

# PHOTOPHYSICAL PROPERTIES OF DIPHENYLACETYLENE AND DIPHENYLBUTADIYNE DERIVATIVES IN SOLUTION PHASE\*

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By using the femtosecond and picosecond transient absorption measurement techniques, we have investigated diphenylacetylene, diphenylbutadiyne, and their methoxy and cyano derivatives in the solution phase. Both the rapid  $S_2 \rightarrow S_1$  internal conversion in the subpicosecond time scale and the triplet formation in the tens of picosecond region were observed for diphenylbutadiyne and its methoxy derivatives, while the dynamic behavior of dimethoxy-diphenylacetylene was quite similar to that of diphenylacetylene. The level inversion of the lowest excited singlet states of dicyano-diphenylbutadiyne was observed. The thermally activated  $S_2 \leftarrow S_1$  internal conversion was not negligible and the sum of the rate constants of  $S_2 \rightarrow S_1$  and  $S_2 \leftarrow S_1$  internal conversions was estimated to be about  $5 \times 10^{11} \text{ s}^{-1}$  at room temperature.

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## 1. Introduction

Recently, characters of the low lying excited singlet states of diphenylacetylene (DPA) and its derivatives have been studied in the solution phase [1–7]. The absorption band of DPA observed at 290 nm was assigned to the  ${}^1B_{1u}$  state, while the lowest excited singlet state was predicted to be  ${}^1A_g$  state [8]. Recent INDO/S calculation predicted that the  $S_1$  state has  $A_u$  symmetry [6]. Under the supersonic beam conditions, the energy gap between the  ${}^1B_{1u}$  and  ${}^1A_g$  states is less

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than  $300\text{ cm}^{-1}$  [9]. Because of the existence of the mutual exclusion principle, the structure of the low lying excited singlet states of DPA should be planar in the gas phase. It should be emphasized here that the  $S_1$  state was experimentally proposed to have a  $g$  symmetry ( $2^1A_g$ ) and that the INDO/S calculation did not give a correct explanation.

In the previous paper [1], we confirmed that the fluorescence state of DPA is the  $S_2$  state and the  $S_1$  state does not emit fluorescence. The strong temperature dependence of the  $S_2 \rightarrow S_1$  internal conversion was demonstrated by using picosecond transient absorption measurement techniques [1]. The questions arisen here are why the internal conversion of DPA between the close lying electronic states is such a slow process and what is the origin of the activation energy. The purpose of this paper is to give an answer of these questions. In order to do so, it is important to assemble our knowledge about the photophysical properties of DPA and related compounds.

The characteristic features of the photophysical process of DPA are the exceptionally long lifetime of the  $S_2$  state and the strong temperature dependence of the  $S_2 \rightarrow S_1$  internal conversion. These characters are believed to be due to the small  $S_2 - S_1$  gap. The strict forbidden character of the  $S_1 - S_0$  dipole transition may be due to the rigid rod-like molecular structure. Although we do not know the exact value of the  $S_2 - S_1$  energy gap of these molecules in the solution phase, the energy gap of DPA and diphenylbutadiyne (DPB) should be different and should change with the substituents. Therefore we hope to extract the information about the mechanism of the  $S_2 \rightarrow S_1$  internal conversion from the energy gap dependence of the transient absorption measurements of DPA, DPB, and their derivatives.

