J. Phys. Chem. A **2005,** *109,* 6799−6804

ARTICLES

Existence of Intramolecular Triplet Excimer of Bis(9-fluorenyl)methane: Phosphorescence and Delayed Fluorescence Spectroscopic and ab Initio Studies

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Received: January 13, 2005

A concerted computational and experimental study has been undertaken to probe the conformational structure and excited-state dynamics of bis(9-fluorenyl)methane (BFM). We have observed that the relative intensity of the delayed excimer fluorescence of BFM is greatly enhanced in comparison with that of the normal fluorescence. This is presumably because the relative concentration of the triplet excimer is enhanced in comparison with the singlet excimer. B3LYP DFT/6-31G(d) calculations indicate that the sandwich conformer of BFM in the singlet ground state is unstable, whereas that in the triplet excited state has a bound state, being very slightly higher in internal and Gibbs free energies than that of the lowest state of the near-orthogonal conformer.

I. Introduction

Diarylalkanes capable of adopting a face-to-face arrangement of the two aromatic rings at an interchromophore separation of ∼3−4 Å are ideal systems in which to probe excimer formation and excimer-dependent photoprocesses.[1,2] Previous work from this laboratory has shown that the resonant two-photon ionization of jet-cooled 1,3-diphenylpropane proceeds very efficiently through the formation and ionization of an intramolecular singlet excimer.[3] Another interesting example of diarylalkanes capable of forming an intramolecular singlet excimer is bis(9-fluorenyl)-methane (BFM), the molecular model of which is shown in Figure 1.

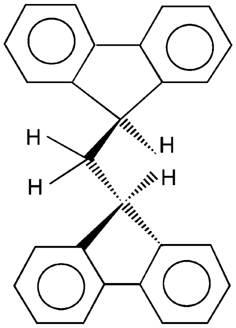

Figure 1. Molecular model of bis(9-fluorenyl)methane.

Boo and co-workers[4] have shown that BFM exhibits weak excimer fluorescence in solution at ambient temperatures. The observation of biexponential decay times of the monomeric fluorescence, and the dual rise times of the excimer fluorescence, led to a conclusion that two conformers of BFM are involved in the two independent excimer formation processes. The faster decaying (rising) component of the monomeric (excimer) fluorescence was attributed to the excimer formation from the trans−gauche conformer, whereas the slower decaying (rising) component of the monomeric (excimer) fluorescence was attributed to the excimer formation from the trans−trans conformer. An Arrhenius plot of the slower excimer formation rate yielded an activation energy of 15.5 kJ/mol.

We have elucidated normal fluorescence and phosphorescence and also delayed fluorescence spectroscopy in the solution phase to explore the extent to which the triplet states are involved in the interconversion of the various conformers. For a detailed understanding of the excited-state dynamics leading to the excimer formation in the singlet and triplet excited states, it is essential to know the ground singlet- (S_0) and triplet-state (T_1) equilibrium conformations of BFM. In this paper, we report the spectroscopic and quantum chemistry studies on BFM, which yield information concerning the conformational structure and the nature of the excited-state conformational changes that are involved in the formation of an intramolecular singlet and triplet excimer.

II. Experimental and Theoretical Methodologies

Ab Initio and DFT Calculations. The ground-state equilibrium geometry of BFM was probed by Kohn−Sham density functional theory (DFT).[5] Becke's three-parameter exchange functional[6,7] and the gradient-corrected Lee−Yang−Parr correlational functional[8] (B3LYP) were used with the 6-31G* basis

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10.1021/jp058019h CCC: $30.25

