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In Search of Through-Solvent Electronic Coupling in Flexible Biradicals

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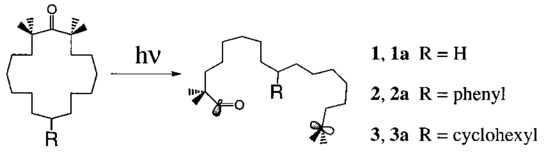
Recently there have been several reports of computations of electronic coupling matrix elements in donor−acceptor (D/A) complexes.[1] These calculations, which were performed at several different levels of theory, were carried out in order to assess the importance of distance, orientation, and solvent on the electron transfer matrix element, *V*. The role of the solvent in electronic coupling is of interest as it addresses the issue of mechanism[2] and medium effects in D/A chemistry, which is of particular importance in biological D/A systems.[3] Direct measurement of *V* is generally not possible in D/A systems because the rate information obtained also depends heavily on nuclear reorganization energies in both the D/A complex and the solvent molecules.[4] For this reason, there is very little experimental data to directly compare with the new calculations.[5]

For the past few years in our laboratory, we have used the spin exchange interaction, $\langle J \rangle$, in flexible alkane chain biradicals as a model for *V* in D/A complexes.[6] Of course, *V* and $\langle J \rangle$ differ by being one- and two-electron quantities, respectively, but both are measures of long-range electronic interactions and should scale together as functions of molecular structure. Biradicals are good model systems for D/A interactions for several reasons: (1) they exhibit a wide range of $\langle J \rangle$ values that are easily measurable using electron paramagnetic resonance (EPR) spectroscopy, (2) they are in general neutral species, so solvent reorganization need not be considered, (3) they are in their electronic ground state at the time of measurement, so the difficulties associated with excited state potential energy surfaces are not present, and (4) it has been shown that in the long-distance limit, the exchange interaction (singlet−triplet energy gap) in neutral biradicals is directly proportional to the overlap between the orbitals containing the unpaired electrons.[7] Since overlap is also a major component of *V*, we[8] and others[9] have argued that what we learn about $\langle J \rangle$ in biradicals should be useful in understanding the nature of other D/A interactions.

Scheme 1



1 - 3 **1a - 3a**

In a previous publication on biradical coupling mechanisms, we have remarked on the insensitivity of $\langle J \rangle$ to solvent polarity and viscosity.[6b] To investigate the role of solvent molecules in more detail, we synthesized ketones **1**−**3** as precursors to biradicals **1a**−**3a**, as shown in Scheme 1. There are two goals of the present set of experiments: (1) to examine the role of a phenyl or cyclohexyl appendage on the side of the main chain that does not directly participate in through-bond coupling and would perhaps mimic a solvent molecule and (2) to look for cooperative effects of the solvent by obtaining the EPR spectrum in “like” and “unlike” solvents such as toluene and methylcyclohexane for each structure. There have been suggestions in the literature that π-bonds can enhance electronic coupling in bridged D/A systems,[1a,10] and a comparison of **2a** and **3a** in the two solvents may allow insight into the magnitude of this effect. Biradical **1a** is a control for these EPR experiments. It has been used previously to study the effect of geometric isomerism on $\langle J \rangle$ values.[11] The details of biradical production,[12] their detection by time-resolved EPR spectroscopy,[6b] and simulation of the EPR spectrum to obtain $\langle J \rangle$[13] are all described in previous papers.

The $\langle J \rangle$ values for all three biradicals in both solvents are plotted as a function of increasing temperature in Figure 1. Accurate extraction of $\langle J \rangle$ was limited to the temperature range shown. On the low-temperature side this was because of the appearance of dynamic effects and/or solubility problems, and on the high-temperature side it was due to decarbonylation of the acyl half of the biradical. An immediate surprise from the data is the absence of any measurable solvent effect. The values of $\langle J \rangle$ at any given temperature for each biradical are identical within experimental error (plus or minus approximately 1 MHz) in both solvents. We have offset them slightly in Figure 1 so that the data points could be seen, but actually they overlap almost completely. Another feature of Figure 1 is that at all temperatures, biradical **3a** with the cyclohexyl appendage has the larger $\langle J \rangle$ value. From this result we can conclude that there is no evidence for through-bond (more correctly, “through-appendage”) π-assistance in this system. The phenyl-substituted biradical **2a** shows nearly identical $\langle J \rangle$ values to those of the unsubstituted structure **1a** at all temperatures.

