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LETTERS

Large Predicted Changes in Geometry Accompanying Charge Separation in Various "Rigid" Multichromophoric Systems in the Gas Phase: An ab Initio MO Study

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UHF/3-21G theory has been used to calculate the gas-phase structures of charge-separated (CS) states of a series of supposedly rigid donor−{bridge}−acceptor systems that are being used experimentally to study electron-transfer processes. It is found that, for most of the systems studied, substantial changes in the interchromophore separation, ranging from 5 to 17 Å, accompany the charge separation process, and that these changes are driven by strong Coulombic interactions between the charged terminal donor and acceptor chromophores. The extent of structural distortion experienced by a CS system depends on the stiffness of the charged chromophores and the connecting bridge, and on the relative orientation of the two chromophores.

Structurally well-defined multichromophoric systems, in which the chromophores are covalently linked to rigid bridges, have provided valuable insight into many important issues of long-range electron transfer (ET) processes,[1] including the dependence of ET dynamics on interchromophore separation[1a,b] and orientation,[2] bridge configuration,[3] orbital symmetry effects,[4] and more recently the nature of solvent-mediated ET processes.[5]

Important examples of rigid systems are **1a**, a member of a "linear" series of bichromophoric systems which have been used for studying the distance dependence of ET dynamics,[1b,c] and the U-shaped molecules **2**, **3a**, **4a**, and **5a** which are being used to study solvent-mediated ET processes.[5] The majority of ET studies carried out on these systems involved photoinduced charge separation. The rate data from these studies are usually used, in conjunction with a suitable ET theory, such as semiclassical theory,[6] to calculate the electronic coupling, V_{el}, for the charge separation process. This calculation entails the evaluation of other important parameters associated with semiclassical theory, such as the solvent reorganization energy and the driving force for the charge separation process. These quantities are not easily obtained from experiment alone and consequently, they normally require the aid of supplementary model calculations.[5e] An important assumption generally made in these calculations is that the geometry of the resulting charge-separated (CS) species is similar to that of its ground-state precursor. We now communicate the results of calculations on the gas-phase structures of the CS states of **1b**−**5b**. They are rather surprising.

Computational Details. Because of the large sizes of the experimental systems **1a**−**5a**, the less substituted molecules **1b**−**5b** were studied. Ground-state geometries were optimized[7a] at the RHF/3-21G level of theory, whereas those for the CS states were optimized at the UHF/3-21G level.[7b] Although there is much to criticize in using a UHF wave function to calculate excited states,[8a] we believe that reasonable excited-state geometries (but not energies) may be obtained using this method.[8b] All geometry optimizations were carried out under C_s symmetry constraint. The CS singlet states obtained for **1b**−**4b** possess A'' symmetry and so are orthogonal to the A' ground states.[8c] The CS states calculated for **4b** and **5b** correspond to giant CS states in which the charges are located at the terminal chromophores. The giant CS singlet state of **5b** has the same

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symmetry as the ground state (A′) and so it could not be calculated at this level of theory. Consequently, the geometry of the lowest triplet state, of A′ symmetry, was optimized, since this state also corresponds to a giant CS state.[9] Full details of the structures and energies of all systems are provided in the Supporting Information.

Results. The geometry of the anion radical, **6b**, of the dicyanovinyl (DCV) model system, **6a**, shows strong pyramidalization at C7 ($\theta = 37°$). The negative charge is associated with the $C(CN)_2$ group and the unpaired spin density is mainly concentrated on C7. The essential geometrical features of **6b** are retained at the UB3LYP/6-31G(d) level. The geometries of model cation radicals of the aromatic chromophores found in the CS states of **1b**−**5b** are essentially planar.[10]

The ground-state structure of **1b**, shown in Figure 1, corresponds closely to the X-ray crystal structure of **1a**.[11] The optimized geometry of the singlet A" CS state of **1b**, $^+$DMN−DCV$^-$,[12] differs little from that of the ground state except for the expected pyramidalization of the DCV group ($\theta = 38°$). The direction of pyramidalization, toward the DMN cation radical, is expected on electrostatic grounds. The gas-phase dipole moment of the CS state is calculated to be 50 D; the experimental value is 68 D (in benzene).[13]

The geometries of the singlet A" CS states of **2**−**4b** are markedly different from those of the corresponding ground states. This is a result of the large change in the center-to-center distance, R_c, between the terminal chromophores which accompanies charge separation (Table 1 and Figure 1). In the case of **2** and **3b**, the strong electrostatic attraction between the DCV anion radical and the aromatic cation radical results in a reduction in the magnitude of R_c, by 4 and 6 Å, respectively. This reduction is largely the result of the terminal, oppositely charged chromophores bending toward each other. Whereas the bending of the naphthalene ring in **2** is slight, that of the anthracene ring in **3b** is quite marked. Interestingly, the "rigid" hydrocarbon bridges in the CS states of **2** and **3b** also bend, resulting in a significant contraction in the distance, R_e, between the ends of the bridges by 1.4 and 1.8 Å, respectively (Table 1).

