# Transannular Interaction in the Excited Triplet States of [2.2]Paracyclophane and Related Compounds

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(Received December 18, 1978)

The triplet-triplet absorption spectra of [2.2]paracyclophane and related cyclophanes (naphthalenophane, pyrenophane, and anthracenophane) were measured. Cyclophanes in which two component subunits fully overlap, show new bands together with monomer-like bands. The electronic structures of triplet states of these cyclophanes were studied theoretically by the "molecules in molecule" method, special attention being paid to the correlations of the electronic structures of cyclophanes with those of corresponding monomers and also to the dependences of the charge transfer interaction upon the overlapping between the component subunits and upon the molecular size.

[2.2]Paracyclophane and other cyclophanes have the conjugated aromatic rings faced to each other and are of particular importance because of the transannular interaction. [2.2]Paracyclophane is regarded as a model of a benzene dimer; especially in the excited state it is a model of a benzene excimer. Thus the electronic structure of this molecule has been studied by several authors.[1)]

Previously, we investigated the singlet states of [2.2]paracyclophane from both experimental and theoretical points of view.[2)] The near and vacuum ultraviolet absorption spectra were well analyzed by considering the configuration interaction (CI) among the ground, locally excited, and charge transfer configurations.

Hausser *et al.* showed in their ODMR (optical detection of magnetic resonance) and ESR studies that in the lowest triplet state, $T_1$, of cyclophanes which contain two same aromatic molecules two unpaired electrons are rather localized in either ring.[3)] In other words, the charge transfer character is not significant in the lowest triplet state.

In this paper, we have studied the triplet-triplet ($T_n \leftarrow T_1$) absorption spectra of several cyclophanes in order to elucidate the character of the lowest triplet state and higher triplet states, $T_n$, and also the dependences of the charge transfer interaction upon the ring overlapping and upon the molecular size.

## Experimental

Cyclophanes studied here are shown in Fig. 1: [2.2]paracyclophane (PC), *anti*-[2.2](1,4)naphthalenophane (*anti*-NP), *syn*-[2.2](1,4)naphthalenophane (*syn*-NP), [2.2](2,7)-pyrenophane (PyP), *anti*-[2.2](1,4)anthracenophane (*anti*-AP), [2.2](1,4)(9,10)anthracenophane ((1,4)(9,10)-AP), and *syn*-[2.2](1,4)anthracenophane (*syn*-AP). [2.2]Paracyclophane (the Aldrich Chemical Company ) was purified by column chromatography and vacuum sublimation. The preparation and purification of other cyclophanes were described previously.[4)]

The $T_n \leftarrow T_1$ absorption spectra of PC, *anti*-NP, *syn*-NP, and PyP were observed at 77 K in 2-methyltetrahydrofuran by an improved "parallel beam method"[5)] in which the exciting light and the monitoring light was set to pass a sample through the same optical path by the use of two sectors synchronized by stepping motors. By setting up the double beam system, the S/N ratio was much improved. Consequently, we could measure the transient spectra with the absorbance less than 0.01. The polarized $T_n \leftarrow T_1$ spectrum of PC was measured by the photoselection method,[6)] two polarizer films being used.

The sensitization method was used for excitation to the triplet states of anthracenophanes since the quantum yields were low for the direct excitation. Biacetyl was added into the sample solution as a triplet sensitizer. Biacetyl was excited with a dye laser pumped with a nitrogen laser at room temperature. Through the energy transfer from triplet biacetyl, anthracenophanes were populated in their $T_1$ states, and their $T_n \leftarrow T_1$ absorption spectra were measured. The details of the excitation and detection systems used for the measurement were described previously.[7)]

## Theoretical

The "molecules in molecule" method was used for the calculation of the energy levels of triplet states of PC in a similar way as for the calculation of singlet states.[2a)]

The energies of the locally excited (LE) configurations for PC were taken to be equal to the observed values of benzene:[8)]

$$E(^3B_{1u}^+) = 3.9\,\text{eV},\ E(^3E_{1u}^\pm) = 4.7\,\text{eV},\ E(^3B_{2u}^-) = 5.6\,\text{eV},$$
$$E(^3E_{2g}^+) = 6.8\,\text{eV},\ E(^3E_{2g}^-) = 9.3\,\text{eV}.$$