In this paper we present the results of the femtosecond and picosecond transient absorption measurements of DPB, *p*-methoxydiphenylbutadiyne (MO-DPB), *p*,*p'*-dimethoxydiphenylbutadiyne (DM-DPB), and *p*,*p'*-dimethoxydiphenylacetylene (DM-DPA) in nonpolar solvents. We also measured the dynamic behavior of *p*,*p'*-dicyanodiphenylacetylene (DC-DPA) and *p*,*p'*-dicyanodiphenylbutadiyne (DC-DPB) in tetrahydrofuran (THF). Both the rapid  $S_2 \rightarrow S_1$  internal conversion in the subpicosecond time scale and the triplet formation in tens of picosecond were observed for DPB and its methoxy derivatives, while the dynamic behavior of DM-DPA was quite similar to that of DPA. The level inversion of the lowest excited singlet states of DC-DPA and DC-DPB was observed. The thermal activation of the  $S_1$  state to the  $S_2$  state was not negligible for DC-DPB and the sum of the rate constants of  $S_2 \rightarrow S_1$  and  $S_2 \leftarrow S_1$  internal conversions was estimated to be about  $5 \times 10^{11}\text{ s}^{-1}$  at room temperature.

## 2. Experimental

Femtosecond transient absorption spectra were measured by using Ar ion laser pumped Ti:sapphire laser (Spectra Physics Tsunami: 70 fs FWHM, 1 W at 80 MHz repetition rate) with 1-kHz regenerative amplifier (Spectra Physics Spitfire) system in Venture Business Laboratory of Osaka University. The third harmonic (267 nm, 40  $\mu\text{J}/\text{pulse}$ ) of the laser was used to excite the sample, while white light generated from the fundamental light of the laser in the flowing water cell was used as probing light. In order to correct the transient absorption spectrum

for the dispersion of the probe light, we measured optical Kerr effect of  $\text{CCl}_4$  and determined the wavelength dependent arrival times of the femtosecond white light at the sample cell. Sample solution was flowed through the quartz cell with an optical path length of 2 mm.

Picosecond transient absorption spectra were measured by using a dye laser photolysis system pumped by second harmonic of a mode-locked  $\text{Nd}^{3+}\text{-YAG}$  laser (Quantel, Pico-chrome YG-503C/PTL-10). The details of this system were described elsewhere [1]. The sample was excited with second harmonic of a rhodamine-6G (295 nm) laser and a transient absorption spectrum between 380 and 980 nm was measured by using a picosecond white light generated in  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixture. Typically the signal was averaged for 30 shots. Correction of the transient absorption spectrum for the dispersion of the probe light was performed in the same manner as the femtosecond measurements. Sample solutions in the quartz sample cell with an optical path length of 10 mm were deaerated by flushing with  $\text{N}_2$  gas.

DPB (Aldrich) was purified by repeated recrystallization from *n*-hexane, while MO-DPB, DM-DPB, DC-DPB, DM-DPA, and DC-DPA were synthesized and purified with HPLC [10]. Spectrograde cyclohexane, *n*-hexane, and THF were used as purchased. Because of low solubility of dicyano-derivatives in non-polar solvents, THF was used to make the DC-DPA and DC-DPB solution.

### 3. Results

Figure 1 shows (a) femtosecond and (b) picosecond time resolved absorption spectra of DM-DPA in cyclohexane measured at room temperature ( $23 \pm 1^\circ\text{C}$ ). Immediately after the laser pulse excitation, transient absorption band peaked around 510 nm was observed. The absorption maximum gradually shifted to 480 nm and

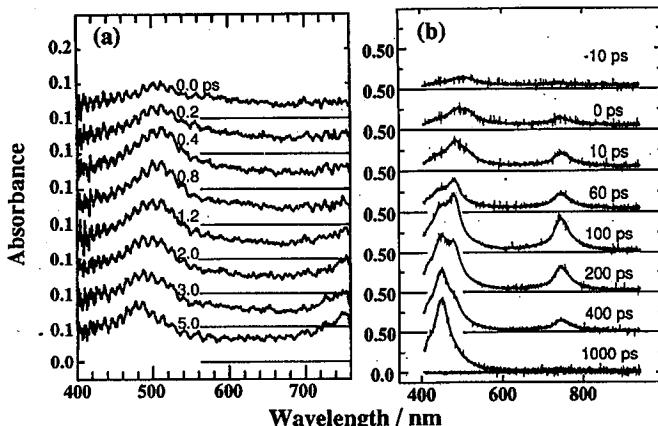


Fig. 1. Femtosecond (a) and picosecond (b) time resolved absorption spectra of DM-DPA in cyclohexane at room temperature. Delay times after the laser pulse excitation were indicated in the figure.