The R_c value for the giant CS state of **4b**, $^+$DMB−N−DCV$^-$,[12] is only 5.4 Å, some 10.5 Å shorter than that in the ground state! This dramatic contraction in the R_c value is due mainly to substantial out-of-plane bending of the central naphthalene ring, by ca. 20°. Model HF/3-21G calculations reveal that out-of-plane bending of a naphthalene ring by 20° requires ca. 7.5 kcal/mol. This energy penalty in $^+$DMB−N−DCV$^-$ is easily met by increased Coulombic stabilization resulting from the close proximity of the terminal chromophores.

The large contractions in R_c for the CS states of **2b**−**4b** are driven by Coulombic attractions between the oppositely charged terminal chromophores. Consequently, charge separation in **5b**, should lead to an increase in the R_c value since both terminal chromophores in the giant CS state $^+$P−N−NQ−MV$^+$,[12] bear positive charges. Indeed, R_c for the giant triplet CS state of **5b** is a massive 21.7 Å, some 17.6 Å greater than that for the ground state. This substantial geometrical change is mainly caused by bending of the naphthalene and naphthoquinone rings each by ca. 9°. Model calculations on **5b** lacking the P and MV^{2+} chromophores suggest that bending of both aromatic rings by 9° incurs an energy penalty of only ca. 2 kcal/mol.

The ground-state geometry of **5b** is also distorted by electrostatic effects, but in this case the forces between the viologen dication and the neutral porphyrin unit are attractive and this leads to an R_c value of only 4.1 Å. In the absence of attractive interactions between the two terminal chromophores, the relaxed value for R_c is estimated to be ca. 13 Å.[14]

