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Electrostatically Driven Geometry Changes Accompanying Charge Separation in Supposedly Rigid Bichromophoric Systems

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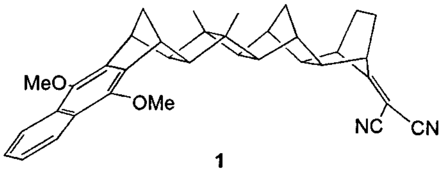
Calculations on the structures of a variety of charge-separated (CS) bichromophoric systems in the gas phase were carried out at the UHF, CIS, and UB3LYP theoretical levels, using the 3-21G, 6-31G(d), and 6-31+G-(d) basis sets. The results indicate that the relatively computationally inexpensive UHF/3-21G method gives a reliable description of the molecular structure and charge distribution in these states. It is predicted that the CS states of most of the bichromophoric systems studied will undergo strong structural distortions due to the Coulombic forces operating between the two charged chromophores. These structural distortions are largely associated with changes in the geometries of the charged chromophores, although the putative "rigid" saturated hydrocarbon bridges connecting the chromophores can also undergo some distortion. In the case of **8b**, the distorted CS geometry predicted by these calculations is consistent with results obtained from recent experimental charge recombination studies on the CS state of the similar system, **8a**. Geometry changes accompanying charge separation or charge recombination processes, on the scale predicted here, might influence the interpretation of rate data based on semiclassical ET theories.

Introduction

In the exploration of long-range electron transfer (ET) processes, molecules in which the donor and acceptor chromophores are connected by a rigid saturated hydrocarbon bridge are playing a central role in the investigation of the distance and orientation dependence of the rate of ET.[1−14] In general, analysis of ET rate data from such systems is carried out within the context of Marcus theory.[15] A simplifying assumption normally used in this type of analysis is that both the chromophore orientation and separation remain unchanged on going from the reactant to the product states. Using this assumption, the important parameters of Marcus theory, namely the driving force, the electronic coupling element, and the internal and solvent reorganization energies for both the forward and the reverse ET processes, are the same and are analyzed in terms of the reactant geometry. While this assumption might be reasonable for *charge-shift* ET processes,[16,17] its validity is far less certain for charge separation reactions, in which the geometry of the dipolar charge-separated (CS) state might be strongly influenced by large electrostatic forces operating between the charged chromophores.

Indeed, electrostatically driven conformational changes have been observed for photoinduced charge separation processes in dyads possessing *semiflexible* (piperidine) bridges in both the gas phase and solution.[18−20] In these systems, the initially generated CS state undergoes an electrostatically driven conformational change of the piperidine ring, from a chair to a boatlike folded conformation, thereby bringing the two oppositely charged chromophores into closer proximity.

While significant electrostatically induced conformational changes might be expected to occur in semiflexible systems, it is assumed, quite reasonably, that they will not occur in systems possessing rigid bridges, such as the norbornylogous bridge which is present in **1**.[8]



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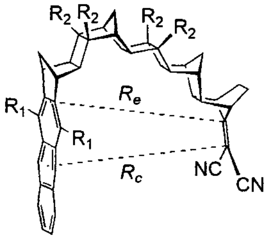
In apparent contradiction of this premise, the results of a recent preliminary ab initio Hartree−Fock study of experimentally relevant charge separation processes occurring in several multichromophoric systems possessing rigid bridges predict that severe structural distortion may accompany charge separation, at least in the gas phase and, presumably, in low polarity solvents as well.[21] For example, the calculated relaxed (gas phase) geometry for the CS state of **2b**, possessing anthracene radical cation and dicyanovinyl (DCV) radical anion chromophores fused to a norbornylogous bridge, differs significantly from that of the ground state (Figure 1a). The center-to-center distance, R_c, between the two chromophores is only 6.2 Å in the CS state, compared to 12.2 Å in the ground state (vide infra).



2a R_1 = OMe; R_2 = CH_2OMe
2b R_1 = H; R_2 = H

Two issues arising from that study on the gas phase structures of CS states[21] will be examined in this paper; a third issue, dealing with the effect of solvation on the structures of CS states, is currently the subject of ongoing analysis. First, the