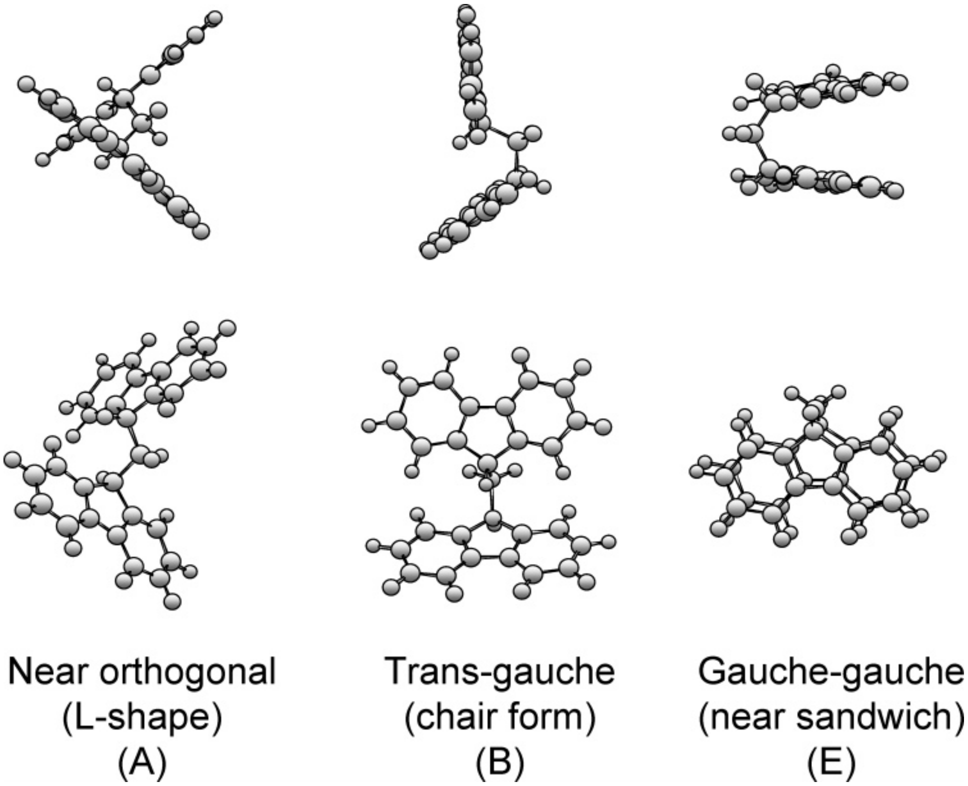


Figure 2. Geometries of three possible ground- and excited-state conformers of bis(9-fluorenyl)methane optimized by the B3LYP DFT/6-31G* method. A and B conformers are optimized in the S_0 and T_1 states. The E conformer is optimized only in the T_1 state, and is assumed to also play an important role in the T_1 and S_1 state.

set. Initial structures for the input file of the DFT calculations were obtained by the PM3 semiempirical calculation.[9] Single point energy calculations at MP2/6-31G level of theory were performed on the B3LYP/6-31G* optimized geometries to compute the relative internal and Gibb free energies of the various low-energy conformers. The zero-point energy corrections were performed on the electronic energy by using the scale factor of 0.963 previously employed for B3LYP/6-31G*.[10] Also, thermal correction to Gibbs free energy at 298 K were carried out how much entropy affects the Gibbs free energy. All calculations were carried out with the Gaussian 98 suite of program[11] on a Cray-T94 at the Ohio Supercomputer Center.

Time-Resolved Fluorescence Measurements. Time-resolved fluorescence measurements were run on a ISA Jobin YVon-SPEX Fluorolog 3-22 fluorometer having dual input and output monochromators. Fluorescence spectra were collected using argon-saturated solutions by exciting at the Soret maxima in S/R mode to correct for changes in the lamp output intensity. We collected the delayed fluorescence signals from BFM excited by 267 nm photons using various delays of 20, 80, and 100 μs and a window of 100 ms.