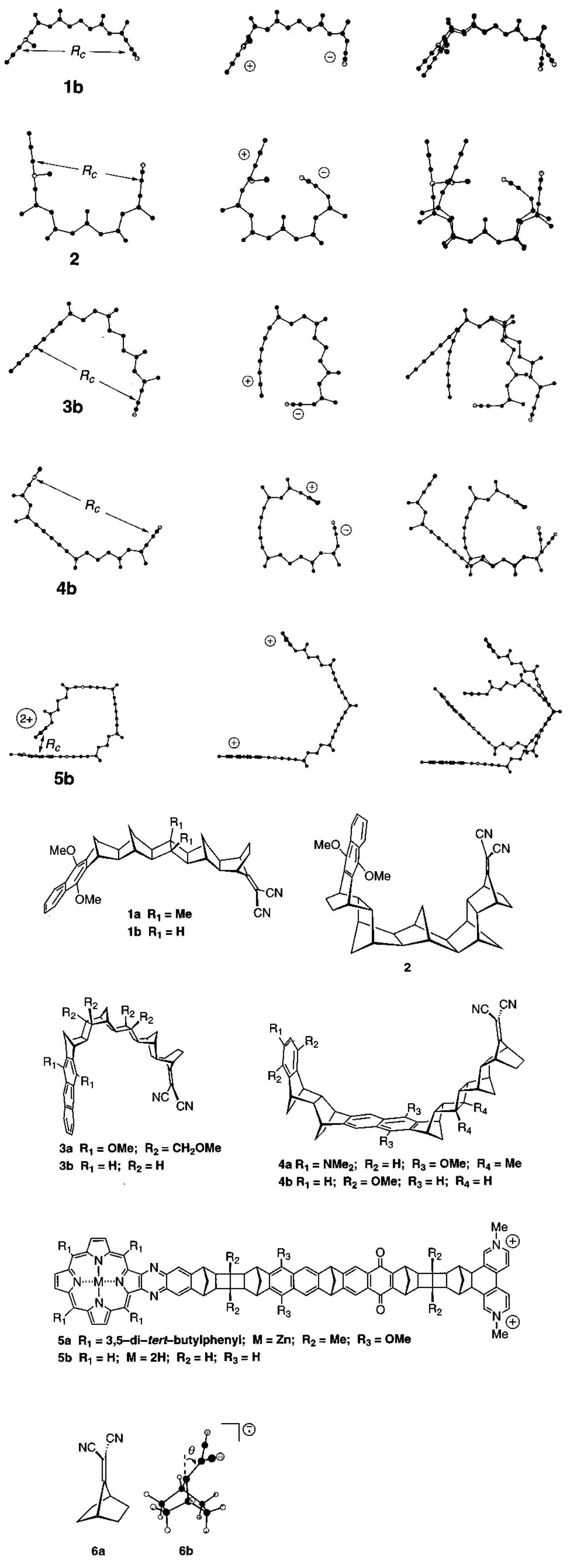

Figure 1. Profiles of (U)HF/3-21G optimized structures for **1b**−**5b** and their giant CS states. The third column shows the superposition of the structures of the ground and CS states.

TABLE 1: Center-to-Center Interchromophore Distances, R_c (Å), and Edge-to-Edge Distances, R_e (Å), of the Bridge for the Ground and Charge-Separated Species of 1b−5b

	1b		2		3b		4b		5b	
	ground	CS	ground	CS	ground	CS	ground	CS	ground	CS
R_c	13.92	12.77	9.54	5.66	12.23	6.22	15.83	5.38	4.13	21.72
R_e	11.78	11.67	9.06	7.66	11.09	9.28				

The extent of structural distortion experienced by a CS system depends on the stiffness of the charged chromophores, the stiffness of the connecting bridge, and the relative orientation of the two chromophores. The latter two factors explain why comparatively little distortion accompanies charge separation in **1b**. In this molecule, the DCV and DMN groups are pointing away from each other. In the optimized CS state, R_c is 12.7 Å. Reducing this distance by 2.4 Å leads to a gain in electrostatic stabilization of only ca. 6 kcal/mol. However, even this modest distortion is not energetically feasible because it would require a massive 62° pyramidalization of the pair of norbornene carbon atoms that are fused to the naphthalene ring.

The sizable calculated changes in R_c which accompany charge separation in **2**−**5b** in the gas phase are consistent with some puzzling experimental findings from solution-phase photoinduced charge separation studies on these systems, illustrative of which are the following two examples.

(1) A charge-transfer fluorescence band is observed to accompany charge recombination (CR) in the giant CS state of **4a**, $^{+}$DMA−DMN−DCV^{-} in nonpolar solvents.[15] This observation of a radiative decay channel for the CR process implies strong electronic coupling (>50 cm^{-1})[15b] between the terminal DMA and DCV chromophores in $^{+}$DMA−DMN−DCV^{-}. A through-bond mediated CR process is unlikely.[16] A solvent-mediated CR mechanism is also difficult to accept if R_c in $^{+}$DMA−DMN−DCV^{-} is the same as that in the ground state (16 Å), since too many solvent molecules would be required to mediate the CR process. However, the calculated small R_c value of ca. 5 Å for $^{+}$DMA−DMN−DCV^{-} would permit CR to proceed efficiently, by either a through-solvent or through-space mechanism.

(2) Although photoinduced charge-separation in **5a**, to form the giant CS state $^{+}$P−DMN−NQ−MV^{+} occurs rapidly, the subsequent CR process is some *3 orders of magnitude slower* than the charge separation process.[5g] This observation is readily explained in terms of the calculated geometry changes which accompany the charge separation process. In the reactant state, R_c is small enough (ca. 4 Å) to permit strong through-solvent or through-space electronic coupling between the terminal chromophores, whereas for the CS state, in which R_c is much larger (ca. 22 Å), this coupling is obviously greatly diminished.

Further evidence in support of the qualitative findings from our calculations comes from the observation of rapid photoinduced ET ($>10^9$ s^{-1}) in **5a** (CH_3CN solvent).[5g] The only reasonable explanation for this result is charge separation taking place directly (through solvent) between the P and MV^{2+} groups which are in electrostatically induced propinquity ($R_c < 8$ Å; vide supra).

Our calculations refer to the gas phase, whereas the experimental ET studies on **1a**−**5a** were carried out in solution. Solvent is expected to attenuate the magnitude of the change in the value of R_c which accompanies charge separation in **1b**−**5b**, and this attenuation should strengthen with increasing solvent polarity. Nevertheless, the experimental results discussed above for **4a** and **5a** suggest that our gas-phase calculations are reflecting (but exaggerating) the geometry changes that accompany charge separation processes in solution. Geometry optimizations on the CS states of **1b**−**5b** using solvent continuum models are currently underway.

