Transient Absorption Spectroscopy of Bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene). Elucidation of Triplet-state Geometry and Triplet-Triplet Absorption

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The cross-conjugated polyenes have been the subjects of researches owing to their intriguing electronic features in the electronically excited[1] and ionized doublet states.[2-5] A previous spectroscopic study shows that the conformation of bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene) (BDCY) in the fundamental state coincides with that of biphenyl (BP) in the first electronically excited state, thereby revealing that the absorption spectrum of BDCY mimics the fluorescence spectrum of BP and *vice versa*.[1] This intriguing spectroscopic behavior is explained by the extent of their extensive π-electron overlap associated with the cross conjugation, to which the angle between the carbocyclic rings is assumed to be achieved.

The molecular structure of BDCY has been studied in the gas phase by means of electron diffraction method,[6] and in crystal by using X-ray diffraction method.[7] In the gas phase, the molecule BDCY was found to have a dihedral angle of 9.7° revealing the slight nonplanarity of the carbocyclic rings.[6] In the crystal, the molecule was found to deviate from planarity to different extents such that the torsional angles about the single and double bonds vary by only 5.1° and 1.2°, respectively.[7] The slight nonplanarity of BDCY molecule, however, is compared with the torsional angle 42° between the two phenyl rings in biphenyl molecule in the gas phase.[8,9] In the solid state, however, the biphenyl molecule is planar,[10-14] indicating that crystal-packing forces can govern the molecular geometry. All six-membered rings are slightly in boat conformations owing to the interactions between the *ortho*-hydrogen atoms across the central double bond.[7]

The main goals of the present study are (1) to directly probe the transient species being formed by the irradiation of the short laser pulse; (2) to clarify the formation and the duration of the excited triplet state, that is to elucidate the decay dynamics by using two types of technologies, one is to measure the time-dependent transient absorption spectra, the other is to measure the decay profiles of some individual transient species in terms of the delay times; (3) to examine the possibility of triplet-triplet absorption by which the transient absorption occurs: (4) to elucidate the electronic and geometrical structures of the ground and excited states with the aid of the DFT and the time-dependent (TD) DFT methods;[15-17] (5) to elucidate the central bond in the cross

conjugation in terms of the density matrix evaluated with the TD DFT calculation; and finally (6) to predict the excitation energies with the aid of the TD DFT methods. We will compare the absorption and the transient absorption spectra with the simulated spectra evaluated with the TD DFT method, by which the electronic state relevant to the electronic absorption can be assigned.

In this work, we present the various spectroscopic and quantum mechanical investigations concerning the static and transient absorptions. We also present the TD DFT calculation results of the geometrical change upon the change of the spin state. Our findings in this work could help to establish the excited-state spectroscopy and dynamics of the cross-conjugated molecules.

Experimental and Theoretical Methodologies

ns Flash photolysis experiment to measure transient absorption spectrum was performed by using a Nd:YAG laser (Spectra-Physics GCR-150), and an intensified CCD (ORIEL INSTASPEC V) and photomultiplier (Hamamatsu 1P28) for multichannel detection of the transient absorption and for temporal measurements of individual transient, respectively.[18] Single-shot triggering was utilized for both detectors by using a pulse generator that triggered a home-built box that received constant Transistor to Transistor Logic (TTL) signals from the flash lamps of the laser. Then, the black box triggered a mechanical shutter placed between an Oriel 150-W Xe-Hg high-pressure arc lamp and the sample chamber, and a Q-switch on the laser. The Q-switch is used to trigger either a Tektronix TDS-640a oscilloscope to measure the traces or a SRS DG-535 pulse generator to trigger the ICCD detector. The detection of the triplet transient absorption required a relatively high concentration of BDCY. In our experiments, an approximately 1.3×10^4 M BDCY solution in cyclohexane was excited with the 355-nm laser pulses.