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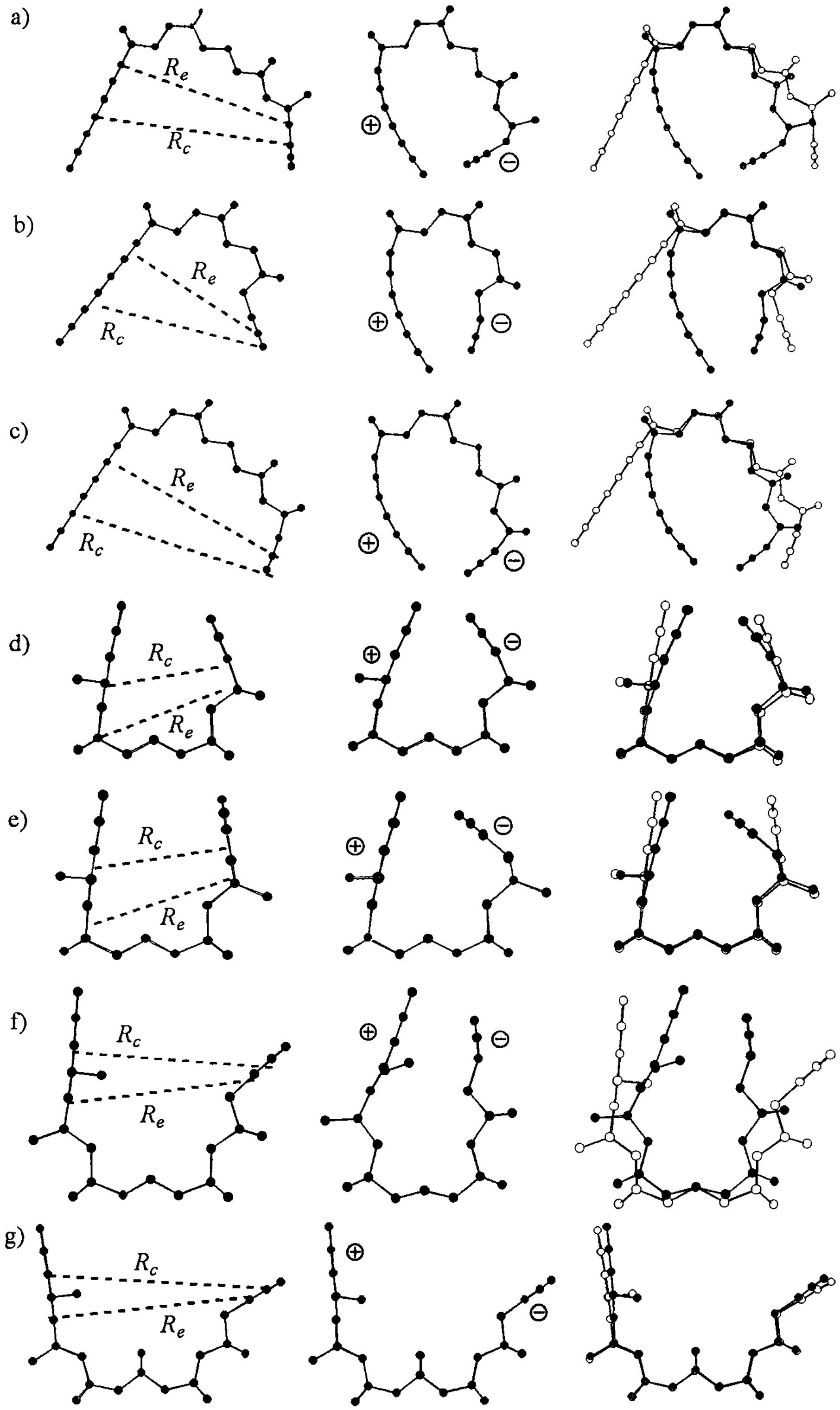
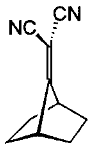


Figure 1. Profiles of the optimized geometries of the ground (RHF/3-21G level) and CS (UHF/3-21G level) states obtained for **2b**−**11**: (a and e) the ground and A″ singlet CS states for **2b** and **9b**, respectively; (b, c, d, f, and g) the ground and A′ triplet CS states obtained for **6b**, **7**, **8**, **10**, and **11**, respectively. The third column shows the superposition of the structures of the ground (white) and CS (black) states.

7-dicyanovinylnorbornane (DCV) group, **3**, was used as the acceptor chromophore in all but one of the systems examined.



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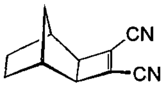

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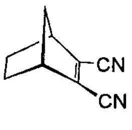

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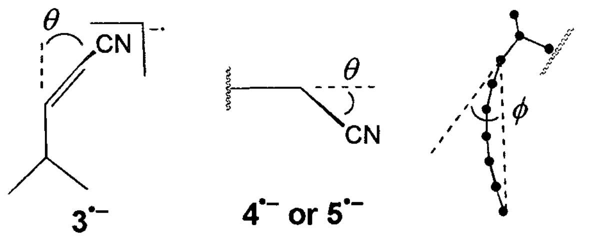
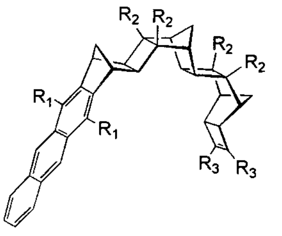
However, the radical anion of **3** displays substantial intrinsic pyramidalization at C7 ($\theta = 37°$ at the UHF/3-21G level; see Scheme 1) which is also exhibited in the CS states of systems possessing this chromophore (e.g., Figure 1a). This intrinsic trait of the DCV radical anion is a major contributor to the overall distortion found for the CS states of such systems. Although it was found that the bridge and donor chromophore also suffered distortions in these CS systems, as may be clearly seen in Figure 1, it is important to determine whether these distortions are