The energies of the CT configurations were calculated by the usual method.[9)] The energy, $E_{CT}(i \rightarrow j)$, for the configuration in which one electron transfers from the $i$-th occupied orbital of one benzene ring to the $j$-th vacant orbital of the other is given by the following equation:

$$E_{CT}(i \rightarrow j) = I_i - A_j - C_{ij}^{I,II}. \quad (1)$$

Here $I_i$ and $A_j$ are the ionization potential for the $i$-th orbital and the electron affinity for the $j$-th orbital, respectively. The Coulombic interaction term, $C_{ij}^{I,II}$, was evaluated with the aid of the Nishimoto-Mataga approximation.[10)]

In actual calculation, $I_i$ and $A_j$ were evaluated by the following equations for the cyclophanes except

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for PC.

$$I_i = I + E_i^+ \quad (2)$$

$$A_j = A - E_j^- \quad (3)$$

Here $I$ and $A$ are the first ionization potential and the electron affinity of an appropriate neutral molecule (naphthalene for naphthalenophane), respectively. $E_i^+$ and $E_j^-$ are the excitation energies of the corresponding cation and anion determined experimentally,[11] respectively. Since the assignment of spectra has some ambiguity for the benzene cation and anion, Eqs. 2 and 3 are not applicable to PC. Therefore we evaluated $I_i$ and $A_j$ by the following equations:

$$I_i = I + (\varepsilon_{HO} - \varepsilon_i), \quad (4)$$

$$A_j = A - (\varepsilon_j - \varepsilon_{LV}). \quad (5)$$

Here $\varepsilon_{HO}$, $\varepsilon_{LV}$, $\varepsilon_i$, and $\varepsilon_j$ are the orbital energies for the highest occupied, lowest vacant, $i$-th, and $j$-th orbitals, respectively. They were calculated with the Pariser-Parr-Pople method.[12]

The molecules of *syn*-series, namely, PC, *syn*-NP, PyP, and *syn*-AP belong to the $D_{2h}$ symmetry, and other cyclophanes to the $C_{2h}$ symmetry. The coordinate systems are shown in Fig. 1. In all cyclophanes that belong to $D_{2h}$, the symmetry of $T_1$ is $^3B_{2g}$ and the allowed transitions are $^3B_{1u} \leftarrow {}^3B_{2g}$ (x-polarization), $^3A_u \leftarrow {}^3B_{2g}$ (y-polarization), and $^3B_{3u} \leftarrow {}^3B_{2g}$ (z-polarization). In the case of $C_{2h}$, $T_1$ is $^3B_g$, and the allowed transitions are $^3A_u \leftarrow {}^3B_g$(x,y-polarization) and $^3B_u \leftarrow {}^3B_g$ (z-polarization).

The semi-empirical SCF MO-CI calculation was also made, using MO's calculated by the Pariser-Parr-Pople method.

## Results and Discussion

[*2.2*]*Paracyclophane (PC).* Figure 2 shows the $T_n \leftarrow T_1$ absorption spectrum and its polarization of PC. We found a very weak band at 550 nm and a broad strong band around 330—400 nm. The polarization experiment using the 313 nm light for excitation shows that the strong band consists of two transitions with the polarizations perpendicular to each other. Therefore, three distinct $T_n \leftarrow T_1$ absorption bands were observed for PC. On the other hand, benzene has only two weak $T_n \leftarrow T_1$ transition bands at 430 nm ($^3E_{2g}^+ \leftarrow {}^3B_{1u}^+$)[8b] and at 280 nm ($^3E_{2g}^- \leftarrow {}^3B_{1u}^+$).[8c] The difference in the $T_n \leftarrow T_1$ absorption spectrum between benzene and PC is clearly due to the transannular interaction in the excited triplet states of PC.