The ground-state equilibrium geometries and the vibrational frequencies were probed by using the Kohn-Sham DFT.[19] Becke's three-parameter exchange functional[20,21] and the gradient-corrected Lee-Yang-Parr correlational functional (B3LYP)[22] were used with the cc-pVTZ basis sets.[23-26] The

TD DFT method[15-17] was also applied to compute the vertical excitation energies with the B3LYP/cc-pVTZ//B3LYP/cc-pVTZ method at the various optimized S_0 geometries. All calculations were carried out with the Gaussian 09 suite of program.[27]

Results and Discussion

We achieved the molecular model of BDCY in the fundamental state optimized with the B3LYP/cc-pVTZ method under the tight D_{2h} option. No imaginary frequency is found in the frequency calculation, indicating that the structure evaluated in the present study is a global or a local minimum. The planar structure of BDCY having a D_{2h} point group has been predicted in our previous study by using a relatively low-level calculation with the B3LYP/6-31G(d) method.[28] The absorption and fluorescence spectra of a 2.0×10^{-5} M BDCY solution in cyclohexane are shown in Figure 1, in which the fluorescence spectrum of biphenyl turned out to be again a perfect mirror image for the absorption one of BDCY, implying that the splitting pattern for the electronic energy levels of the singlet excited state of BDCY is similar to that of the ground state of BP. The electronic structure seen in the absorption spectrum of BDCY (Fig. 1(a)) disappears in the fluorescence spectrum of BDCY (Fig. 1(c)), revealing that the energy separation occurred in the singlet excited-state BDCY molecule does not occur in the singlet ground-state BDCY molecule.
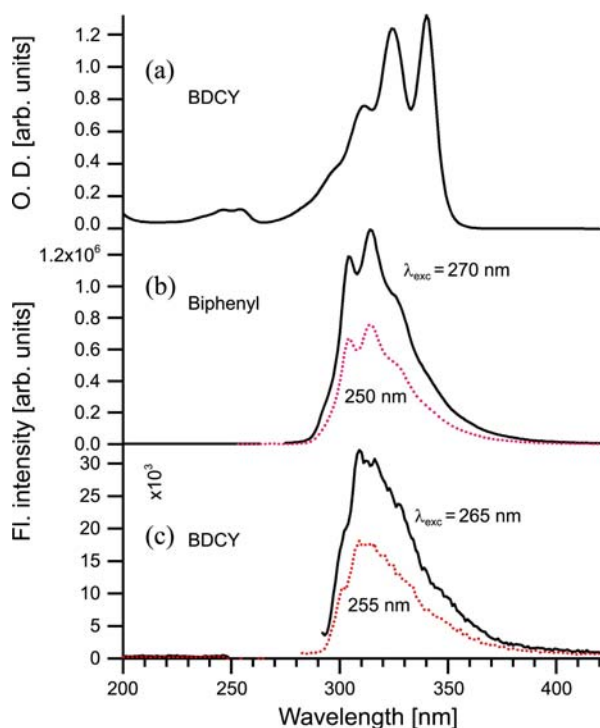
We present in Figure 2 transient absorption spectra of a 1.3×10^{-4} M BDCY solution in cyclohexane measured by using an excitation wavelength, $\lambda_{exe} = 355$ nm after various delays. Note that as shown in Figure 1(a), the absorption spectrum spans the wavelength region from 265 to 360 nm, and thus our excitation laser sources of 266 and 355 nm covers only the absorption edges. Therefore, the weak transient signals shown in Figure 2 may be attributed to the weak absorption intensities. The transient absorption spectra measured by using the excitation source of 266 nm are basically the same as those measured by using that of 355 nm. Thus, we do not present here the spectra measured for 266 nm. The transient absorption occurs spanning the region of 340-650 nm. Note that 800 nm is the detection limit for transient absorption. Extraordinary long-lived triplet-excited species (5 ms) is observed in Figure 2. The temporal evolution of the transient absorption monitoring at 360 nm was measured by using the excitation laser of 355 nm, in which the lifetime of the 360 nm transient was found to be 250 ± 10 μs.

