D surface; (ii) the Ph moiety lies outside cavity (below D), with CN near the cavity entrance.

and methyl ester (MeE) groups of DBA, as reflected in the diversity of conformations found in available structural data for related systems.[17] Having established by preliminary calculations that for a given DBA framework geometry, the conformations of the MeO and MeE groups have small effects on the D to A coupling (i.e., the influence on H_{CS} and H_{CR} is relatively modest),[18] we simply adopted a single set of conformations in all calculations reported below (at D the MeO's are rotated perpendicular to the D plane with one on the convex outer ("up") side and one on the concave inner ("down") side of the plane; at A the MeE's are in the olefinic plane, with one of the two carbonyls directed "in" and the other "out" (i.e., respectively cis and trans to the olefin)).[19]

The CR process is symmetry allowed in C_s symmetry (the highest symmetry available to **1** and **4**), while the CS process is formally forbidden (the LUMOs of D and A have a′ and a″ symmetry respectively, in C_s symmetry). The DBA framework in the structures obtained above maintains a quasi-C_s plane despite the nonsymmetric MeO and MeE conformations and the presence of solvent. Nevertheless, symmetry-breaking of the DBA wave function is found to have an important role in the influence of solvent on the electronic coupling of D and A (vida infra).

Results for H_{CS} and H_{CR}

With Solvent Removed. As a point of reference for interpreting the influence of solvent on H_{CS} and H_{CR}, we first consider the results for the solvent-free DBA systems (see Table 1), using the same DBA structures as optimized in the presence of the solvent (see above). On the basis of the diabatic dipole moment differences obtained in the GMH method,[8,9] one can define an effective donor−acceptor distance $R_{\mathrm{DA}} = |(\mu_x - \mu_{\mathrm{CT}})/e|$, where μ_x is the mean dipole moment[20] for the two states with the electron on the donor (DBA and D*BA), μ_{CT} is the dipole moment for the $\mathrm{D^+BA^-}$ state, and e is the electronic charge. The resulting R_{DA} are (±0.3 Å) **1**: 11.8 Å; **4**: 7.1 Å. Table 1 lists the two H_{ab} values of interest, as well as the number of geometries at which the calculations were performed. The observation that the solvent-free H_{CS} and H_{CR} values cover narrow ranges for the set of structures considered, in comparison with the ranges found with the solvent present, underscores the fact (noted above) that the calculated DBA geometry is not greatly affected by solvent.[15]

As expected on the basis of symmetry considerations (i.e., based on the quasi-C_S geometry of the DBA framework), H_{CS} is significantly smaller than H_{CR}. This result and detailed examination of the wave functions demonstrate that the asymmetry found in the optimized geometries has not radically altered the C_S-like properties of the molecular orbitals. It is also clear that H_{CR} and H_{CS} decrease with increasing number of bonds between D and A and do *not* correlate with the physical distance between D and A. This does not mean, however, that the coupling is through-bond (tb) mediated in both cases. In fact, the coupling for **4** derives almost entirely from through-space (ts) overlap of D and A. Removal of a portion of the bridge, which we denote as a [2/6] truncation ([*n*/*m*] indicates removal of the section of the bridge between (but not including) the *n*th and *m*th atoms of the basal covalent linkages ("rails"), proceeding from D to A and terminating the dangling bonds with H atoms), results in little change in the CS or CR matrix elements ($H_{\mathrm{CS}} = 0.2\ \mathrm{cm}^{-1}$, $H_{\mathrm{CR}} = 1.1\ \mathrm{cm}^{-1}$). Further removal of bridge atoms ([1/7] truncation) leads to $H_{\mathrm{CS}} = 0.2\ \mathrm{cm}^{-1}$, $H_{\mathrm{CR}} = 3.1\ \mathrm{cm}^{-1}$. In contrast, a [1/6] truncation of **1** reduces H_{CS} and H_{CR} by 2 orders of magnitude ($H_{\mathrm{CS}} = 0.04\ \mathrm{cm}^{-1}$, $H_{\mathrm{CR}} = 0.3\ \mathrm{cm}^{-1}$). Thus, at the level of the INDO wave functions employed here,[10,11] we conclude that the coupling in **4** is largely ts, whereas in **1** it is largely tb. The coupling in **1** is larger than in **4**, even with the greater R_{DA} in **1**, due to the weaker distance dependence of H_{ab} for tb coupling than for ts coupling.[1,21]