In order to analyze the $T_n \leftarrow T_1$ absorption spectra, we performed the semi-empirical SCF MO-CI calculation and the "molecules in molecule" calculation. Figure 3 shows the calculated ("molecules in molecule" method) and observed energy levels of the triplet

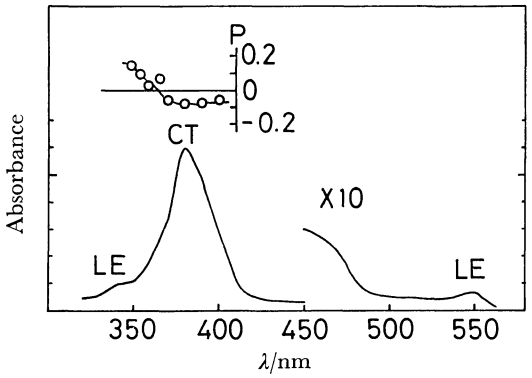


Fig. 2. The $T_n \leftarrow T_1$ absorption spectrum of PC and the polarization, P.

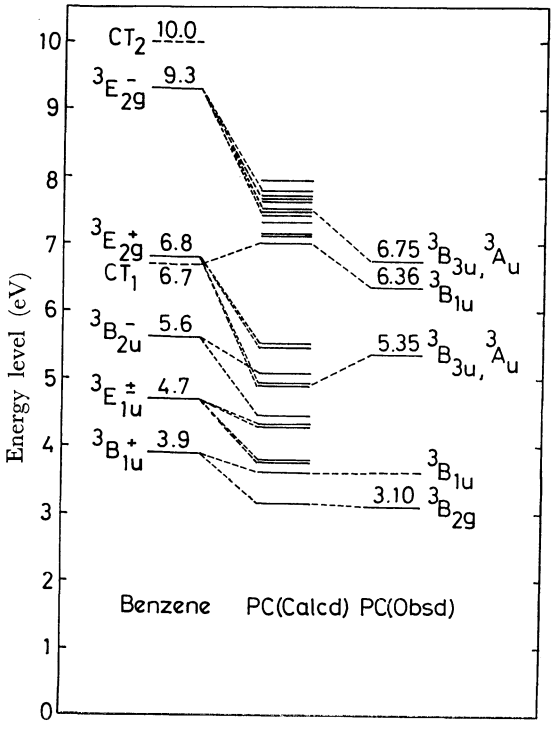


Fig. 3. Observed and calculated energy levels of the triplet states of PC and observed levels of benzene.

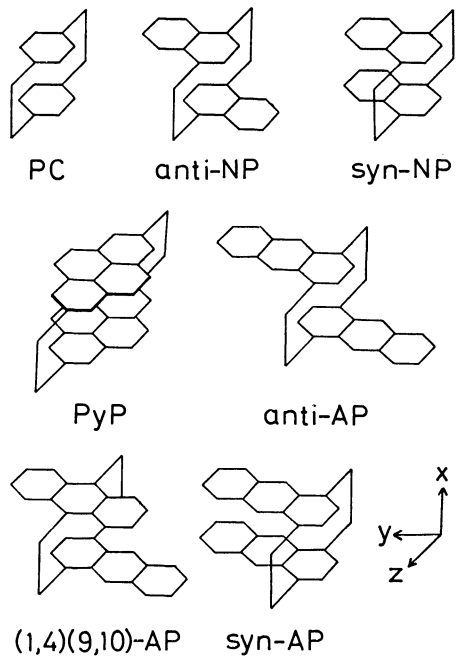


Fig. 1. The molecular structures of PC, *anti*-NP, *syn*-NP, PyP, *anti*-AP, (1,4)(9,10)-AP, and *syn*-AP.

states of PC, together with the observed levels of benzene. The zeroth-order LE levels of $^3B_{1u}^-$, $^3E_{1u}^+$, and $^3B_{1u}^+$ of benzene strongly interact with the $CT_1$ level, and those of $^3E_{2g}^+$ and $^3E_{2g}^-$ with $CT_2$.