Figure 3 presents the molecular structures of the singlet ground-state and triplet excited-state BDCY molecules optimized with the B3LYP/cc-pVTZ and UB3LYP/cc-pVTZ methods constraining D_{2h} and D_{2d} symmetries, where the U refers to the unrestricted method. The constraint for the D_{2d} symmetry in the triplet state is based on the preliminary calculation in which a perfect perpendicular geometry involving the carbocyclic rings is found to be lowest in energy. The prediction of the perpendicular geometry is
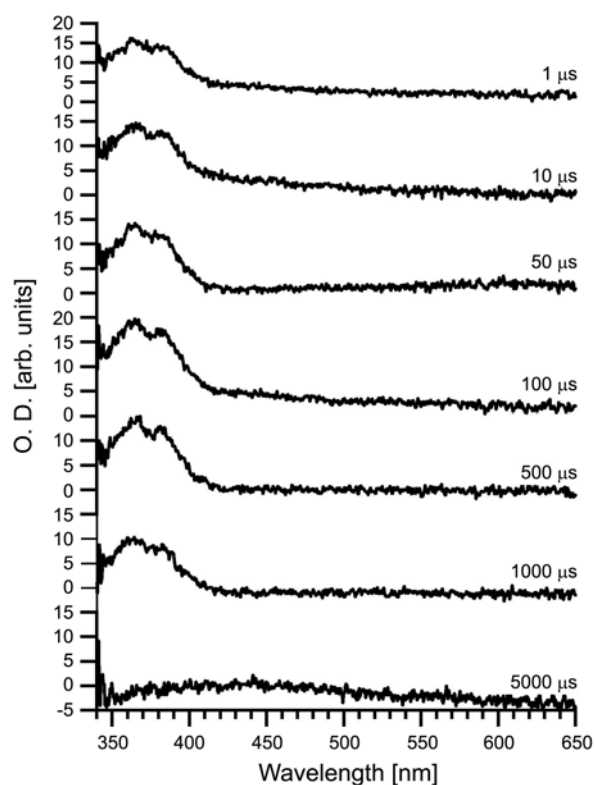

Figure 1. Static absorption and fluorescence spectra of a 2.0×10^{-5} M bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene) solution in cyclohexane are compared with fluorescence spectrum of a 2.0×10^{-5} M biphenyl solution in cyclohexane. (a) Absorption spectrum of BDCY. (b) Fluorescence spectrum of biphenyl. (c) Fluorescence spectrum of BDCY. The excitation wavelengths λ_{exc} are indicated in the individual fluorescence spectra.

Figure 2. Transient absorption spectra of a 1.3×10^{-4} M bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene) solution in cyclohexane measured after various delays. The excitation wavelength is 355 nm.
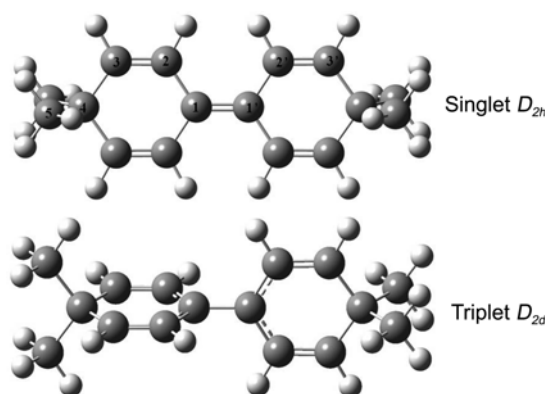
Figure 3. Geometrical structure of triplet excited-state bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene) molecule optimized with the B3LYP/cc-pVTZ method constraining a D_{2d} symmetry is compared with that of the ground singlet-state one optimized with the B3LYP/cc-pVTZ method constraining a D_{2h} symmetry.