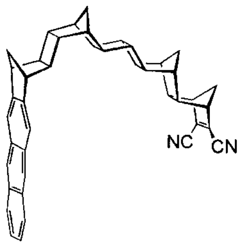
SCHEME 1





6a R_1 = OMe; R_2 = CH_2OMe; R_3 = CO_2Me

6b R_1 = H; R_2 = H; R_3 = CN



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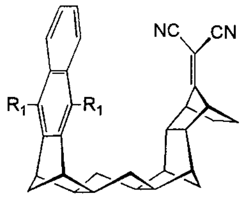
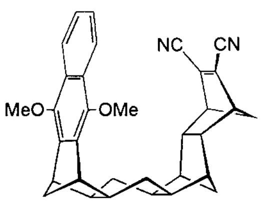


8a R_1 = Ph

8b R_1 = OMe



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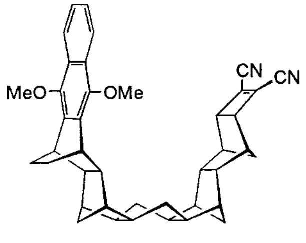
induced by the proximate pyramidalized DCV radical anion or whether they may also occur in the CS states of systems possessing acceptor groups whose radical anions are not intrinsically pyramidalized. This issue has now been addressed by carrying out UHF/3-21G calculations on the CS states of systems **6b**, **7,** and **9**−**11** in which the acceptor is either 1,2-dicyanocyclobutene (DCC), **4**, or 1,2-dicyanonorbornene (DCN), **5**. While both DCC and DCN acceptors have similar redox properties to the DCV acceptor, **3**, UHF/3-21G level calculations show that the radical anions of **4** and **5** are essentially planar about the double bond. The calculated relaxed structures of the CS states of **6b** and **9** will be compared with those of **2b** and **8b** which possess the DCV acceptor.



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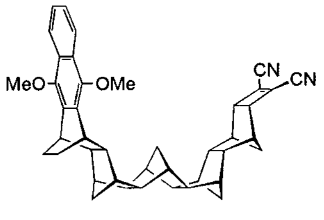

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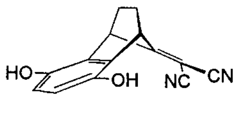

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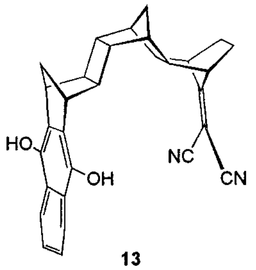

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The second issue concerns the reliability of the UHF/3-21G theoretical model, which was used in our initial study, to calculate the geometries of the CS states. Because of the large sizes of the molecules used in that study, we were limited to using single configuration noncorrelated SCF wave functions. An important requirement of any theoretical model that is used for investigating electrostatically induced changes in molecular geometry is that it should give an accurate description of the charge distribution in the charge-separated state of the molecule. Our use of the UHF/3-21G theoretical model for such investigations is questionable on two counts.

First, the 3-21G basis set[22] is too compact and the omission of polarization basis functions and, possibly, diffuse basis functions might lead to distorted charge distributions. Second, the lack of electron correlation in the HF method could lead to a poor description of the wave function and hence to innacurate charge distributions. These problems have now been investigated by carrying out more extensive calculations on charge-separated states of a selection of molecules, namely **2b**, **12**, and **13**, using more extended basis sets and including varying degrees of electron correlation with the CIS[23] and DFT (B3LYP)[24,25] methods.[26]

Computational Details

Geometry optimizations on all systems were carried out under C_s symmetry constraint, which is certainly valid for the ground states, but which is assumed to be a reasonable constraint for the CS states of **2b** and **6b**−**13**. There is an incentive to enforcing C_s symmetry on the geometries of the CS states of these dyads beyond that of computational economy: the singlet CS states for systems **2b**, **8b**, **12**, and **13** possess A″ state symmetry which therefore enables their calculation by UHF and DFT techniques—provided the CS state is the lowest energy state possessing this symmetry (vide infra). In contrast, the singlet CS states for **6b**, **7**, and **9**−**11** which possess the 1,2-dicyanoethene moiety, have A′ state symmetry and, therefore, it was not possible to examine the singlet CS state using UHF and DFT methods. However, the lowest energy UHF/3-21G A′ triplet states calculated for **6b**, **7**, and **9**−**11** are charge separated; consequently, relaxed triplet CS geometries for these molecules could be obtained at the UHF level. Given the comparatively large donor−acceptor separations in **6b**, **7**, and **9**−**11**, it is likely that the triplet and singlet CS states in each of these molecules will have similar relaxed geometries.[27] Geometry optimizations were, therefore, carried out on the A′ ground states of **2b** and **6b**−**13**, at the RHF/3-21G level (=HF/3-21G), and on the A″ singlet CS states of **2b**, **8b**, **12**, and **13**, and the A′ triplet CS states of **6b**, **7**, and **9**−**11**, at the UHF/3-21G level.