We can see from Fig. 3 that the lowest triplet state of benzene ($^3B_{1u}^+$) is split into two states, $^3B_{2g}$ and $^3B_{1u}$ in PC. The $^3B_{2g}$ state is slightly lower than the $^3B_{1u}$ state and is of the neutral exciton nature. The weight of $^3B_{1u}^+$ of benzene in the $T_1$ state of PC is more than 80%. Hausser *et al.* recently showed that the zero-field splitting parameter, *D*, of PC is reduced only by 15% with respect to the corresponding monomer, *p*-xylene.[3b] This is consistent with the present result. The present result is also consistent with the result calculated by Hillier *et al.*[1c]

Contrary to the $T_1$ state, there are no previous studies on higher triplet states. From theoretical consideration we can see that the transitions from the $^3B_{2g}$ state to the $^3B_{3u}$ and $^3A_u$ states (polarized parallel to the ring), and to the $^3B_{1u}$ state (polarized perpendicularly to the ring) are allowed. These states are shown in Fig. 3. The $^3B_{1u}$ state located at about 7 eV in the column of PC (calcd) is mainly of the CT character. As is clearly seen in this figure, the theoretical study predicts that three bands appear in the observed wavelength region. This prediction agrees well with the experimental result. The semi-empirical SCF MO-CI calculation shows that the intensity ratio of the $T_n \leftarrow T_1$ absorption spectrum is 1 : 0.38 : 0.03 for the $^3B_{1u} \leftarrow {}^3B_{2g}$, $(2^3B_{3u} \leftarrow {}^3B_{2g} + 2^3A_u \leftarrow {}^3B_{2g})$, and $(1^3B_{3u} \leftarrow {}^3B_{2g} + 1^3A_u \leftarrow {}^3B_{2g})$ transitions. With the aid of this intensity ratio together with the calculated and observed transition energies, the three $T_n \leftarrow T_1$ absorption bands are assigned as follows. The most intense band at 380 nm is the CT band ($^3B_{1u} \leftarrow {}^3B_{2g}$) characteristic of the transannular interaction. The band around 340 nm which is polarized perpendicularly to the above CT band, is assigned to the LE band $(2^3B_{3u} \leftarrow {}^3B_{2g} + 2^3A_u \leftarrow {}^3B_{2g})$ and the parentage of this transition is the $^3E_{2g}^- \leftarrow {}^3B_{1u}^+$ transition of benzene. The weak band at 550 nm is ascribed to the LE band $(1^3B_{3u} \leftarrow {}^3B_{2g} + 1^3A_u \leftarrow {}^3B_{2g})$ which comes from the forbidden transition ($^3E_{2g}^+ \leftarrow {}^3B_{1u}^+$) of benzene.

The polarization of the absorption of PC at 313 nm (the excitation wavelength for the measurement of the $T_n \leftarrow T_1$ absorption spectrum of PC) is not clear, since the absorption band in this region consisting of two forbidden transitions, $^1B_{1g} \leftarrow {}^1A_g$ and $^1B_{2g} \leftarrow {}^1A_g$,[2a,13] is only vibrationally allowed. By the polarized absorption spectra of PC crystal measured on the ac plane, the absorbance at 313 nm of the c// spectrum is about twice larger than that of the a// spectrum.[2a] The c axis is parallel to the long axis of the molecule. On the basis of this, the present experiment of the $T_n \leftarrow T_1$ absorption is explained as follows. The degree of polarization, P, is expected to be 1/2 when the $T_n \leftarrow T_1$ transition is polarized parallel to the $S_n \leftarrow S_0$ transition used for excitation, and $-1/3$ when it is polarized perpendicularly. The band around 380 nm shows the negative value of P. This is consistent with our assignment that the band is the CT band the polarization of which is perpendicular to the benzene plane. In the $T_n \leftarrow T_1$ absorption band around 340 nm, P becomes positive. This indicates that the transition parallel to the $S_n \leftarrow S_0$ excitation is involved in this region.

It is interesting that the CT band was more distinctly observed in the $T_n \leftarrow T_1$ absorption spectrum than in the usual $S_n \leftarrow S_0$ absorption spectrum. This may be because of the weak $T_n \leftarrow T_1$ transition of the component molecule, benzene; that is, the transition localized in one ring is rather weak in the case of PC, and therefore the transition over two rings (CT transition) is observed clearly without the hindrance of LE bands.

anti- *and* syn-*NP*. Figure 4 shows the $T_n \leftarrow T_1$ absorption spectra of *anti*- and *syn*-NP together with that of naphthalene. In the case of naphthalene, the very strong $T_n \leftarrow T_1$ absorption is observed in the visible and ultraviolet regions. The most intense band at 417 nm is known to be polarized parallel to the long axis of the molecule and is assigned to the $^3B_{3g}^- \leftarrow {}^3B_{1u}^+$ transition.[14] The band in the shorter wavelength side is regarded as a vibrational structure. In the $T_n \leftarrow T_1$ absorption spectrum of *anti*-NP, a distinct peak at 447.5 nm was observed but the vibrational structure was not clear. We could not find other bands in the longer wavelength region up to 900 nm. In the spectrum of *syn*-NP, a peak was observed at 465 nm. This is similar to the band of *anti*-NP. In addition, a new broad band was observed around 612.5 nm.