somewhat surprising because a perpendicular geometry has not been predicted in the molecular structure of biphenyl in the singlet ground state.[8,9] We presume that only the repulsion between the *ortho*-hydrogen atoms of the two rings cannot explain the perpendicular geometry. In the singlet structure, the bond length associated with the central C_1-$C_{1'}$ bond is calculated to be 1.379 Å, being slightly longer than the adjacent double C_1=C_2 bond length of 1.338 Å. In the triplet structure, however, the bond length associated with C_1-$C_{1'}$ is shown to significantly elongate to 1.481 Å. Note that the central C_1-$C_{1'}$ bond length is close to the terminal C_4-C_5 single bond length of 1.552 Å. We presume that the central C-C bond in the triplet state still involves slightly double bond character, thereby indicating that the cross conjugation across the C_1-$C_{1'}$ central bond still occurs.

We performed the electron population analysis for the singlet and triplet BDCY molecules, which may yield information about the electron densities of the bonds associated with the cross conjugation. In quantum chemical calculations, the electron density as a function of coordinates **r**, $\rho(\mathbf{r})$ is defined so that $\rho(\mathbf{r})d\mathbf{r}$ is the number of electrons in a infinitely small volume $d\mathbf{r}$. For closed-shell molecules, $\rho(\mathbf{r})$ can be represented in terms of a sum of products of basis functions, φ:

$$\rho(\mathbf{r}) = \sum_{\mu}^{basis\ functions} \sum_{\nu} P_{\mu\nu}\phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}) \qquad (1)$$

where $P_{\mu\nu}$ is the density matrix. In many cases, bond strength and bonding pattern might be rendered in term of the density matrix. In the ground state, it is found that the density matrix element involving the 2s orbitals of C_1 and $C_{1'}$ atoms is relatively high in comparison with that involving the 2p orbitals of the corresponding atoms. In the triplet state, it is shown that the density matrix element involving the 2p orbitals of C_1 and $C_{1'}$ atoms is relatively high in comparison with that involving the 2s orbitals of the corresponding atoms. When the density matrix elements are condensed to all the electrons of the atoms, the density matrix elements

corresponding to the C_1-$C_{1'}$ and C_1-C_2 in the ground stat are found to be 0.5395 and 0.4015, respectively. In the triplet excited state, however, the reverse order is found such that those corresponding to the C_1-$C_{1'}$ and C_1-C_2: are 0.3512 and 0.4334, respectively. Consequently, in the triplet state the electron density attributed to the C_1-$C_{1'}$ atoms is significantly decreased. On the other hand, the electron density attributed to the C_1-C_2 atoms is found to be slightly enhanced upon the electron excitation.

No imaginary frequencies are found when we performed the frequency calculations on the optimized triplet geometries with the B3LYP/cc-pVTZ//B3LYP/cc-pVTZ method. Figures 4(a)-(b) compare the experimental static absorption spectra with the simulated singlet absorption spectrum calculated with the singlet TD DFT B3LYP/cc-pVTZ//B3LYP/cc-
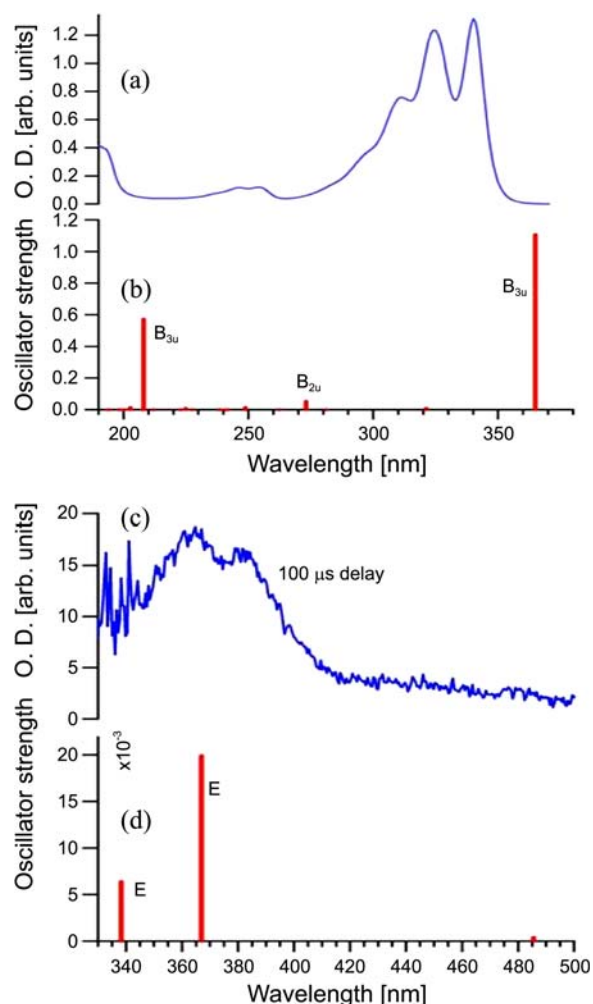