a new band appeared in the red region with increasing delay time. The 480 and 760 nm bands were dominant at 10 ps after the laser pulse excitation, while at longer delay times than 500 ps only the 440 nm band of which the decay time was beyond the scope of our measurements was observed. The lifetime of the 510 nm band was estimated to be about 3.5 ps, which was shorter than we reported previously [5]. This can be due to the poor time resolution of the picosecond measurements. The rise and decay times of the transient absorbance monitored at 760 nm were about 3.3 and 200 ps, respectively. The rise time of the 440 nm band was about 180 ps, which is close to the decay time of the 760 nm band. Therefore

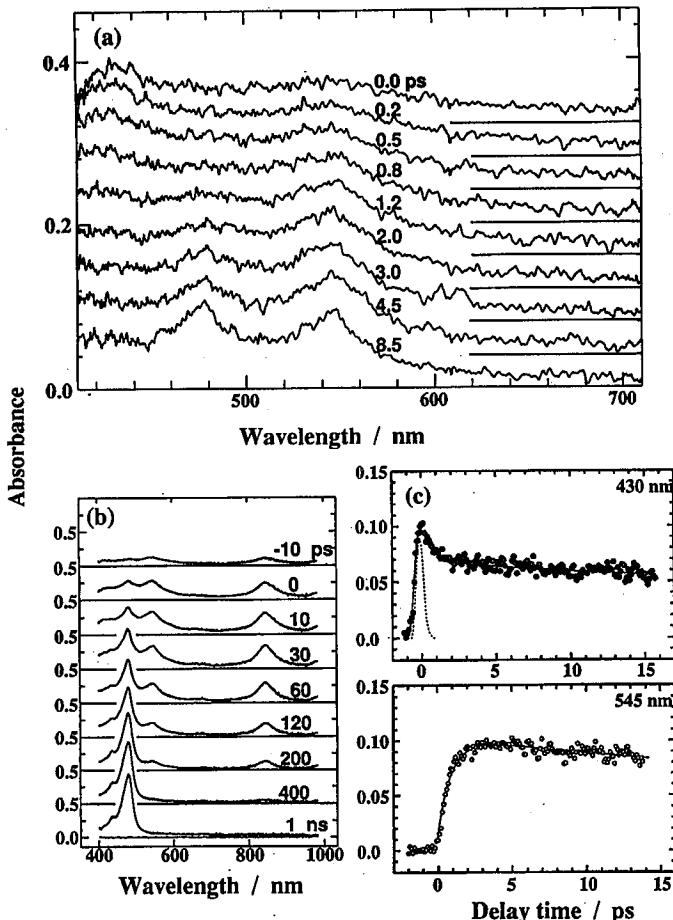


Fig. 2. Femtosecond (a) and picosecond (b) time resolved absorption spectra and time dependence of the transient absorbance of DM-DPB (c) in cyclohexane. Delay times after the laser pulse excitation and the monitoring wavelengths are indicated in the figure. Solid lines in (c) show the best fit of the time dependence, while the broken line shows the cross correlation between the excitation and interrogating pulses.

the 760 nm band was due to the precursor of the  $T_1$  state. Since the fluorescence lifetime was found to be less than 10 ps, the fluorescence state gave the 510 nm band. From the similarity of the dynamic behavior of DM-DPA to that of DPA, we can safely assign the 440, 510, and 760 nm bands to the  $T_n \leftarrow T_1$ ,  $S_n \leftarrow S_2$ , and  $S_n \leftarrow S_1$  transitions of DM-DPA, respectively. Since no  $S_1$  fluorescence was observed, the  $S_1$  state was dipole forbidden from the ground state.