In order to interpret these spectra, the LE and CT levels were also analyzed with the "molecules in molecule" method. The lowest triplet states of *anti*- and *syn*-NP's have mainly a character of $T_1$ ($^3B_{1u}^+$) of naphthalene. Froines and Hagerman showed that the phosphorescence bands of *anti*- and *syn*-NP shifted

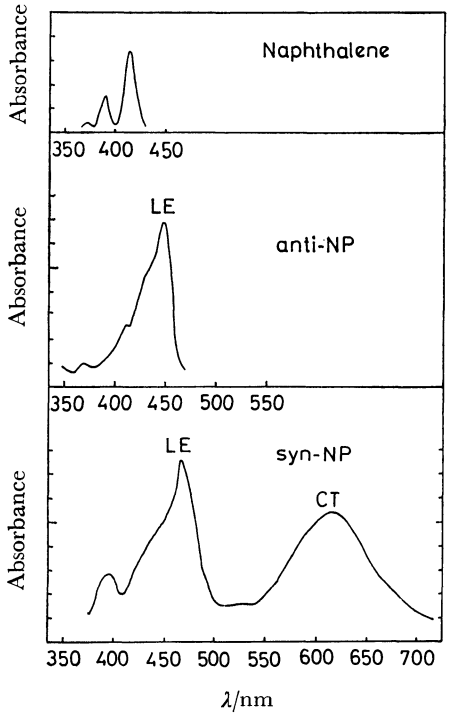


Fig. 4. The $T_n \leftarrow T_1$ absorption spectra of naphthalene, *anti*-NP, and *syn*-NP.

by 1700 $cm^{-1}$ and 2700 $cm^{-1}$, respectively, to the longer wavelength side from the monomer, 1,4-dimethylnaphthalene, and that the vibrational structures in the phosphorescence spectra of *anti*- and *syn*-NP were rather similar to the monomer's.[15] According to Hausser *et al.* the *D* value of *anti*-NP is reduced by $\approx 10\%$ with respect to 1,4-dimethylnaphthalene.[3a] Therefore, it is concluded that the CT character of $T_1$ state of NP is small.

Because of the similarity of the spectral shapes, both the $T_n \leftarrow T_1$ absorption bands of *anti*-NP at 447.5 nm and of *syn*-NP at 465 nm are attributed to the LE transitions polarized parallel to the long axes of the molecules. Their parentage is the $^3B_{3g}^- \leftarrow {}^3B_{1u}^+$ transition of naphthalene. On the other hand, we attributed the new band of *syn*-NP around 612.5 nm to the CT band ($^3B_{1u} \leftarrow {}^3B_{2g}$) polarized perpendicularly to the ring plane. The calculated energy levels of the zeroth-order CT states clearly shows that the CT band appears in the longer wavelength side of the LE band at 465 nm. The next problem is why the $T_n \leftarrow T_1$ CT band can be observed in *syn*-NP but not in *anti*-NP. The spacial overlapping of two rings is larger for *syn*-NP than for *anti*-NP. Because of this difference in the overlapping, it is expected that the interaction between the zeroth-order CT level and the zeroth-order lowest triplet LE level is larger for *syn*-NP than for *anti*-NP. This means that absorption intensity of the CT band is larger for *syn*-NP than for *anti*-NP.

Very recently, Subudhi and Lim observed the $T_n \leftarrow T_1$ absorptions of the intramolecular excimers from fluid solutions of di(1-naphthyl)alkanes.[16] The transient absorption spectrum of 1,2-di(1-naphthyl)-ethane observed 150 μs after excitation has a broad band around 470 nm , and the band is continuing up to 600 nm. The band around 470 nm may correspond to our "LE band" observed with *anti*- and *syn*-NP's. Since the LE bands are conceivably rather insensitive to the geometry of the molecule, they are observed at similar positions for *anti*- and *syn*-NP's and also for di(1-naphthyl)alkanes.