The end-to-end distance distributions mentioned above can help explain some of the observed behavior in Figure 1. To generate such curves we used a rotational isomeric state (RIS) model[14] that accounts for excluded volume interactions and computes the energy of every possible RIS state with anti, gauche+, and gauche− conformations about each bond. The energies of conformations of bonds close to the appendages were obtained from MM2 minimizations of model compounds, usually 5-phenyl- and 5-cyclohexylnonane. The MM2 mini-

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[5] An advance in this regard has recently been presented by Kumar and co-workers (Kumar, K.; Waldeck, D. H.; Zimmt, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 243), who reported a strong solvent dependence of electron transfer rates in two rigid D/A complexes of different geometries. Cave et al. presented a theoretical analysis of this data (Cave, R. J.; Newton, M. D.; Kumar, K.; Zimmt, M. B. *J. Phys. Chem.* **1995**, *99*, 17501), modeling it using generalized Mulliken−Hush theory. The results showed that changes in *V* were most likely responsible for the observed effects.

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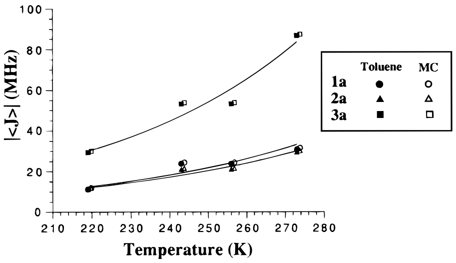

Figure 1. $|\langle J\rangle|$ plotted as a function of temperature for biradicals **1a**–**3a** in toluene and methylcyclohexane (MC). The $\langle J\rangle$ values were obtained by simulation of time-resolved EPR spectra obtained as described in ref 6b.

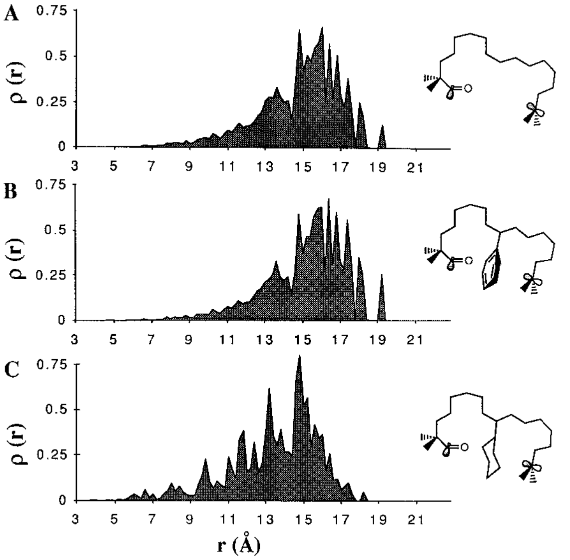

Figure 2. Normalized RIS calculations of probabilities $\rho(r)$ vs end-to-end distance r for biradicals (A) **1a**, (B) **2a**, and (C) **3a** at 280 K.

mizations show that the phenyl-substituted model compound gives an energy minimum for a *trans* conformation about the bonds α and β to the carbon atom bearing the phenyl group, whereas the gauche conformation is lowest in energy for the bonds in the chain coming from the cyclohexyl appendage. In fact, the gauche conformation lies above the *trans* by 2.6 kcal mol^{-1}. The methyl groups and carbonyl moiety were included in the calculations, but the closed shell analogs (obtained by adding hydrogen atoms to the radical centers and changing geometries to those of sp^3 carbons) were used rather than molecules with radical centers.