Bis(9-fluorenyl)methane (BFM) was prepared following a slightly modified procedure of Wowzonek and Dufek.[12] In a 250 mL three-necked round-bottomed flask, equipped with a gas inlet tube and a gas outlet, was placed 5.16 g (31.0 mmol) of fluorene and 30 mL of petroleum ether. A mixture of 37.5 mL of 1.6 M BuLi in hexane (60 mmol) and 20 mL of petroleum ether was added dropwise to the reaction mixture. After stirring at room temperature with N_2 bubbling in for 18 h, the color of the reaction mixture turned orange. 2.02 g (9.41 mmol) of 9-(chloromethyl)fluorene dissolved in petroleum ether was added dropwise to the reaction mixture. The reaction mixture was stirred for 30 h. Unreacted fluorenyllithium and butyllithium were allowed to decompose by reaction with ethanol. Lithium hydroxide was removed by an extraction with water. Excess solvent was removed by a simple distillation. Remaining fluorene and 9-(chloromethyl)fluorene solids were removed by sublimation. The resulting product was recrystallized over acetone to afford 0.37 g (1.1 mmol) of BFM (yield = 12%). The purity was checked by TLC and NMR and identified by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.

III. Results and Discussion

B3LYP DFT calculations predict two low-energy conformers for the S_0 ground and T_1 excited states of BFM, as shown in Figure 2. Conformer A is of “crossed” or “perpendicular” structure (a L-shape) in which the long in-plane axes of the two fluorene moieties are nearly perpendicular, whereas B is a less symmetrical structure of slightly higher energy by 2.4 kJ/mol (MP2 single point calculation in Table 1) in energy with the two long in-plane axes parallel (a chair form). The E conformer is not converged in the S_0-state optimization; however, it is optimized as a stable form in the T_1 state and is assumed to also play an important role in the S_1 and T_1 states. A and B conformers are optimized in the S_0 and T_1 states.

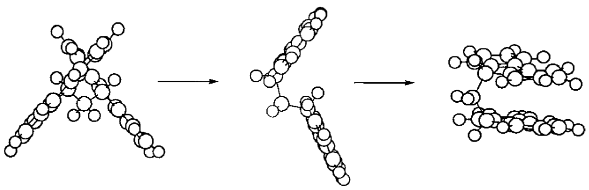
If we consider the entropy effect, the trans−gauche conformer is most stable. But the Gibbs free energy difference between the two structures is very small, indicating that the interconversion between the conformers is almost thermoneutral. However, the face-to-face structure (conformer E) is found to be unstable in the S_0 state. Even when we use the input data having the sandwich structure for the DFT optimization of the face-to-face structure, the optimization process does not lead to a convergence. Also the conversion to one of structures A and B is not achieved presumably owing to the sizable torsional barrier involving the $-CH_2-$fl rotation, where fl denotes a fluorenyl ring.

TABLE 1: Electronic and Zero-Point Energies, Entropy, and Relative Internal and Gibbs Free Energies of Nearly Orthogonal and Trans−Gauche Conformers of the Singlet Ground State of Bis(9-fluorenyl)methane Calculated with Various Levels of Theory at the Geometries Optimized with the B3LYP DFT/6-31G* Method

conformer	electronic energy (hartree)		ZPE (hartree)[a]	thermal correcn to energy at 298.15 K (kJ/mol)[b]	rel energy (kJ/mol) at 298.15 K		entropy at 298.15 K (J/(mol·K))	thermal corrcn to Gibbs free energy at 298.15 K (kJ/mol)[c]	rel Gibbs free energy (kJ/mol) at 298.15 K	
	B3LYP/ 6-31G(d)	MP2/6-31G// B3LYP/ 6-31G(d)	B3LYP/ 6-31G(d)	B3LYP/ 6-31G(d)	B3LYP/ 6-31G(d)	MP2/ 6-31G// B3LYP/ 6-31G(d)	B3LYP/ 6-31G(d)	B3LYP/ 6-31G(d)	B3LYP/ 6-31G(d)	MP2/6-31G// B3LYP/ 6-31G(d)
nearly orthogonal	−1040.954123	−1036.115876	0.386635	51.1	0	0	609.7	−128.2	0	0
trans−gauche	−1040.951038	−1036.114819	0.386480	51.1	7.7	2.4	618.5	−130.8	5.1	−0.2

[a] Scaled by 0.963. [b] Contribution from translational, rotational and vibrational energies except the zero-point energy at 298.15. [c] Contribution from translational, rotational and vibrational energies at 298.15 K except the zero-point energy, and Δ(pV)(=RT) and $-TS_{298.15}$ where T = 298.15 K and $S_{298.15}$ is given in Table 1.