*Pyrenophane (PyP).* The $T_n \leftarrow T_1$ absorption spectra of PyP and pyrene are shown in Fig. 5. In pyrene, the $T_n \leftarrow T_1$ spectrum has a sharp band at 413 nm polarized parallel to the long axis ($^3A_g^- \leftarrow {}^3B_{1u}^+$) and another band at 518 nm polarized parallel to the short axis ($^3B_{3g}^- \leftarrow {}^3B_{1u}^+$).[17] On the other hand, the $T_n \leftarrow T_1$ absorption spectrum of PyP has three bands: a sharp band at 380 nm, a weak band at 480 nm, and a strong band at 625 nm. From the consideration of the spectral shape, the sharp band of PyP can be clearly assigned to the LE band ($^3B_{3u} \leftarrow {}^3B_{2g}$) corresponding to the 413 nm band of pyrene ($^3A_g^- \leftarrow {}^3B_{1u}^+$).

The energy separation between the two absorption peaks of pyrene is about 5000 $cm^{-1}$, and the separation between the sharp band and the weak band of PyP is 5400 $cm^{-1}$. Because of this similarity the weak band at 480 nm was assigned to the LE band ($^3A_u \leftarrow {}^3B_{2g}$) corresponding to the 518 nm band of pyrene ($^3B_{3g}^- \leftarrow {}^3B_{1u}^+$). The strong band in the red region can be assigned to the CT transition ($^3B_{1u} \leftarrow {}^3B_{2g}$). It is interesting that the CT band was clearly observed

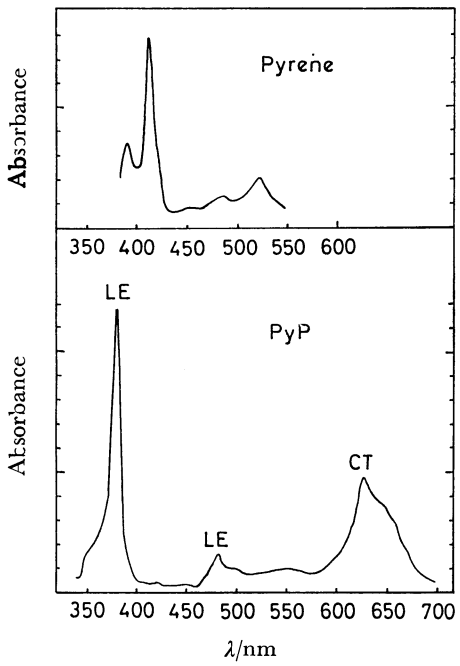


Fig. 5. The $T_n \leftarrow T_1$ absorption spectra of pyrene and PyP.

for PyP as well as for *syn*-NP. This may be due to the whole overlapping of two component subunits.

anti-, *(1,4)(9,10)-, and* syn-*AP.* We measured the $T_n \leftarrow T_1$ absorption spectra of *anti*-, (1,4)(9,10)-, and *syn*-AP by the sensitization method as mentioned in experimental section. The transient spectra observed by the method are confirmed to be the $T_n \leftarrow T_1$ spectra of AP's, since the spectra are quenched by oxygen and the observed rise times of the spectra are

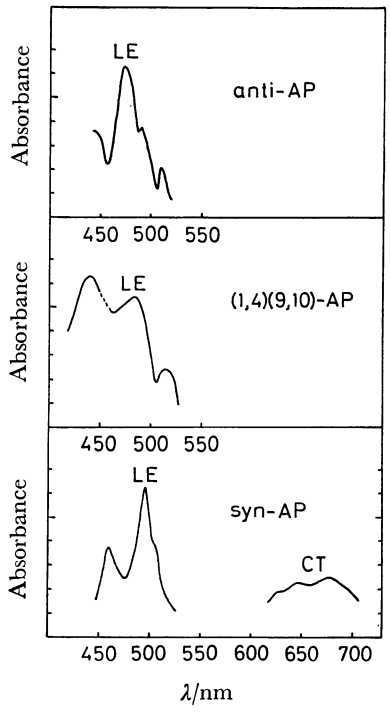


Fig. 6. The $T_n \leftarrow T_1$ absorption spectra of *anti*-, (1,4)-(9,10)-, and *syn*-AP.