Femtosecond time resolved absorption spectra of DM-DPB in cyclohexane is shown in Fig. 2a. Immediately after the laser pulse excitation, the band around 430 nm was observed. The 430 nm band was gradually replaced by the 545 nm band with increasing delay time. As shown in Fig. 2b, at the delay times longer than a few hundreds of picoseconds the long-lived band was observed at 475 nm, which should be assigned to the  $T_n \leftarrow T_1$  transition of DM-DPB [5]. The decay curve shown in Fig. 2c was fitted to the double exponential function and the decay time constant of the short-lived component measured at 430 nm was estimated to be  $680 \pm 120$  fs. The rising part of the transient absorbance monitored at 545 nm consisted of a small portion of the instrumentally limited component and the exponentially rising component with a time constant of  $640 \pm 150$  fs. Because of the agreement between the decay time of the 430 nm band and the rise time of the 545 nm band, the 430 nm band should be ascribed to the higher excited singlet state ( $S_2$ ) of DM-DPB. The bands observed in the intermediate delay times were ascribed to the  $S_n \leftarrow S_1$  transition of DM-DPB. Although we could not observe the short-lived band of DPB in cyclohexane between 400 and 700 nm, the  $S_2$  lifetime of  $600 \pm 160$  fs was obtained from the rise time of the  $S_n \leftarrow S_1$  absorption

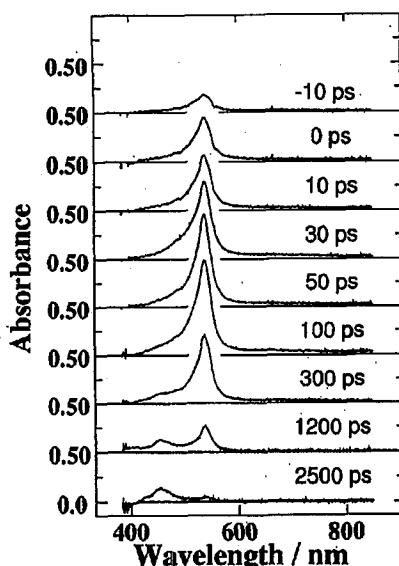


Fig. 3. Picosecond time resolved absorption spectra of DC-DPA in THF at room temperature. Delay times after the laser pulse excitation were indicated in the figure.

around 540 nm. The lifetimes of the  $S_1$  state of DM-DPB and DPB were estimated to be 190 and 30 ps, respectively [5].

The first absorption band of DM-DPB in *n*-hexane was observed around 330 nm and the oscillator strength of this band and the radiative lifetime ( $\tau_r$ ) of the upper state were estimated to be almost the unity and about 1 ns, respectively. If the first absorption band is due to the  $S_1$  state of DM-DPB, the fluorescence yield should be as large as  $\tau(S_1)/\tau_r \approx 0.2$ . The failure of detecting the fluorescence implies that the major part of the first absorption band does not correspond to the  $S_1 \leftarrow S_0$  transition. Transition moment between the  $S_1$  and  $S_0$  states should be

