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An Unequivocal Demonstration of the Importance of Nonbonded Contacts in the Electronic Coupling between Electron Donor and Acceptor Units of Donor−Bridge−Acceptor Molecules

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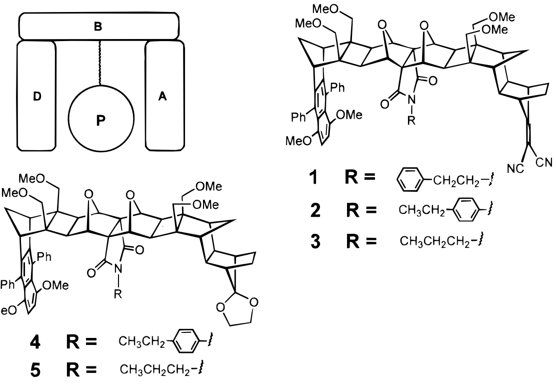
Because of their ubiquity, electron transfer (ET) reactions have received considerable attention over the past few decades. The current view of a superexchange mechanism to treat the electronic interaction for electron-transfer processes in the nonadiabatic limit has been quite successful. Although it is widely believed that covalent linkages between donor and acceptor units provide the dominant pathway for this mechanism,[1] recent work suggests that other pathways involving hydrogen-bonded linkages[2,3] and nonbonded interactions[4,5] can be important. This work assesses the importance of nonbonded contacts by comparing three different unimolecular ET systems that differ by the juxtaposition of a pendant group between the electron donor and acceptor units. This design provides an avenue to quantify the importance of an aromatic moiety's placement on the electron-transfer rate. The work presents unequivocal evidence that electronic coupling through nonbonded moieties can compete effectively with covalent linkages, when the mediating moiety lies between the electron donor and acceptor groups.

This study utilizes a U-shaped donor−bridge−acceptor (DBA) dyad in which a pendant moiety (P) is placed between the electron donor and acceptor units by a covalent linkage to the bridge (see the cartoon in Chart 1). Through systematic change of the pendant molecular unit it is possible to demonstrate its importance to the ET and the role of its placement on the efficiency of ET. This approach has several advantages over earlier approaches. First, the moiety that mediates the superexchange interaction (solvent molecule in earlier studies[4,5]) is clearly located between the donor and acceptor groups. Second, the nature of P can be changed, and a homologous series of DBA molecules can be studied in a single solvent, thereby minimizing any differences in the reaction free energy and outer sphere reorganization energy that may result from solvation changes. These systems also promise an ability to change the geometry of the mediating unit and to investigate how its nuclear dynamics impact the ET.

Chart 1



The ET rates of **1**−**3** in Chart 1 were studied in three different solvents (acetonitrile, dichloromethane, and tetrahydrofuran) as a function of temperature. The general synthetic strategy for these molecules and the specific synthesis of **3** has been reported elsewhere.[6] (See Supporting Information for NMR data.) The molecules in Chart 1 have the same electron donor unit, 1,4-dimethoxy-5,8-diphenylnaphthalene. Molecules **1**, **2**, and **3** have a 1,1-dicyanovinyl (DCV) acceptor unit, and ET occurs when the naphthalene moiety is electronically excited by 375 nm light. These donor and acceptor units have been used for intramolecular ET studies in the past.[1c] Molecules **4** and **5** have a 1,3-dioxolane unit in place of the DCV acceptor. These molecules do not undergo ET and are used as experimental controls. A comparison of the ET rate constant for **1**, **2**, and **3** provides information on the effectiveness of an aromatic ring for mediating the electronic coupling in the ET, as compared to that of an alkyl unit, and addresses the importance of its placement. The ET rate constant was determined by subtracting the excited-state relaxation rate of the control molecules (**4** and **5**) from that of the ET molecules (**1**,**2**, and **3**) (see Supporting Information for more details).