In order to check the sensitivity of molecular geometry and charge distribution to electron correlation and the basis set size, geometry optimizations of the A′ ground states and the A″ singlet CS states of **2b**, **12**, and **13** were carried out using DFT, CIS,[23] and MP2 methods and the 3-21G and 6-31G(d)[28−30] basis sets and, in the case of **12**, the 6-31+G(d) basis set[28,29,31,32] as well. All DFT calculations were carried out using B3LYP level of theory.[24,25,33,34] In the case of **2b**, the CS state could not be located using the B3LYP method; the converged A″ singlet state found using this method corresponds to local excitation of the dimethoxynaphthalene (DMN) chromophore. All calculations pertain to gas-phase structures. Attempts to study solvent effects on the geometries of the CS states of the dyads described here have so far met with failure. We were unable to achieve SCF convergence for our systems using a variety of solvation

TABLE 1: Selected Data for the Ground and CS States of 2b, and 6b−11 Obtained from Geometry Optimizations at the (U)HF/3-21G Level

system	state	R_c[a] (Å)	R_e[b] (Å)	θ[c] (deg)	ϕ[d] (deg)	μ (D)	charge donor	charge acceptor
2b	^{1}A′ ground	12.23	11.09		0.5	7.83	0.049	−0.190
	^{1}A″ CS	6.22	9.28	38.2	33.1	19.23	0.897	−0.762
6b	^{1}A′ ground	9.54	7.91	−2.7	0.5	7.03	0.053	−0.209
	^{3}A″ CS	4.71	6.56	19.2	38.5	15.31	0.899	−0.849
7	^{1}A′ ground	11.77	11.07	5.6	0.5	20.59	0.050	−0.132
	^{3}A″ CS	6.28	9.15	16.7	38.2	7.90	0.869	−0.752
8b	^{1}A′ ground	5.73	6.45		3.6	17.90	0.018	−0.194
	^{1}A″ CS	4.37	6.29	36.9	8.4	7.50	0.807	−0.741
9	^{1}A′ ground	5.07	6.25	5.0	5.2	6.49	0.019	−0.135
	^{3}A″ CS	4.16	5.96	13.6	12.5	18.42	0.810	−0.776
10	^{1}A′ ground	8.84	8.37	−2.0	−3.0	6.25	−0.006	−0.230
	^{3}A″ CS	3.77	5.09	20.9	−2.4	12.9	0.791	−0.838
11	^{1}A′ ground	11.39	10.21	−1.9	−3.0	4.83	−0.006	−0.231
	^{3}A″ CS	10.81	9.91	0.8	−3.0	43.71	0.778	−0.847

[a] The center-to-center separation between the chromophores (see Figure 1). [b] The bridge edge-to-edge separation (see Figure 1). [c] The degree of pyramidalization of the DCV group or the degree of folding of the 1,2-dicyanoethene group (see Scheme 1). [d] The degree of out-of-plane bending of the donor group (see Scheme 1).

continuum models.[35−37] All calculations were carried out using the Gaussian 94[38] and Gaussian 98[39] suite of programs.

Results and Discussion

Effects of Modification of the Acceptor on the Geometries of CS States. Dyads **2b** and **6b**−**11** comprise a donor (anthracene or naphthalene) and an acceptor (DCC, DCV, or DCN) which are fused to a rigid norbornylogous bridge with bridge lengths ranging from 8 to 11 bonds. The U-shaped curvature of these systems makes them attractive systems for investigating photoinduced charge separation by solvent-mediated superexchange coupling mechanisms. In fact, **2a**, **6a**, and **8a** are being experimentally studied for such purposes.[11,40−42] Clearly, the size of the cavity between the donor and the acceptor, measured by the center-to-center interchromophore separation, R_c (see **2** and Figure 1 for the definition of R_c), will markedly influence the efficacy of the solvent-mediated electronic coupling processes and it is therefore important to ascertain whether the cavity size in these systems changes upon charge separation.

Relevant structural data from the (U)HF/3-21G optimized gas phase geometries of the ground and CS states of **2b**, **6b**, and **7** are summarized in Table 1, and profiles of the structures are shown in Figure 1. As reported previously,[21] the anthracene−DCV system **2b** is predicted to undergo a dramatic structural distortion upon conversion from the ground state to the A″ CS state, the most notable consequence being the 6 Å contraction in the value of R_c, from 12.2 Å in the ground state to only 6.2 Å in the CS state. This contraction is due not only to the expected 38° pyramidalization of the DCV radical anion group but also to a large out-of-plane bending of the anthracene radical cation ($\phi = 33°$, see Scheme 1) and, to a lesser extent, some distortion of the putatively rigid norbornylogous bridge. These distortions are clearly seen in the superposition of the profiles of the geometries of the ground and CS states of **2b** (Figure 1a). The cavity size of **2b** is therefore significantly smaller in the CS state than it is in the ground state.

To what extent this type of distortion of the CS state of **2b** occurs in solution is a moot point (however, see below), although one may confidently predict that it will be most significant in nonpolar solvents, such as hexane, and progressively less so in solvents of increasing polarity. Photoinduced charge separation studies carried out on **2a** in polar aromatic solvents, such as benzonitrile, indicated that solvent-mediated ET was occurring. The results of these investigations were analyzed with the tacit assumption that the ground and CS state geometries of **2a** are identical.[11,40] This may be a valid assumption for the forward charge separation process in polar solvents, but it might well break down for the subsequent charge recombination (CR) process, or even for photoinduced charge separation in weakly polar solvents. However, due to the nature of the chromophores, dyad **2a** is not suitable for investigating these caveats.