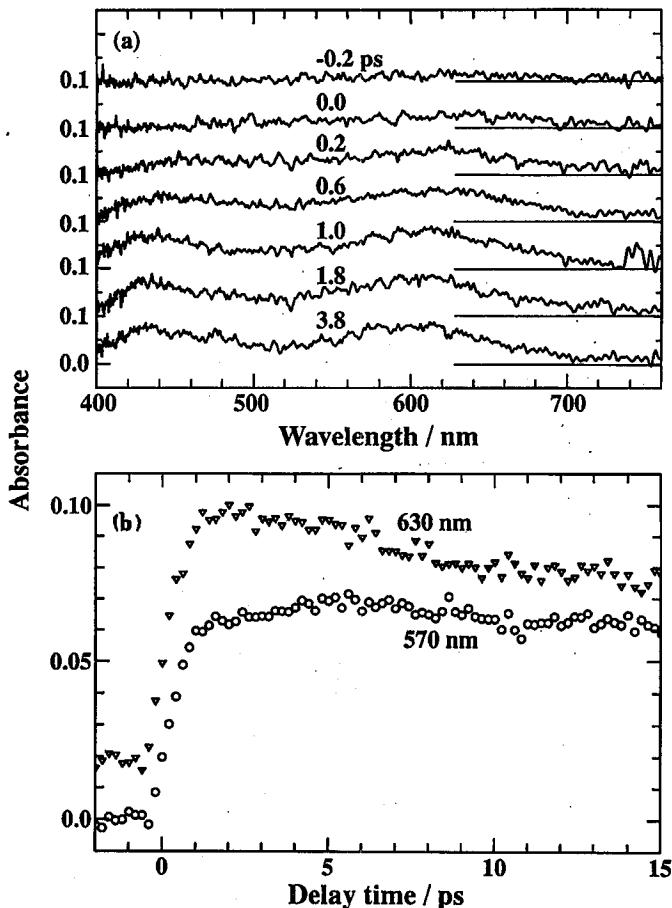


Fig. 4. Femtosecond time resolved absorption spectra (a) and the time dependence of the transient absorbance (b) of DC-DPB in THF. Delay times after the laser pulse excitation and the monitoring wavelengths are indicated in the figure.

significantly smaller than that of the first absorption band. The situation was the same for DPB and seemed to be quite similar to that of DPA, where the  $S_1$  state is nonfluorescent in the solution phase and the first absorption band was assigned to the  $S_2(^1B_{1u}) \leftarrow S_0$  transition.

Picosecond time resolved absorption spectra of DC-DPA in THF at room temperature are displayed in Fig. 3. Just after the excitation of DC-DPA, transient absorption band around 540 nm was observed, while at longer delay times than 2 ns the 440 nm band was dominant. The lifetime of this band was about 1.1 ns which was in a good agreement with the fluorescence lifetime. Therefore the 540 nm band was ascribed to the  $S_1$  state of DC-DPA. The lifetime of the 440 nm band, which may be assigned to the  $T_n \leftarrow T_1$  transition of DC-DPA, was much longer than the range of our measurements. Because of the high fluorescence yield ( $\approx 0.5$ ) of this compound, the  $S_1$  state is one-photon allowed from the ground state and has  $B_{1u}$  symmetry. These results clearly show that the level inversion of the  $S_2$  and  $S_1$  states occurs with the introduction of the cyano groups to DPA. Figure 4 shows (a) femtosecond transient absorption spectra of DC-DPB in THF and (b) time dependence of the transient absorbance monitored at 430, 570, and 630 nm. At short delay times, we observed transient absorption bands around 430 and 630 nm. At 570 nm, we observed the rising component with a time constant of about 2 ps. At 630 nm, the decaying component with the similar time constant was observed. The lifetime of these bands coincided with each other (about 70 and 60 ps at 295 and 170 K, respectively) and the triplet band at 490 nm showed the rise with the same time constant. As shown in Fig. 5, the intensity ratio of the 570 and 630 nm bands depended on the temperature and the contribution of the 630 nm band increased with decreasing temperature. The 570 and 630 nm bands should be assigned to two different excited singlet states. Since the  $^1B_{1u}$  state was one-photon allowed from the ground state but the  $^1A_g$  state was not accessible, it is reasonable to assign the 630 nm band to  $^1B_{1u}$ . The results of the temperature dependence indicate that the state which gives the 630 nm band is lower than the