With Solvent Present. To assess specific solvent effects we now consider the results obtained for **1** and **4** with solvent present. The results are reported in Table 1, together with available experimental estimates of H_{CS}.[3]

The results for **1** display several intesting features. *n*-Pentane has essentially no effect on H_{CS} or H_{CR}. Since the straight chain bridge is essentially on a direct line from D to A, and given the expected weak interaction between *n*-pentane and the D−B−A, the small effect of *n*-pentane on H_{ab} is not unexpected. With MeCN or PhCN present somewhat larger effects are observed on both H_{CS} and H_{CR}, with a larger effect in the CS case. The three geometries for PhCN with **1** have the solvent on the concave side of the DBA surface, straddling D and B (case i), straddling B and A (case ii), or on the face of D (case iii). Case iii, where PhCN is not proximate to B, leads to an insignificant change in H_{CR} and increases H_{CS} by a factor of 2.7. The geometries with PhCN under the bridge (i and ii) produce larger CS coupling. However, a significant part of this increase arises from wave function symmetry breaking in the DBA moiety due to strong interactions with PhCN (vide infra).

The results for system **4** are much more dramatic. In this case, solvent in the cavity might be expected to enhance the electronic coupling through specific superexchange effects, especially since the coupling in this system is dominated by ts coupling when no solvent is present. Indeed, this is the case. For **4**, *n*-pentane has a marked effect on the CS and CR coupling elements when it is in the cavity, consistent with previous calculations for model systems.[22] However, shifting the *n*-pentane either to the exterior face of the anthracene or below the cavity (out-of-cavity results) produces matrix elements (CR and CS) similar to those found with no solvent present. MeCN in the cavity behaves similarly to *n*-pentane. The two structures have, respectively, the CH_3 and CN portions of the MeCN in the cavity, and little difference is seen between them.

The largest solvent alteration of the coupling occurs for PhCN. For this solvent both the CR and CS matrix elements are considerably larger on average than for either of the two preceding solvents. The spread in matrix elements is quite large as well, pointing up orientation (and position) effects for the PhCN within the cavity. The larger H_{ab} obtained for one of the "out-of-cavity" PhCN calculations is somewhat misleading since the CN group and the ipso carbon are, in fact, partially within the cavity. The other out-of-cavity result places the PhCN on the external face of D, and essentially no change relative to the solvent-free result is observed. It is clear that placement of the PhCN within the cavity leads to a much larger H_{ab}.

Discussion

It is important to note that the trends observed above for H_{CS} are similar to those found experimentally for these systems (see Table 1). That is, the CS matrix element for system **1** is relatively insensitive to choice of solvent but the CS matrix element for system **4** shows large variations with solvent. We do see somewhat greater sensitivity to the presence of PhCN for **1** than is observed experimentally. The averages reported in Table 1 are Boltzmann-weighted rms values. Thus the enhancements reflected in the rms values are a property of thermally accessible configurations.

The elucidation of the mechanism for the solvent-induced enhancement of the electronic coupling is of considerable interest. Two possible mechanisms for solvent-enhanced coupling might be termed "indirect" (via asymmetrical solvent configurations, which induce symmetry breaking in the DBA wave function and/or structure leading to larger ts (DA) or tb (DBA superexchange) D/A coupling) or "direct" (where solvent-mediated (DSA) superexchange interactions are important in the overall coupling). In the indirect case one would expect relatively little effect on H_{CR}, since it is already allowed by symmetry (it may even be diminished due to loss of constructive interference effects), but a significant increase in H_{CS}, since symmetry breaking disrupts the destructive interference operative in C_S symmetry, thereby leading to finite coupling (either ts or tb). The maximum size of H_{CS} for the indirect mechanism might be expected to be of the order of H_{CR}, the symmetry-allowed value. However, if both H_{CR} and H_{CS} are enhanced dramatically by solvent, then symmetry-breaking effects cannot be solely responsible, thus implicating direct solvent-mediated superexchange coupling. Accordingly, of the two systems examined here, **1** appears to manifest the indirect solvent effect, while **4** seems to be dominated by the direct effect. As noted above, in **1** the observed enhancements are much larger for CS than for CR. In addition, case iii for PhCN interacting with **1**, wherein no direct effects are likely, leads to at least half of the H_{CS} increase observed for cases i and ii. On the other hand, in **4**, both H_{CS} and H_{CR} are enhanced dramatically, and the effect is quite dependent on the solvent type, position, and orientation, whereas removal of the bridge has virtually no effect on the coupling, as shown by the example given in Table 2. In addition, placement of PhCN on an external face of the D (where only indirect effects could be operative) leads to essentially no enhancement, further implicating specific solvent-mediated superexchange coupling for **4**.