The 11-bond dyad **7** is structurally similar to **2b** with the result that both have comparable ground state R_c values of 11.8 and 12.2 Å, respectively. Dyad **7** differs from **2b** in that it is endowed with the DCN acceptor. As expected for norbornene double bonds,[43] this group shows weak endo pyramidalization of about 5.6°. Remarkably, the triplet A″ CS state of **7** is predicted to suffer the same degree of collapse of the cavity as predicted for the corresponding CS state of **2b**—the R_c values are 6.3 and 6.2 Å, respectively—even though the pyramidalization of the DCN radical anion is increased by only 11°, relative to the neutral species. In both **7** and **2b**, the bridge undergoes the same degree of distortion, upon conversion from the ground state to the CS state, as measured by the calculated 1.9 Å decrease in the edge-to-edge distance, R_e, between the two ends of the bridge (see **2** and Figure 1 for the definition of R_e). However, the magnitude of the out-of-plane bending angle, ϕ, of the anthracene radical cation (see Scheme 1) in the CS state is greater in **7** than it is in **2b**, by 5°.

Solvent-mediated charge separation using the dyad **6a** has recently been investigated.[44] Unlike the case of **2a**, the driving force for charge separation from the locally excited state of **6a** is sufficiently large to be studies in low dielectric alkylbenzene solvents. We have explored the structure of the CS state for this dyad using the similar, but computationally more tractable molecule **6b**, in which the cyclobutene dicarboxylate ester acceptor in **6a** has been replace by the DCC group in **6b** and the methoxy groups have been omitted from the bridge of **6b**. As in the case of **2b** and **7**, the triplet A″ CS state of **6b** shows severe diminution in the size of the cavity, with R_c decreasing from 9.5 Å, in the ground state, to only 4.7 Å in the CS state. The bridge undergoes a contraction of 1.4 Å in the process (as measured by the difference in the R_e values for the ground and CS states). The small R_c value predicted for the gas phase CS state of **6b** is due to a combination of an out-of-plane bending of the anthracene radical cation ($\phi = 38.4°$), and pyramidalization of the DCC radical anion ($\theta = 20°$), as shown in Figure 1b. In their paper on the photophysics of **6a**, Zimmt and Waldeck state that they found no particular evidence supporting any large structural changes occurring in **6a** in the charge separation process in alkylbenzene solvents,[44] although we feel that the negative evidence is not decisive.

The 8-bond dyads **8b** and **9** also display cavity contraction in their CS states, the respective R_c values diminishing by 18% and 24%, compared to their ground-state structures. This change might not seem significant at first sight but the R_c values for the ground states of these systems are small (<6 Å) and, bearing in mind the inverse dependence on R_c of both the Coulombic contribution to the driving force, $-\Delta G$, and the solvent reorganization energy, λ_s, for CS and CR processes, an 18−24% decrease in the value of R_c should have a marked effect on the magnitudes of $-\Delta G$ and λ_s.

The major structural change in the CS state of **8b** is the 37° pyramidalization associated with the DCV radical anion; there is little out-of-plane bending of the naphthalene radical cation ($\phi = 8°$) and the geometry of the centrally located cyclohexane ring in the bridge is the same in the CS state as in the ground state. In fact, from the R_e values, the entire bridge in **8b** suffers little distortion upon charge separation, contracting by only 0.2 Å. The smaller degree of structural distortions of the bridge and DMN radical cation in **8b**, compared to those calculated for the CS states of **2b**, **6b**, and **7**, is probably due to the DCV and DMN chromophores achieving their optimal separation in the CS state without requiring significant structural change. The closest distance between the nitrogen atoms of the DCV radical anion group and the carbon atoms of the DMN ring is only 3 Å, which is close to the sum of the van der Waals radii of carbon and nitrogen (2.8 Å). This optimal separation is mainly achieved through the intrinsic pyramidalization of the DCV radical anion without having to resort to energetically more costly distortions of the DMN and the bridge.

Similar arguments obtain for the CS state of **9**, although the degree of pyramidalization of the DCN radical anion group (14°) is less than that calculated for the DCV radical anion moiety of **8b** (37°), reflecting the intrinsic tendency for the former group to be essentially planar.

The 11-bond dyads **10** and **11** are very similar, except that the central bridge unit is a cyclohexane ring in the case of **10**, and a norbornane unit in the case of **11**. The R_c values in the ground states of **10** and **11** are 8.8 and 11.4 Å, respectively, and are significantly greater than those for the ground states of **8b** and **9** (5.7 and 5.1 Å, respectively). Consequently, in their CS states, more substantial distortion of the structures of **10** and **11** is required, than for **8b** and **9**, to bring the oppositely charged chromophores into optimal separation. A sizable distortion is calculated to occur in the CS state of **10**, resulting in a 57% contraction in R_c, to a value of 5.1 Å (Table 1 and Figure 1f). In this structure the closest distance between the nitrogen atoms of the DCC radical anion group and the carbon atoms of the DMN ring is 3.5 Å. The main source of this distortion is a flattening of the central cyclohexane ring, with its flap angle increasing from 122° to 152° (in the case of **8b** and **9**, the corresponding change in this angle is less than 3°). However, this mode of distortion is thwarted in the CS state of **11**, due to the replacement of the comparatively flexible cyclohexane ring with a rigid norbornane unit. Consequently, charge separation in **11** leads to negligible change in cavity size (Figure 1g). Thus, R_c decreases by only 0.4 Å, while the flap angle of the central norbornane unit increases by only 0.4°.