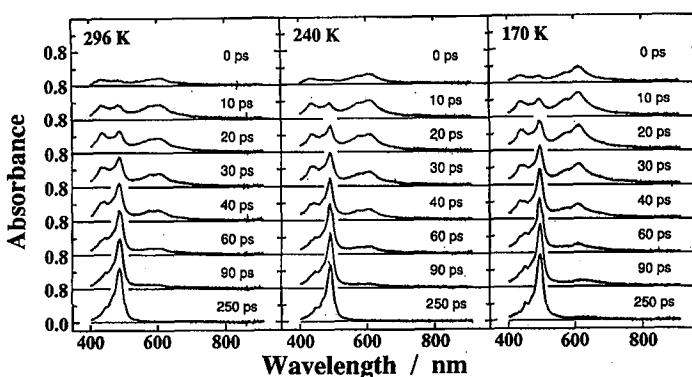


Fig. 5. Picosecond time resolved absorption spectra of DC-DPB in THF at various temperatures. Delay times after the laser pulse excitation were indicated in the figure.

other state. Therefore we can assign the 570 and 630 nm bands to the  $S_n \leftarrow S_2$  and  $S_n \leftarrow S_1(B_{1u})$  transitions of DC-DPB, respectively. The introduction of the cyano groups to DPB also results in the level inversion of the lowest excited singlet state. The observed agreement of the decay times of the  $S_1$  and  $S_2$  states indicates that the  $S_2 \leftarrow S_1$  back internal conversion is not negligible and the sum of the rate constants of the  $S_2 \rightarrow S_1$  and  $S_2 \leftarrow S_1$  internal conversions is  $\approx 1/2 \text{ ps}^{-1}$ . The larger fluorescence yield of DC-DPB than that of DPB should be due to the longer lifetime of the  $^1B_{1u}$  state.

#### 4. Discussion

Since a large frequency difference of the C≡C stretching mode between the  $S_2$  and  $S_1$  states was observed by the transient Raman spectral measurements [7], the internal conversion should require the excitation of the C≡C stretching mode either in the  $S_2$  or  $S_1$  state. The sum of the  $S_2-S_1$  gap and the activation energy of the  $S_2 \rightarrow S_1$  internal conversion of amino-DPA was close to the frequency of the C≡C stretching in the  $S_1$  state [3, 4], which suggests that the C≡C stretching mode is excited in the  $S_1$  state.

From the temperature dependence measurements of DM-DPA in *n*-hexane, we obtained the frequency factor and activation energy of the  $S_2 \rightarrow S_1$  internal conversion to be  $6.8 \times 10^{12} \text{ s}^{-1}$  and  $830 \text{ cm}^{-1}$ , respectively, which were similar to those of MO-DPA and DPA [1, 3, 5]. The vibrational level density should significantly increase with the introduction of methoxy groups, but the methoxy substitution hardly affected the frequency factor and activation energy of the  $S_2 \rightarrow S_1$  internal conversion. From these facts we can safely conclude that the total vibrational level density is not important but the density of the vibronic levels with the excitation of the C≡C stretching mode should be important for the  $S_2 \rightarrow S_1$  internal conversion. At room temperature the rate constants of the  $S_2 \rightarrow S_1$  internal conversion of DPBs were almost one order of magnitude larger than those of DPAs but they were rather similar to the frequency factors of DPA. We found that the temperature dependence of the  $S_2$  lifetime of DPB was expected to be small [5]. These results suggest that the  $S_2-S_1$  gap of DPB is larger than the frequency of the C≡C stretching vibration. Once the energy gap becomes larger than the energy of C≡C stretching, the excitation of this mode as at least a part of the combination tone in the  $S_1$  state during the internal conversion is possible.