well explained in terms of the fact that the related energy transfer process is diffusion controlled. The $T_n \leftarrow T_1$ absorption spectra of *anti*-, (1,4)(9,10)-, and *syn*-AP are shown in Fig. 6. $T_n \leftarrow T_1$ absorption spectra could not be observed for *anti*- and *syn*-AP in the shorter wavelength region than 450 nm, because of the ground state absorption and of scattering of the exciting light.

Anthracene shows the strong $T_n \leftarrow T_1$ absorption band at 425 nm with the polarization parallel to the long axis of the molecule ($^3B_{3g}^- \leftarrow {}^3B_{1u}^+$).[14] Contrary to the cases of NP and PyP, the $T_n \leftarrow T_1$ absorption spectra of AP cannot be interpreted from a simple analogy with the monomer. In *syn*-AP, we found a new band in the red region.

Although it is difficult to assign clearly the bands observed with the three AP's, the strong bands around 500 nm may be due to the LE transition of anthracene, in view of their positions and intensities.

From the calculation of the zeroth-order CT energy level, the CT band is expected to appear for *syn*-AP in the longer wavelength region than the LE band around 500 nm in consistence with the experimental result. The reason why the CT band is observed for *syn*-NP but not for *anti*-NP can be applied to the cases of AP's.

*Trend in* syn-*Series.* In order to elucidate the dependence of the CT interaction upon the molecular size, the spectra of *syn*-series should be compared. Figure 7 shows the correlation of triplet energy levels of *syn*-series and corresponding monomers. The lower zeroth-order CT levels presented in the columns of monomers interact with the $T_1(^3B_{1u})$ states, and the higher CT with the higher LE ($^3E_{2g}$, $^3B_{3g}$, and $^3A_g$). The energy separation between $T_1$ and $CT_1$ levels are almost the same in naphthalene, pyrene, and anthracene. In fact, in all of *syn*-NP, PyP, and *syn*-AP spectra the new CT bands are found around 600 nm.

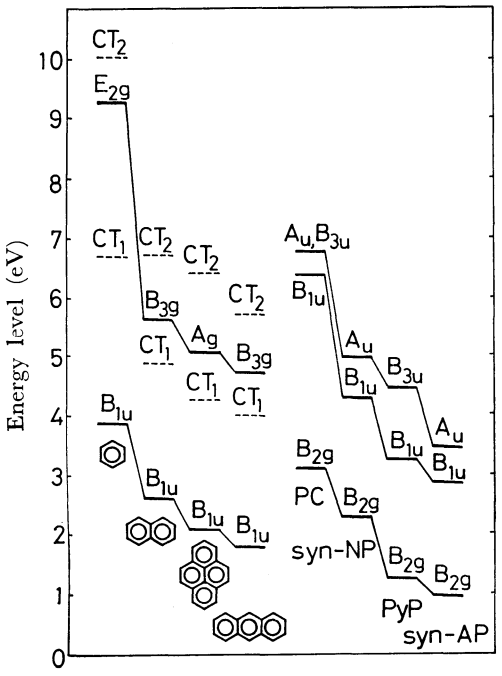


Fig. 7. Energy levels of triplet states of benzene, naphthalene, pyrene, anthracene, PC, *syn*-NP, PyP, and *syn*-AP. The zeroth-order CT levels are also presented in the columns of monomers.

## Conclusion

(1) The $T_1$ states of PC and related compounds are the neutral exciton states.
(2) Higher triplet levels of cyclophanes are well analyzed in terms of the interaction among the zeroth-order LE and CT levels.
(3) CT bands are observed for the *syn*-series : PC, *syn*-NP, PyP, and *syn*-AP in which overlapping between the aromatic rings is large.

The authors should like to express their sincere thanks to Dr. Toshihiko Hoshi, Aoyama Gakuin University, for his kind advice in preparing the polarizer film.

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