The significance of **8b** is that recent photophysical studies by Koeberg, de Groot, and Verhoeven Lokan and ourselves on the structurally related dyad **8a** have confirmed our predicted structure for the CS state of **8b**. Although this work will be presented in full elsewhere,[42] we point out here that the CS state of **8b** was found to display charge transfer (CT) fluorescence in a wide range of solvent polarity. From the solvent dependence of the CT fluorescence maximum, the dipole moment of the CS state of **8a** was estimated to be 20 D, corresponding to an R_c value of 4.2 Å. These data agree well with a predicted dipole moment of 17.9 D (Table 1) and an R_c value of 4.37 Å. Intriguingly, the experimental data imply that the "collapsed" geometry for the CS state of **8b** is independent of solvent polarity, at least within the range of solvents studied (*n*-hexane–acetonitrile).

TABLE 2: Selected Data for the Ground and CS States of 12 Obtained from Geometry Optimizations at Various Theoretical Levels

	R_c (Å)	R_e (Å)	θ^a (deg)	μ (D)	charge	
level					DHB	DCV
			Ground State			
HF/3-21G	4.447	2.194		3.49	0.150	−0.092
HF/6-31G(d)	4.415	2.179		4.98	0.085	−0.187
HF/6-31+G	4.449	2.190		4.80	−0.482	0.912
B3LYP/3-21G	4.479	2.203		4.44	0.270	−0.030
B3LYP/6-31G(d)	4.437	2.178		4.92	0.222	−0.112
			CS State			
HF/3-21G	3.818	2.228	42.8	13.33	0.743	−0.546
HF/6-31G(d)	3.834	2.212	40.7	13.56	0.682	−0.664
HF/6-31+G	3.879	2.220	39.5	13.86	1.064	−0.205
B3LYP/3-21G	3.859	2.238	40.2	12.09	0.757	−0.466
B3LYP/6-31G(d)	3.898	2.217	36.7	12.41	0.730	−0.559
CIS/3-21G	3.809	2.203	36.0	12.41	0.681	−0.489
CIS/6-31G(d)	3.810	2.172	30.8	12.43	0.590	−0.595
CIS/6-31+G	3.874	2.181	29.5	12.33	0.258	−0.449

[a] The degree of pyramidalization of the DCV group, see Scheme 1 for its definition.

TABLE 3: Selected Data for the Ground and CS States of 13 and 2b[a] Obtained from Geometry Optimizations at Various Theoretical Levels

		R_c (Å)	R_e (Å)	θ^b (deg)	μ (D)	charge	
system	level					donor	DCV
				Ground State			
13	HF/3-21G	8.369	6.926		9.33	0.083	−0.189
13	HF/6-31G(d)	8.441	6.968		9.27	0.012	−0.249
13	B3LYP/3-21G	8.356	6.948		8.71	0.173	−0.130
13	B3LYP/6-31G(d)	8.428	6.982		8.79	0.146	−0.161
2b	HF/6-31G(d)	12.392	11.172		8.14	−0.025	−0.253
				CS State			
13	HF/3-21G	4.586	5.885	44.5	6.42	0.682	−0.682
13	HF/6-31G(d)	4.700	5.923	41.4	8.49	0.693	−0.813
13	B3LYP/3-21G	4.456	5.875	43.7	3.06	0.557	−0.457
13	B3LYP/6-31G(d)	4.499	5.856	40.8	6.25	0.645	−0.632
13	CIS/3-21G	4.511	5.792	42.1	7.49	0.701	−0.677
13	CIS/6-31G(d)	4.623	5.840	38.5	9.09	0.669	−0.771
2b	HF/6-31G(d)	6.231	9.222	36.4	19.22	0.840	−0.845
2b	CIS/3-21G	5.788	8.878	34.5	17.66	0.877	−0.708

[a] See Table 1 for the (U)HF/3-21G data obtained for the ground and CS states of **2b**. [b] The degree of pyramidalization of the DCV group; see Scheme 1 for its definition.

This agreement between experiment and theory for the CS state of the **8a/b** system lends credibility to our predicted (gas phase) geometries for the CS states of the other dyads presented here and in our earlier study.[21] The finding that **8a** appears to retain its "collapsed" cavity structure, even in polar solvents, should provide encouragement to carry out further experimental studies of the CS state of **6a** that might lead to the determination of its structure.

How Reliable Is the UHF/3-21G Level in Predicting Geometries of CS States? The adequacy of the (U)HF/3-21G theoretical model in predicting properties of CS states was verified by comparing the geometries and dipole moments for the CS states of **2**, **12**, and **13** calculated at various other levels of theory. Specifically, the effect of the inclusion of d-type polarization functions and diffuse functions on the heavy atoms was investigated using the 6-31G(d) and 6-31+G(d) basis sets.[28−32] The sensitivity of the geometries and charge distributions of the open-shell CS states of **2b**, **12**, and **13** were explored using the CI-singles (CIS) and B3LYP methods. The latter method is particularly interesting since it includes a large degree of the electron correlation energy. The results for **12** are presented in Table 2 and those for **2b** and **13** are presented in Table 3.