Introduction of the cyano groups to DPA and DPB appeared to result in the level inversion of the  $^1B_{1u}$  state and  $2^1A_g$  states. Both CN-DPA and DC-DPA, of which the  $S_1$  states have  $B_{1u}$  symmetry and the fluorescence yield was high ( $\approx 0.5$ ), do not show any anomalous dynamic behavior but they act as usual aromatic compounds. The higher excited singlet state was not observed with our excitation wavelength and time resolution, which may be due to the large  $S_2-S_1$  energy gap of these compounds. On the other hand, both the  $S_1$  and  $S_2$  states of DC-DPB were observed and they were in the equilibrium. The sum of the forward and backward internal conversion rate constants between the  $S_2$  and  $S_1$  states were obtained to be about  $5 \times 10^{11} \text{ s}^{-1}$  which was one order of magnitude smaller than the  $S_2 \rightarrow S_1$  internal conversion rate constants of DPB and DM-DPB. Since the  $S_2 \leftarrow S_1$  internal conversion of DC-DPB can be thermally activated, the energy

gap of this transition should be at most of the order of  $k_B T$ . Therefore the energy gap is much smaller than the frequency of the C≡C stretching vibration, of which the excitation is necessary for the internal conversion. Without the assistance of the thermal activation, the C≡C stretching mode cannot be excited either in the  $S_2$  or  $S_1$  state. Thus we can expect that the  $S_2 \rightarrow S_1$  internal conversion is slow for the molecules with the smaller  $S_2 - S_1$  energy gap than the effective vibrational frequency and that such compounds should show strong temperature dependence. This is the case for various DPA derivatives and DC-DPB. The energy gap of DPB and diphenylpolyenes are larger than the effective vibrational frequency and the  $S_2 \rightarrow S_1$  internal conversion of these molecules takes place without the assistance of the thermal activation.

The lowest excited singlet states of diphenylpolyenes longer than diphenylhexatriene have the similar level ordering of the lowest excited singlet states to that of DPA [11], but the characters of the  $S_2(^1B_u) \rightarrow S_1(2A_g)$  internal conversion of diphenylpolyenes seems to be quite different from those of DPA [12]. Increasing the polyene chain length, the  $2^1A_g$  state lowered more than the  $^1B_u$  state and the  $S_2 - S_1$  energy gap increased from  $1605\text{ cm}^{-1}$  (diphenylhexatriene) to  $4780\text{ cm}^{-1}$  (diphenyltetradecaheptaene) [13]. The  $S_2 \rightarrow S_1$  internal conversion of diphenylpolyenes seemed to be energy gap independent and the  $S_2$  lifetimes were quite short ( $\approx 0.2\text{ ps}$ ) [14]. Moreover the temperature dependence of the  $S_2 \rightarrow S_1$  internal conversion was expected to be much smaller than that of DPA.

The  $S_1$  state of DPA is nonfluorescent, while many diphenylpolyenes emit fluorescence from the  $S_1$  state and the  $S_2$  fluorescence appears on the higher-energy side of the  $S_1 \rightarrow S_0$  fluorescence [13, 15]. Such difference may be partially due to the rapid  $S_1 \rightarrow T_1$  intersystem crossing of DPA but the more strict forbidden factor of the  $S_1 - S_0$  dipole transition of DPA compared with that of diphenylpolyenes should be responsible for the nonfluorescent character of the  $S_1$  state of DPA.

The strict forbidden character of the  $S_1 - S_0$  dipole transition of the DPA and DPB derivatives suggests that the molecule keeps the planar and linear structure in the excited singlet state and that the  $S_1$  state is the parity forbidden  $g$  state in the solution phase. Since the fluorescence from the  $^1B_{2u}$  state is observed under the supersonic beam conditions [9], this state may not be the candidate of our  $S_1$  state. Taking account of the lifetime of the  $S_1$  state, we should detect the  $S_1$  fluorescence of DPA if the transition moment between  $S_1 - S_0$  is similar for DPA and diphenylhexatriene. The more rigid structure of DPA and DPB than diphenylpolyenes makes the mutual exclusion principle, which is expected for the molecules with the inversion symmetry, hold strictly and prevents the observation of the fluorescence from the  $S_1$  state.

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