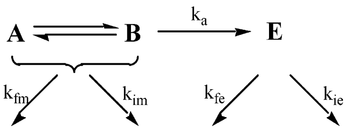
It is theoretically shown that the structures A and B are not distinguishable at the level of theory used. We presume that the conformational change from the excited state of B conformer to the excimer geometry would be favorable as shown below because the direct conversion from conformer B to E requires only a single fl−CH$_2$ rotation, whereas the direct conformational change from conformer A to E would be unfavorable as it should involve cooperative rotational motions around the two fl−CH$_2$ bonds (joining the CH$_2$ carbon atom to the C$_9$ carbon atom of the fluorenyl ring). Note that the cooperational motions indicates a sequential excimer formation involving rotation around one fl−CH$_2$ bond, followed by rotation around the second fl−CH$_2$ bond.



The first rotation induces the conformational change from structure A to structure B, whereas the second yields the face-to-face structure characteristics of the intramolecular singlet excimer. Thus, the excimer formation from the photoexcited A conformer represents a sequential two-step process involving an intermediate B conformer. As the above analyses indicate, we presume that the tg conformer (conformer B) plays an important role in the conversion to the excimer structure and thus in the excimer fluorescence. But it should be noticed that it does not mean that the relative concentration of conformer B is predominant in the solution in comparison with that of conformer A.

The intramolecular excimer formation in covalently linked diaryl compounds requires an intramolecular vibrational energy redistribution (IVR) from the initially excited ring mode of the chromophore into the low-frequency chain and interchromophore vibrations that represent the reaction isomerization coordinate.[1,13] With sufficient accumulation of energy in the reactive modes, the molecule can undergo the activated conformational change from the initial S$_1$ geometry to the face-to-face geometry of the excimer. This will lead to a strong quenching of the fluorescence from the locally excited (LE) state of the molecule without corresponding increase in the intensity of the excimer fluorescence.[1]

The observation of the excimer fluorescence from fluid solutions of BFM at ambient temperature[4] requires lengthy comments. The formation and decay of the intramolecular excimer (E) in solution can be described by the following mechanism:[13]



Here k_{fm} and k_{fe} are rate constants for fluorescence from the excited state of the BFM conformer (A and B), and excimer (E), respectively, k_{im} and k_{ie} are the corresponding rate constants for radiationless transitions, and k_{a} denotes the rate of excimer formation. In this scheme, it is assumed that the excimer is identical to the excited sate of the folded conformer, and that the back dissociation of the excimer to the excited state of conformer B can be neglected. For simplicity, we also assume

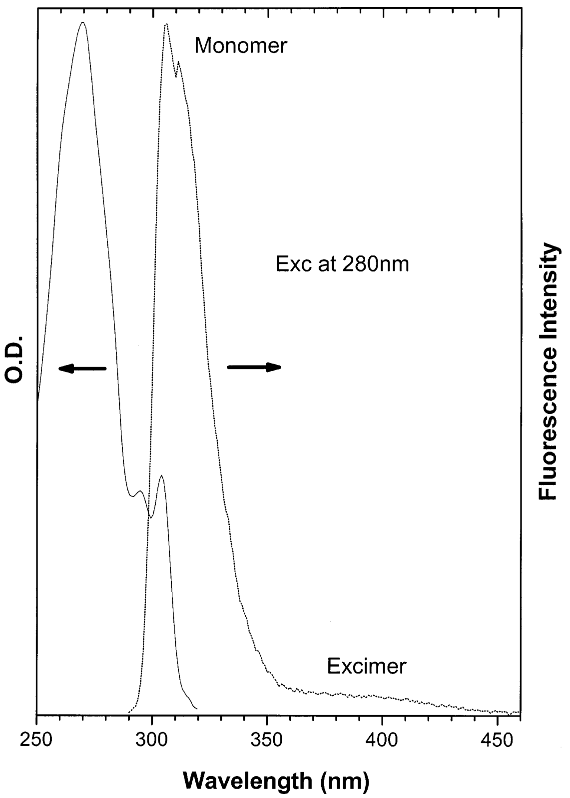


Figure 3. Absorption and fluorescence spectra of bis(9-fluorenyl)methane solutions in cyclohexane (absorption, 9.70 × 10^{-5} M; fluorescence, 4.85 × 10^{-5} M).