TABLE 2: Influence of PhCN and Bridge on Coupling in 4[a]

system	H_{CS} (cm^{-1})	H_{CR} (cm^{-1})
full bridge		
no solvent	0.05	3.6
solvent	18.5	231
[2,6] truncated bridge		
no solvent	0.19	1.09
solvent	21.7	230.6

[a] Based on results for PhCN rotated 120° out of the quasi-C_s plane (see footnote *j* of Table 1).

In summary, exploratory DBA/single solvent molecule calculations demonstrate that solvent-mediated coupling can be the dominant contributor to H_{ab} in certain DBA systems. In such cases, the coupling magnitude is sensitive to both the nature and the placement of the solvent. In solution, multiple solvent molecules interact simultaneously with the DBA. Thus, it will be interesting to characterize the magnitudes and time correlation functions for H_{ab} using more realistic distributions of solvent environments and the associated fluctuation dynamics. Such simulations would also be of considerable value for investigations of coupling in bimolecular electron-transfer systems, for example, in contact and solvent-separated ion pairs. Recent developments[22] in merged quantum mechanical/molecular mechanical coupled potentials make it feasible to characterize D/A electronic coupling in structurally complex systems, with inclusion of dynamical fluctuations. We will pursue such investigations in the near future.

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(10) The GMH approach requires the calculation of the adiabatic energies and dipole moment matrix for the states of interest.[8,9] We have used the Zerner parametrization of INDO (ZINDO[11]) and calculated restricted Hartree–Fock wave functions for the ground state of the system for each molecular geometry.[12] Excited states were generated by diagonalizing the configuration interaction Hamiltonian obtained using all single excitations from the HOMO of the ground state (the donor HOMO in all cases) into all virtual orbitals of the system. The resulting states can be thought of as being constructed in the field of the ground-state ion (D^+BA) using the orbitals appropriate to the neutral ground state (DBA). The GMH analysis employs the component of each dipole vector in the direction of the dipole difference vector for the initial and final adiabatic states (two-state case) or by the average of such differences when several et processes are considered for a given system, as in the present case.

(11) ZINDO: A comprehensive semiempirical SCF/CI package, written by M. C. Zerner and co-workers, University of Florida, Gainesville, FL. See, for example: Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589.

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(14) For DBA **4** the "in-cavity" structures for each solvent have MM2 energies within a 1.2 kcal/mol range (except for one PhCN structure which is 2.3 kcal/mol above the minimum-energy one), while the out-of cavity structures display ranges of ≤2 kcal/mol and all lie several kcal/mol above the "in-cavity" structures. For DBA **1** the MM2 energy ranges are, respectively, 0.2, 2.1, and 2.9 kcal/mol, for *n*-pentane, MeCN, and PhCN.

(15) The optimized DBA framework geometry is little affected by the presence of solvent, as reflected by the fact that when solvent is removed, while maintaining the geometries as optimized with solvent, the energies are all within $\sim kT$ at room temperature (0.4 and 0.8 kcal/mol, respectively, for **1** and **4**).

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(18) Calculated H_{CS} values vary by ≤ 1 cm^{-1} over a wide range of MeO and MeE conformations. For H_{CR}, variations of ≤15% are found as long as the MeE groups remain in the olefin plane (out-of-plane conformers yield values larger by as much as 40%).

(19) For the *isolated* DBA systems we estimate on the basis of MM2 energies that the *up/down in/out* conformations is within ~3 kcal/mol of the lowest energy (*down/down out/out*) structure.

(20) In the cases examined here, the CS and CR dipole moment differences differed by ≤6% in magnitude and less that 7° in direction.

(21) Solvent-free calculations were performed for molecules **2** and **3** of ref 3, yielding for **2**: $H_{CS} = 0.03$ cm^{-1}, $H_{CR} = 0.46$ cm^{-1}, and for **3**: $H_{CS} = 0.21$ cm^{-1}, $H_{CR} = 2.7$ cm^{-1}.

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