Assuming that the UHF/3-21G optimized geometries for the CS states of **1b**−**5b**, are reliable,[8b,17] then the following important conclusions may be drawn:

(1) The large calculated geometry changes in the CS states of **2**−**5b** stem mainly from out-of-plane bending of the charged DCV and aromatic groups in these molecules, driven by Coulombic interactions. However, bending of the putative ”rigid” hydrocarbon bridges may also be a significant contributor to the overall structural distortion suffered by the CS state (e.g., **2** and **4b**). The distortion is particularly marked in those CS systems possessing one or more aromatic rings embedded within the “rigid” bridge (e.g., **4b** and **5b**); this is the result of the combination of a fairly soft out-of-plane bending potential for aromatic rings, and a strong leverage effect exerted by the charged chromophores attached to the ends of the long hydrocarbon “wings”.

(2) Using supposedly rigid U-shaped systems, such as **2**−**5b** to study solvent-mediated charge separation processes may give ambiguous results because the cavity dimensions in the reactant and CS state of these systems are substantially different. This problem should be most acute for low polarity solvents. *One way to circumvent the problem is to study charge-shift ET processes instead of CS processes, since changes in Coulombic interactions are minimal in the former.*

(3) Geometry changes accompanying charge separation or CR processes, on the scale predicted here, will influence the interpretation of rate data using semiclassical ET theories in the following ways: (*a*) The geometry changes will be associated with one or more low-frequency skeletal breathing modes which should be incorporated into the semiclassical treatment, either explicitly, by using a multi-quantized mode model, or through adjustment of the low-frequency solvent reorganization energy term.[5e] (*b*) Both solvent reorganization energy and driving force terms are strongly dependent on the interchromophore separation, R_c, the former decreasing (increasing) and the latter increasing (decreasing) with decreasing (increasing) R_c. The seriousness of this problem depends on both solvent properties (such as polarity) and the degree to which the transition structure geometry for charge separation resembles that of the CS product. We are investigating this problem by locating the transition structures for charge separation in **1b**−**5b**.

(4) The predicted geometry changes that accompany charge separation in **1b**−**5** are further examples of the harpooning mechanism[18a,b] which is known to occur in flexible systems.[18c] Our results suggest that harpooning might be more widespread in charge separation processes than previously thought.[19]

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Supporting Information Available: Calculated energies and Cartesian coordinates of the optimized geometries for all molecules described in the manuscript. This material is available free of charge on the Internet at http://pubs.acs.org.

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(8) (a) The omission of electron correlation is serious. Also, the $<S^2>$ values for the CS states of **1b**−**5b** are too large, viz., 1.07−1.18 for the singlet CS states of **1b**−**4b**, and 3.6 for the triplet CS state of **5b**. (b) For example, geometry optimization of the CS state of a shorter analogue of **1b** using the configuration interaction singles method (CIS/3-21G) gave essentially the same geometry as that using the UHF/3-21G method (see data on structure **12** in the Supporting Information). (c) The CS states were identified from inspection of the Mulliken populations and natural orbital populations associated with the chromophores.

(9) It is reasonable to assume that, since both A′ singlet and triplet giant CS states of **5b** have the same electronic configuration and are nearly degenerate, they should possess very similar geometries.

(10) See Supporting Information.

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(12) DMN = dimethoxynaphthalene; DMA = dimethylaniline; A = anthracene; DMB = dimethoxybenzene; N = naphthalene; NQ = naphthoquinone; P = porphyrin; MV^{2+} = viologen dication.

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(16) There are too many bonds between the terminal chromophores in **4a** for a through-bond mediated electronic coupling mechanism to be significant.

(17) This point will be checked by carrying out CIS calculations on smaller analogues of **2b** and **3b**. However, replacing the P^+ and MV^+ groups in the CS state of **5b** with pyridinium groups and optimizing the ground-state geometry of the resulting molecule gave an R_c value of 20.8 Å, which is nearly the same as that calculated for the giant CS triplet state of **5b**. This finding reinforces our confidence that the UHF/3-21G calculated geometries of the CS states are reliable.

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(19) Only one stable geometry has been located for the CS state for each of the molecules **1b**−**5b**. Thus, the charge separation process in these molecules is envisaged to take place by a concerted mechanism, without proceeding via an intermediate CS state possessing a geometry resembling that of reactant.