that the rate constants for the radiative and nonradiative decays of BFM are independent of the conformation. Because the excimer can form only from conformer B, the solution of the rate equation under photostationary conditions leads to[13]

$$\frac{I_e}{I_m} = f\left(\frac{k_a}{k_{fm}}\right)\left(\frac{k_{fe}}{k_{fe}+k_{ie}}\right) \tag{1}$$

where f is the fraction of the excited state with conformation B. The ratio of the emission intensity I_e/I_m therefore depends on several factors: the rate constant for excimer formation relative to the radiative decay rate of the precursor conformers, k_a/k_{fm}, fraction of the excimer decaying by radiative process, $k_{fe}/(k_{fe} + k_{ie})$, and the fraction of the molecules in the B conformation.

The most noteworthy feature of the emission characteristics of BFM in solution is that excimer fluorescence is very weak relative to dinaphthylpropanes,[13] dipyrenylpropanes,[13] and dibiphenylpropanes[13] that exhibit intramolecular excimer formation. The I_e/I_m ratio is in fact an order of magnitude smaller in BFM than in the diarylpropanes (Figure 3). Because the observed activation energy (15.5 kJ/mol)[4] for excimer formation is very similar to the values (15.5−16.3 kcal/mol)[14] for the diarylpropanes, the unusually weak excimer fluorescence of BFM is very likely due to the small fraction of conformer B which is in equilibrium with conformer A, or due to the large radiative decay rate of the fluorene moiety in BFM. The radiative decay rate of fluorene is at least 1 order of magnitude greater than that of naphthalene or pyrene, and an order of magnitude larger than that of biphenyl.[15] The question of which of these two explanations is more valid cannot be answered without measuring the conformer distribution of BFM in solution by NMR.[16,17]

We measured phosphorescence spectrum of BFM at liquid nitrogen temperature, which is shown in Figure 4. Here we observe two prominent peaks at 427.5 and 458.3 nm. The 427.5 nm is presumed to be 0_0^0 band for the phosphorescence. Note that at liquid nitrogen temperature, the conformational change is hindered owing to the restriction of the fl−CH_2 bond rotation and thus the excimer phosphorescence should contribute very slightly the total phosphorescence intensity.

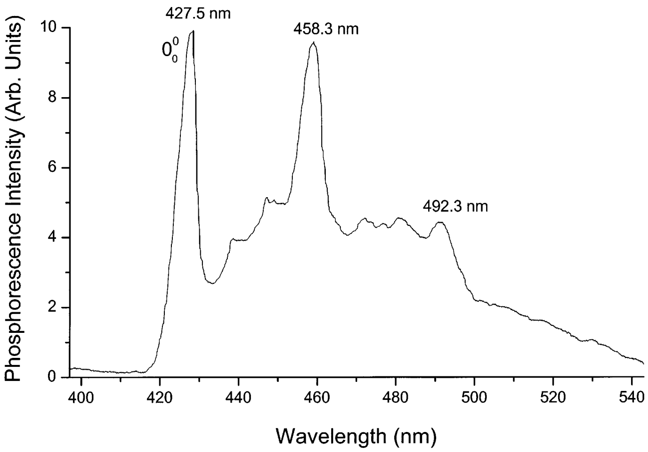


Figure 4. Normal phosphorescence of a 1.3 × 10^{-5} M bis(9-fluorenyl)methane solution in methylcyclohexane at liquid nitrogen temperature. The excitation wavelength is 300 nm.