The ET rate constants as a function of temperature are shown in Figure 1 for compounds **1**, **2**, and **3**. In each solvent studied the ET rate for **2** is significantly faster than that found for the other compounds. The larger ET rate constant for **2** compared to **3** demonstrates the benefit of placing an aromatic unit between the electron donor and acceptor rather than an alkyl unit. The larger ET rate constant for **2** compared to that for **1** demonstrates the importance of the aromatic unit's placement between the donor and acceptor groups. Molecular modeling calculations of the molecular geometries of **1** and **2** show that the phenyl ring in compound **2** is in the "line-of-sight" between the donor and acceptor groups (see Figure 2), whereas the phenyl ring in compound **1** is shifted down from the line-of-sight position.[7] The very similar rates for **3** and **1** corroborate this conclusion. In short, the propyl **3** and 2-phenylethyl **1** pendant units are similar with respect to their influence on the ET, but the *p*-ethylphenyl unit

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[7] The images in Figure 2 were calculated at the MM2 level. More sophisticated geometry calculations are underway. Preliminary calculations on **2** at the HF3-21G level indicate that the phenyl ring is located on a line of sight between the donor and acceptor, but it is twisted (~70°) from the plane of the imide ring.

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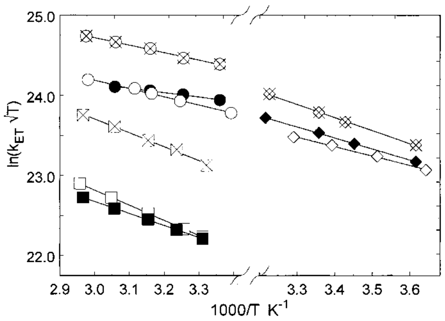


Figure 1. These plots show the temperature dependence of the ET rate constant k_{ET} in three solvents: acetonitrile (squares), dichloromethane (diamonds), and tetrahydrofuran (circles). The filled symbols represent the data for **1**, the open symbols with an × represent the data for **2**, and the open symbols represent the data for **3**. The lines are linear regression fits to the data (see Supporting Information for the best fit slopes and intercepts).

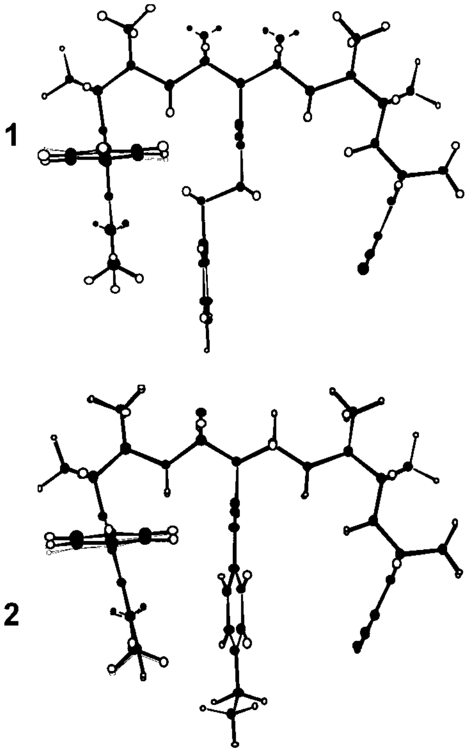


Figure 2. This figure shows ball-and-stick renderings of MM2 optimized structures of the DBA molecules **1** and **2**. The phenyl ring of the pendant group in **2** is on the line-of-sight between the donor and acceptor units.

in **2** is markedly different. These comparisons imply enhanced tunneling when the phenyl ring is in line-of-sight.