1. Ground States. As may be expected, the optimized ground state geometries of **2b**, **12**, and **13**, in particular their R_c and R_e values, are largely insensitive to both the basis set and the

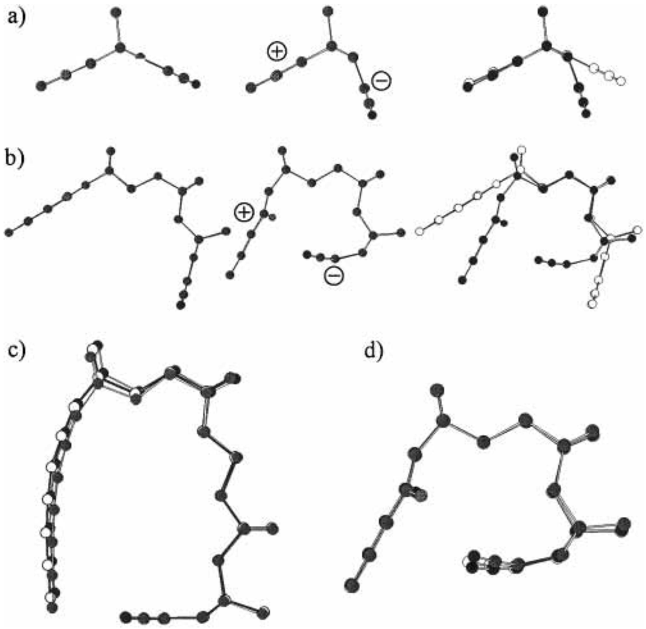

Figure 2. (a and b) Profiles of the optimized geometries of the ground (RHF/3-21G level) and A″ singlet CS (UHF/3-21G level) states obtained for **12** and **13**, respectively. The third column shows the superposition of the structures of the ground (white) and CS (black) states. (c) Superposition of the HF/3-21G (shaded), HF/6-31G(d) (white), and CIS/3-21G (black) optimized CS state geometries of **2b**. (d) Superposition of the HF/3-21G (shaded), B3LYP/6-31G(d) (white), and CIS/6-31G(d) (black) optimized CS state geometries of **13**.

method used (i.e., (R)HF or B3LYP). Even the dipole moments of these species are relatively insensitive to the basis set and method.

2. Charge-Separated States. In the case of the CS state of the 2-bond dyad **12**, the results obtained at the HF/3-21G level are comparable to those obtained using various other basis sets and methods (Table 2). All methods satisfactorily reproduce the sizable pyramidalization at the DCV radical anion (Figure 2a), although the degree of pyramidalization decreases slightly at higher levels of theory and with increasing flexibility of the basis set. While there is some variation in the dipole moment and the total charges on the dihydroxybenzene (DHB) radical cation and the DCV radical anion, all calculations predict a large dipole moment (ca. 13 D) and a high degree of charge separation.

For the 7-bond dihydroxynaphthalene (DHN)-DCV dyad, **13**, there is a ca. 3.8 Å decrease in R_c and a ca. 1.1 Å decrease in R_e in going from the ground to the CS state at all levels of theory (Figure 2b). That the optimized structure of the CS state of **13** is practically the same for all methods studied is clearly revealed from inspection of the superposition of the CS state structures optimized using UHF/3-21G, B3LYP/6-31G(d), and CIS/6-31G(d) levels as shown in Figure 2d. In addition to the expected pyramidalization of the DCV radical anion moiety in the CS state of **13**, significant distortion of the both the bridge and the DHN radical cation group occurs, with the O−H bonds pointing toward the DCV radical anion in an electrostatically stabilizing orientation. This OH-DCV radical anion interaction, together with the close proximity of the two chromophores in the CS state of **13**, is the likely cause of the surprising prediction that the calculated dipole moment for this state is smaller than that calculated for the ground state. The B3LYP/3-21G calculation on the CS state of **13** gives a smaller dipole moment and smaller charges on the chromophores, compared to the other levels; this may be due to a smaller (O)H−N separation (1.46 Å) obtained at this level compared to that obtained for the other levels (>1.78 Å).

In the case of the A″ singlet CS state of the 11-bond dyad **2b**, only the HF/3-21G, HF/6-31G(d), and CIS/3-21G calculations are reported, because the A″ state obtained using the B3LYP method was not a CS state but corresponded to local excitation of the anthracene group. Also, the dyad is too large for a CIS/6-31G(d) level calculation to be feasible. In **2b**, all theoretical levels predict substantial geometrical changes upon formation of the CS state (Figure 1a and Figure 2c), with R_c and R_e decreasing by ca. 6.2 and ca. 2.0 Å, respectively (Table 3). Overall, the UHF/3-21G optimized geometry of the CS state of **2b** is similar to that calculated using the UHF/6-31G(d) and CIS/3-21G methods, as may be seen from the superposition of their structures (Figure 2c). For example, the values of R_c and R_e for the CS state of **2b** at the CIS/3-21G level are each ca. 0.4 Å smaller than the corresponding UHF/3-21G quantities. Unlike the case of **13**, the calculated dipole moment for the CS state of **2b** is substantially larger than the ground state value, by 11.1 D (UHF/3-21G) and 9.5 D (CIS/3-21G).