The distributions calculated in this manner at a temperature of 280 K for **1a**–**3a** are plotted in Figure 2. The plots for **1a** and **2a** are remarkably similar, with the only major difference being the probability of finding chains with longer end-to-end distances. In particular, the probability of the all-*trans* conformation is larger for **2a**, as predicted by the MM2 minimizations discussed above. The remaining part of the distributions for **1a** and **2a** show very few differences and help explain why the $\langle J\rangle$ values for these two biradicals are the same at each temperature. The $\langle J\rangle$ value can be computed by averaging over the entire distribution the value of a suitable exponential function for J with distance, for example $J = J_0 \exp(-\lambda(r - r_0))$.[15] The distribution for **3a** also reflects the outcome of the MM2 minimizations in that the all-*trans* conformation is not present, being of too high energy. The rest of the distribution is also quite different from those in Figure 2A,B; it is spiky and favors many shorter distances. The cyclohexyl system is therefore biased toward shorter end-to-end distances and thus should always have the larger $\langle J\rangle$ if the interaction depends mostly on this distance and not on other parameters, such as strong through-bond coupling.[16] Using the formula above and the distributions in Figure 2 leads to values for $|\langle J\rangle|$ of 42, 31, and 67 MHz for **1a**, **2a**, and **3a**, respectively, at 280 K.[17] These numbers compare favorably with the observed experimental trend of 31, 29, and 87 MHz for the same structures. We conclude that the stereoelectronic effect we had hoped to see in this series of molecules is dominated by sterics rather than electronics.

It is somewhat surprising that the solvent effects are so minimal. We can suggest two reasons why they are difficult to observe in flexible systems. The first is that the biradicals are still highly coiled in solution even at these low temperatures. The distributions in Figure 2 confirm this for all three biradicals. However it seems unlikely that the average J value is determined only by the most highly coiled conformers, which have no solvent molecules between the ends of the chain. Chains with the largest individual $\langle J\rangle$ values contribute the least to the observed spectrum because the spin polarization generated is weak when $\langle J\rangle$ is large. On the EPR time scale all of the conformations are undergoing rapid interchange,[18] and therefore a snapshot of the biradicals at this spectroscopically defined "f-stop" would show a fuzzy sphere (at higher temperatures) or fuzzy ellipse (at lower temperatures), with the radical centers spending most of their time on the edges of these topologies.[19] This would mean that most of the time the radicals couple through the rest of the molecule and very little of the time couple through-solvent. We call this the "through-excluded volume" coupling mechanism, which is really a sum of through-vacuum, through-bond, and through-solvent mechanisms, with through-solvent being less important because the solvent molecules are always being pushed out of the way or "excluded" by the rest of the molecule.

A second reason for the absence of major solvent effects has to do with the density of states through which the radical centers can couple. In liquid solution the rapid motion of the solvent molecules modulates the energies of the molecular orbitals to such an extent that there is, at any given time, always at least one very good pathway through which a superexchange-type coupling can occur, regardless of the nature of the orbital, i.e., σ or π. This seems reasonable when one considers that the widths of the electronic bands in the UV–vis spectrum of, say, toluene, are approximately 1 eV for both the $\pi-\pi^*$ and the $\sigma-\sigma^*$ transitions, which is comparable to their separation in absolute energy. Which of these explanations is correct is a subject of present experimental and theoretical interest to us.

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(15) All terms in this equation have their standard meanings: J_0 is the value of J at the distance of closest approach of the radical centers (r_0 = 3.5 Å), and λ is a falloff parameter generally accepted to be about 1.0 $Å^{-1}$.

(16) Contribution from through-bond coupling arises in $\langle J\rangle$ as the chains populate more extended conformations, i.e., as the temperature is lowered. The extreme limit of this is when all chains assume the geometry of the *all-trans* conformer. On the basis of our results from other similar structures, we expect this mechanism to begin to dominate at temperatures below 220 K, which is outside the range considered here.

(17) For these calculations we used values of 3.5 Å for r_0, 8.4×10^{10} s^{-1} for J_0, and 1.1 $Å^{-1}$ for λ.

(18) If conformational exchange is not fast, then dynamic effects are observed. The simulation routine then fails, and $\langle J\rangle$ cannot be determined. In all cases reported here, $\langle J\rangle$ is obtained from simulations that were successful, so we assume that all $\langle J\rangle$ values reported here are in the fast-exchange limit.

(19) A way to envision the emergence of an elliptical topology at lower temperatures is to consider the extreme condition of slowly approaching absolute zero. If the chains can overcome all rotational barriers, a completely extended (and highly ordered) *all-trans* chain would result. This topology is described by a rigid rod. The high-temperature limit is the "fuzzy sphere", which must acquire more *trans* bonds (and become more ordered) as the temperature is lowered. It is clear that a topology between that of a sphere and a rod is an ellipse. At our experimental temperatures, motion of the chain is still fast, so that the "fuzzy" terminology still applies.