Figure 4. Static and transient absorption spectra are compared with the simulated singlet and triplet absorption spectra calculated with the TD DFT B3LYP/cc-pVTZ//B3LYP/cc-pVTZ method. (a) Static singlet absorption spectrum. (b) Simulated singlet absorption spectrum achieved with the TD DFT B3LYP/cc-pVTZ method. (c) Transient absorption spectrum measured after 100 μs delay, for which the excitation wavelength is 355 nm and the monitoring wavelength is 360 nm. (d) Simulated triplet absorption spectrum achieved with the TD DFT B3LYP/cc-pVTZ method. The electronic states are indicated near the peaks.

Notes

pVTZ method. Note that the simulated singlet absorption spectrum corresponds to electronic excitation from S_0 to S_1. Unfortunately, the simulated spectrum is not found to be consistent with the experimental one. The inconsistency may be attributed to possible deviation from the coplanarity under the solvent environment. It is shown in the present study that the electronic excitation energies are quite dependent upon the dihedral angle made by the two planes of a BDCY molecule. It is shown in the previous study that the TD DFT B3LYP/cc-pVTZ//B3LYP/cc-pVTZ calculations overestimate within only $6.83 \pm 5.17\%$ the 0_0^0 bands of 13 compounds containing at least one phenyl group.[29] The rms deviation is shown to be as low as 0.177 eV.[29] We present in Figures 4(c)-(d) the transient absorption spectrum measured at a delay of 100 µs, for which the excitation wavelength is 355 nm and the monitoring wavelength is 360 nm, and the simulated absorption spectrum of the triplet excited-state BDCY molecule calculated with the TD DFT B3LYP/cc-pVTZ//B3LYP/cc-pVTZ method at the D_{2d} optimized geometry involving the perpendicular geometry, respectively. Note that the simulated triplet absorption spectrum corresponds to electronic excitation from the first triplet state (T_1) to the second triplet state (T_2). Also note that the simulated spectra shown in Figures 4(b) and 4(d) were shifted to red by using a scaling factor of 0.930 eV, the value used previously.[29] We found two significantly high oscillator strengths in the transient absorption region in the present study. The peak intensities and positions involving the two E electronic states coincide with the experimental data, which implies that the transient absorption corresponds to the T_1 and T_2.

Conclusions

We measured ns transient absorption spectra for bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene). Temporal measurements for individual transient species were also made to elucidate the decay kinetics of the triplet species. A transient absorption spans about 340-650 nm, presumably due to triplet-triplet absorption. The lifetime of the triplet excited state is found to be quite long as 250 ± 10 µs. The B3LYP/cc-pVTZ calculations show that the carbocyclic rings in the singlet-state is coplanar in the singlet ground state, while in the triplet excited state, the rings are perfectly orthogonal, reducing the electronic delocalization effect. The static and transient absorption spectra were assigned *via* the time-dependent DFT method. The analysis of the electron density matrices evaluated with the time-dependent DFT method using the cc-pVTZ basis set indicates that electron density involving the central C-C bond is significantly reduced upon the change of the spin state from the singlet to the triplet state.

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