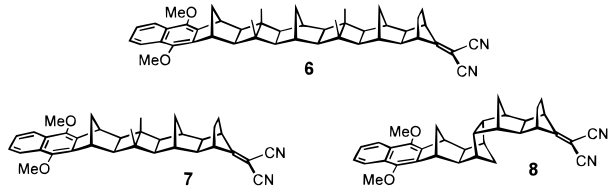
In each solvent system, the ET rate displays a temperature dependence. A fit of the data (see Supporting Information) provides activation energies between 2 and 4 kcal/mol. The similarity of the activation suggests that the Franck−Condon terms (the reaction free energy Δ_rG and the reorganization energies λ) are similar for the three compounds. The ET activation energies for **1**−**3** display a solvent dependence, decreasing by a factor of ~2, upon changing the solvent from acetonitrile to tetrahydrofuran (see Supporting Information). If the Franck−Condon factors are not changing for the compounds in a single solvent, the difference in the rate constants reflects a change in the electronic coupling |V|. This logic is supported by the very similar rates that are observed for **1** and **3** in each of the different solvents. From an analysis of the temperature dependence in each solvent and assuming that the reorganization energy in a given solvent is the same for each of the molecules **1**−**3**, it is possible to extract reliable relative electronic couplings. Table 1 presents the relative electronic couplings in acetonitrile. The results reveal that the coupling in **2** is 2.5 times larger than in **3** and 30% larger than in **1**. Similar differences in the electronic couplings are found in tetrahydrofuran and CH_2Cl_2 (see Supporting Information).

Table 1: Comparison of Rate Constants k_{ET} and Relative Electronic Couplings $|V_{rel}|$ in Acetonitrile Solvent at 300 K

compd	1	2	3	6	7	8
k_{ET} (ns^{-1})	0.25	0.64	0.245	0.16	30.	2.2
$\|V_{rel}\|^a$	1.9	2.4	1			

[a] The electronic couplings are compared to the value for **3**

Chart 2



Comparison of these rate constants with those from earlier studies supports the conclusion that ET in **1**−**3** is occurring through the pendant group and not through the covalent bonds of the bridge (see Table 1). In all three dyads, **1**−**3**, the bridge is 12 bonds long and has two *cisoid* kinks. The rate constants for **1**−**3** are all larger than that for the all-*trans* 12-bond DMN−DCV (see **6** of Chart 2) for the same solvents.[1a] This comparison becomes more significant when one realizes that ET through an all-*trans* bridge is much faster than that through a bridge having two *cisoid* kinks.[8] For example, the ET rate constant for the all-*trans* **7** is up to 14 times larger than that for **8**, which has two *cisoid* links.[8] These considerations suggest that the propyl chain in **3** mediates ET more efficiently than does its 12-bond, double-kinked, covalent bridge! A caveat to these comparisons is that the Δ_rG and λ could be changing, because of the smaller donor−acceptor separation in **1**−**3** (9.0−9.9 Å), compared to that in **6** (~14 Å). Initial investigations indicate that the free energies in these systems are similar,[9] however more studies are required to better quantify these considerations.

A comparison of ET rates in the different DBA molecules **1**, **2**, and **3** demonstrates the importance of the molecular functionality that lies between the donor and acceptor units, even though it does not covalently link them. By changing the pendant unit that lies between the electron donor and acceptor, it has been possible to explore how its nature and its placement impact the ET rate. A more quantitative study of these systems and their electronic coupling is underway. Nonbonded contacts are ubiquitous in chemical and biological systems, and it will be interesting to investigate a wider range of systems. In particular, we are currently synthesizing variants of **2**, in which the ethyl substituent of the phenyl ring is replaced by groups having different electronegativities, to delineate how the donor−acceptor electronic coupling depends on the electronic properties of the pendant aromatic group.

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Supporting Information Available: Rate data and NMR data on **1**−**3** (PDF). This material is available free of charge via the Internet at http:://pubs.acs.org.

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(9) The oxidation potential of the dimethoxynaphthalene in **6** is 0.1 eV smaller than dimethoxydiphenylnaphthalene group in **1** to **3**, and the ground to locally excited-state energy of **6** is 0.2 eV larger than in **1** to **3**, implying about 0.3 eV more driving force for the reaction. However, the Coulomb stabilization of the charge transfer state in **6** is about 0.2 eV smaller than in **1** to **3**. This suggests that the reaction free energies will be close to one another, within 0.1 to 0.2 eV.