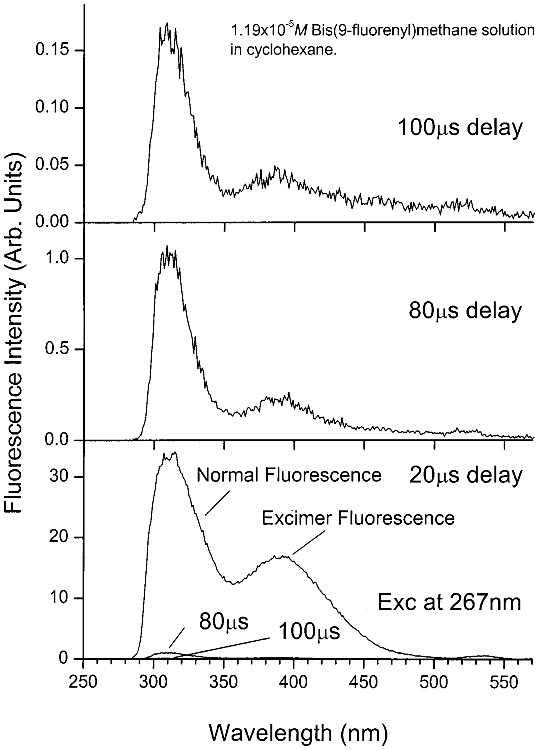


Figure 5. Delayed fluorescence spectra of a 1.19 × 10^{-5} M bis(9-fluorenyl)methane solution in cyclohexane.

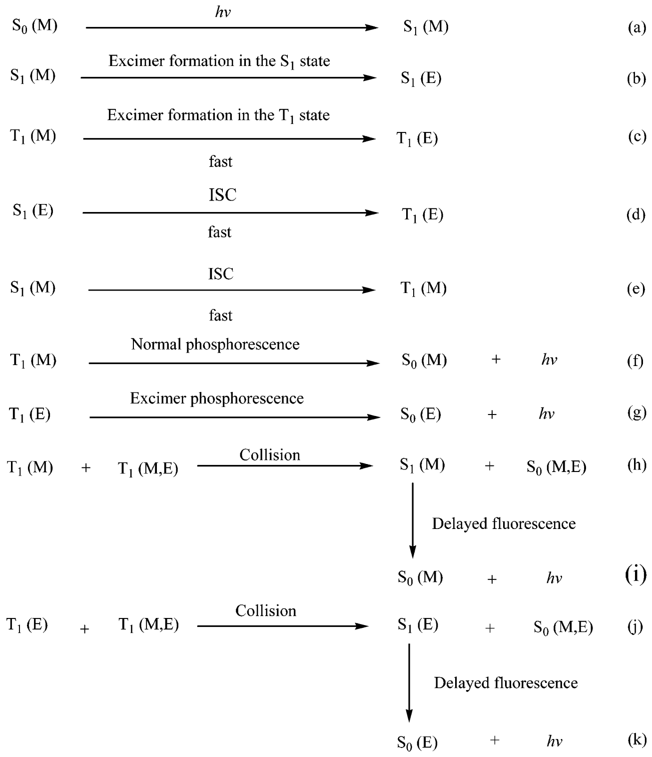
The observation of phosphorescence has prompted us to measure delayed fluorescence at room temperature. As shown in Figure 5, we have observed that the relative intensity of the delayed excimer fluorescence of BFM is greatly enhanced in comparison with that of the normal fluorescence. This is presumably because the relative concentration of the triplet excimer is close to that of the triplet monomer. Note that the triplet excimer can be converted to excited singlet excimer state via collision processes as shown in Scheme 1, in which (d) and (j) processes are assumed to be relatively predominant.