The nett Mulliken population charges[45] associated with the donor and acceptor chromophores in the ground and CS states for **2b**, **12**, and **13** do not vary significantly with either basis set or theoretical method (see Tables 2 and 3), the exception being the results obtained using the 6-31+G basis set on the ground and CS states of **12**. These anomalous results are due to the presence of the diffuse basis functions.[46] Additional calculations carried out at the HF, B3LYP, and MP2 levels on charged model monochromophoric systems, containing either the DCV radical anion or an aromatic (e.g., anthracene or DHB) radical cation give similar total chromophore charges to those obtained from the CS states of the dyads **2b**, **12**, and **13** at the HF/3-21G level.

In summary, the results from this section indicate that the UHF/3-21G method does give a fairly reliable account of the molecular structure and charge distribution, the results being comparable to those obtained using either the CIS or B3LYP methods with more flexible basis sets.

Conclusions

The following salient conclusions may be drawn from this study.

1. Gas phase calculations carried out on the CS states of the “rigid” dyads **2b**, **12**, and **13** using three different methods, UHF, CIS, and UB3LYP, and basis sets of varying flexibility, 3-21G, 6-31G(d), and 6-31+G(d), indicate that the UHF/3-21G method gives a reasonably reliable description of the molecular structure and charge distribution in these states. This opens up the possibility of exploring giant CS states at reasonable computational cost. A drawback to using a simple UHF wave function in these calculations is that the CS state in question must be the lowest energy state having that particular symmetry. If this is not the case, or in the case where a system does not possess any symmetry, then higher levels of theory must be employed, such as CIS or multiconfigurational methods (e.g., CASSCF, CI, MRCI) or time-dependent DFT[47] methods.

2. It is predicted that CS states of the dyads **2b**, **6b**−**10**, and **13**, possessing supposedly rigid frameworks undergo—at least in the gas phase—strong structural distortions that are caused by the Coulombic forces operating between the two of charged chromophores. This distortion is akin to the harpooning mechanism which has been found to operate in semiflexible systems,[18−20] but differs from it in that only a single, distorted CS structure is predicted for each system studies herein. That

is, we believe that the charge separation process, taking place from the locally excited states of **2b**, **6b**−**10**, and **13**, and the accompanying structural distortion mode are concerted, though not necessarily synchronous processes.

3. The structural distortions found in the CS states of **2b**, **6b**−**10**, and **13** are largely associated with changes in the geometries of the charged chromophores, namely out-of-plane bending of the aromatic radical cation and pyramidalization of the radical anion, although the latter is not a requirement for causing strong distortion in the CS state. For example, the geometries of the CS states of both **2b** (Figure 1a) and **6b** (Figure 1b) are strongly distorted, even though pyramidalization of the DCC radical anion in the CS state of **6b** is not as marked as that for the DCV radical anion in the CS state of **2b**.

4. Even the "rigid" norbornylogous bridge can suffer a degree of, albeit weak, distortion in some of the CS systems investigated, for example, the CS states of **2b** (Figure 1a) and **7** (Figure 1c). More substantial distortion of the bridge may be achieved by the inclusion into the bridge of more flexible components, such as a cyclohexane ring (e.g., **10**, Figure 1f) or by one or more aromatic rings, as noted in our earlier study.[21]

5. Our predictions of large electrostatically induced structural distortions in the CS states of the dyads presented here refer to the gas phase. It is necessary to determine the extent to which such distortions occur in solution because the large majority of charge separation processes are studied in solution. Solvent is expected to attenuate the degree of distortion and this attenuation should strengthen with increasing solvent polarity. Unfortunately, attempts to carry out geometry optimizations on the CS states of the dyads listed in this paper using a variety of solvation continuum models have led to failure for a variety of technical reasons. This problem is still being actively pursued. It is noteworthy that self-consistent reaction field calculations were successfully carried out on the radical anion of **3** and they revealed that the degree of pyramidalization of the DCV group is essentially retained even in high dielectric media.[35,48] Therefore, a substantial contribution to the decrease in interchromophore separation may be retained for DCV-based dyads, even in high polarity solvents.

6. The results of experimental charge recombination studies on the CS state of **8a** in a broad range of solvent polarities are fully consistent with the formation of a distorted geometry similar to that predicted for **8b**. This agreement, together with other supporting experimental evidence,[21] suggests that structural distortions in the CS states of dyads in solution may be a more general occurrence than is presently believed.

7. Geometry changes accompanying charge separation or charge recombination processes, on the scale predicted here, will markedly influence the interpretation of rate data using semiclassical ET theories in the following ways: (a) The predicted 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 multiquantized mode model, or through adjustment of the low frequency solvent reorganization energy term. (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 potential 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. The problem should be particularly marked for charge recombination processes from structurally distorted CS states. For example, the close proximity between the oppositely charged chromophores should give rise to characteristic effects, such as CT fluorescence, as was found for the case of CR occurring from the CS state of **8a**.[41]

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