TABLE 2: Electronic and Zero-Point Energies, Entropy and Relative Internal and Gibbs Free Energies of Nearly Orthogonal, Trans−Gauche, and Near Sandwich of Triplet Bis(9-fluorenyl)methane Calculated with Levels of Theory at the Geometries Optimized with the B3LYP DFT/6-31G* Method

conformer	electronic energy (hartree)		ZPE (hartree)[a]	thermal corrcn to energy at 298.15 K (kJ/mol)[b]	rel energy (kJ/mol) at 298.15 K		entropy at 298.15 K (J/(mol·K))	thermal corrcn to Gibbs free energy at 298.15 K (kJ/mol)[c]	rel Gibbs free energy (kJ/mol) at 298.15 K	
	B3LYP/ 6-31G(d)	MP2/6-31G// B3LYP/ 6-31G(d)	HF/4-31G// B3LYP/ 6-31G(d)	HF/4-31G// B3LYP/ 6-31G(d)	B3LYP/ 6-31G(d)	MP2/ 6-31G// B3LYP/ 6-31G(d)	HF/4-31G// B3LYP/ 6-31G(d)	HF/4-31G// B3LYP/ 6-31G(d)	B3LYP/ 6-31G(d)	MP2/6-31G// B3LYP/ 6-31G(d)
nearly orthogonal	−1040.844157	−1035.938332	0.365140	46.0	0	0	570.8	−121.7	0	0
trans−gauche	−1040.841366	-−1035.937611	0.364978	46.0	6.9	1.4	570.3	−121.6	7.0	1.6
near sandwich	−1040.836211	−1035.936609	0.364397	45.8	18.7	2.4	565.7	−120.4	20.2	3.9

[a] Scaled by 0.893. [b] Contribution from translational, rotational and vibrational energies except the zero-point energy at 298.15. [c] Contribution from translational, rotational and vibrational energies at 298.15K except the zero-point energy, and $\Delta(pV)(=RT)$ and $-TS_{298.15}$ where T=298.15K and $S_{298.15}$ is given in Table 2.

SCHEME 1



B3LYP DFT/6-31G(d) calculations were carried out to explore whether the sandwich conformer of BFM in the triplet excited state has a local minimum in the potential energy surface. As expected, conformers A and B are found to be the global and local minima, respectively, in the triplet-state potential energy surface. The structural parameters of the triplet conformers A and B are found to be almost identical with those of the singlet conformers A and B, respectively. The most noteworthy thing is that the face-to-face conformer of BFM in the triplet excited state is found to have a local minimum in the triplet potential energy surface. Single point calculation with the MP2/6-31G//B3LYP/6-31G(d) method show that the near-face-to-face conformer is very slightly higher in internal and Gibbs free energies by only 2.4 and 3.9 kJ/mol, respectively, than the corresponding near-orthogonal conformer. The triplet E conformer is found to have low entropy in comparison with the triplet A and B conformers, indicating that the folded form could involve strain by which the spacing between the two chromophores is widened in the terminal site. The ring repulsion is manifested in conformer E in Figure 2 in which the two other conformers optimized by the B3LYP/6-31G(d) method are also shown. Table 2 compares the internal and Gibbs free energies of three conformers predicted by a combined study involving the DFT and MP2 calculations.

IV. Conclusions

B3LYP DFT calculations predict two low-energy conformers having crossed and perpendicular structures for the S_0 state of BFM. The most noteworthy feature of the emission characteristics of BFM in solution is that excimer fluorescence is very weak relative to dinaphthylpropanes, dipyrenylpropanes, and dibiphenylpropanes that exhibit intramolecular excimer formation. The I_e/I_m ratio is in fact an order of magnitude smaller in BFM than in the diarylpropanes. The relative intensity of the delayed excimer fluorescence of BFM is greatly enhanced in comparison with that of the normal fluorescence. This is presumably because the relative concentration of the triplet excimer is close to that of the triplet monomer. As expected in the theoretical calculation, the face-to-face conformer of BFM in the triplet excited state is found to have a local minimum, being very slightly higher in internal and Gibbs free energy by only 2.4 and 3.9 kJ/mol, respectively, than the corresponding near-orthogonal conformer.

Acknowledgment. This work was supported by a grant from the Office of the Basic Energy Science of the U.S. Department of Energy, in part by a Korea Research Foundation Grant (KRF-2001-041-D00115), and in part by Korea Basic Science Institute. The computational work described herein was made possible by a grant from the Ohio Supercomputer Center.

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