# The Electronic Spectra of Paracyclophadiynes

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The electronic absorption spectra of [3,3]-paracyclophadiyne and [4,4]-paracyclophadiyne have been investigated in solution and in the crystalline state. A *trans*-annular interaction between the diacetylene group and the benzene ring has been found, and a theoretical study has been made to confirm the assignment. The bathochromic shift and the CT band from the benzene ring to the diacetylene group are particularly noticeable for [3,3]-paracyclophadiyne, where the inter-group distance is significantly shorter than the normal van der Waals distance.

The *trans*-annular interaction between the different groups in composite molecules is a problem of great interest, because the mechanism of the electronic interaction between contact groups at close distances is not yet fully elucidated. A well-known case is that of [2,2]-paracyclophane, where a bathochromic shift of the UV absorption is observed. The CT bands of the complexes between TCNE and cyclophanes are also red-shifted by the *trans*-annular layer interaction.[1] The electronic structure and spectrum of [2,2]-paracyclophane were investigated by Vala *et al.*[2] and by Iwata *et al.*[3] and a significant change in spectrum from that of benzene was interpreted in terms of the presence of the CT transition between the benzene rings.

Recently a series of paracyclophadiynes were synthesized by Misumi and his collaborators;[4] a crystallographic study was carried out on one of these compounds in this laboratory. Each of the molecules consists of a diacetylene group and a benzene ring (Fig. 1), and the CT effect can be expected between the two groups. In this paper the electronic absorption spectra of 4,6-[10]-paracyclophadiyne ([3,3]-paracyclophadiyne) and 5,7-[12]-paracyclophadiyne ([4,4]-paracyclophadiyne) will be investigated in order to ascertain the *trans*-annular effect on the UV spectra. The inter-group CT transition is observed in [3,3]-paracyclophadiyne, while it is not found in [4,4]-paracyclophadiyne. A theoretical calculation for interpreting these spectra will be presented, and the assignment of the spectra will be presented in detail.

## Experimental

The samples of [3,3]-paracyclophadiyne and [4,4]-paracyclophadiyne were gifts from Professor Misumi of Osaka University. The absorption spectra in solution were measured by means of a Carl Zeiss spectrophotometer, PMQ II. The crystalline absorption spectra of [3,3]-paracyclophadiyne were measured by means of thin crystals obtained by sublimation. A microspectrophotometer, composed of a Carl Zeiss monochromator and an Olympus microscope, was used for the crystalline spectral measurements. The crystal structure of [3,3]-paracyclophadiyne will be described in a separate paper. The crystalline data are as follows: monoclinic; space group $P2_1/a$; $a=14.509$; $b=8.539$, $c=10.623$ Å, and $\beta=112.37°$.[5] The crystal develops the ab plane by sublimation. The thin crystal of [4,4]-paracyclophadiyne were obtained from an acetone-water solution and were used for spectral measurements. The crystalline data were obtained by oscillation and Weissenberg photographs; $a=8.441\pm0.03$, $b=13.14\pm0.03$, $c=12.73\pm0.03$ Å, $\alpha=90.4\pm0.3°$, $\beta=90.4\pm0.3°$, and $\gamma=92.8\pm0.3°$. The crystal develops the ac plane.

## Theoretical Calculations

The electronic energy levels of [3,3]-paracyclophadiyne are calculated by the molecular orbital method. The orthogonalized SCF MO for the diacetylene group, $\phi_{aj}$, and the benzene ring, $\phi_{bi}$, are calculated, and the ground configuration of the molecule is given as;

$$\Phi_0 = |\phi_{a1}(1)\cdots\bar{\phi}_{an}(2n)\phi_{b1}(2n+1)\cdots\bar{\phi}_{bm}(2n+2m)| \quad (1)$$

The excited configurations of each group will be denoted as $\Phi_{ai\to aj}$ and $\Phi_{bi\to bj}$. The singlet configuration of the charge transfer from the benzene ring to the diacetylene group may be described as;

$$\Phi_{bi\to aj} = \frac{1}{\sqrt{2}}\{|\cdots\phi_{bi}(2n+2i-1)\bar{\phi}_{aj}(2n+2i)\cdots| \pm|\cdots\phi_{aj}(2n+2i-1)\bar{\phi}_{bi}(2n+2i)\cdots|\} \quad (2)$$

The configurational energies and the matrix elements are calculated by using the Hamiltonian including the inter-group interaction:

$$\mathscr{H} = \sum_i\left\{-\frac{\hbar^2}{2\mu}\nabla_i^2 + V(\mathbf{r}_{ai}) + V(\mathbf{r}_{bi})\right\} + 1/2\sum_{i,j}e^2/r_{ij}. \quad (3)$$

The calculation of the excited energy levels is carried out by the composite molecule method. That is, the matrix elements between $\Phi_0$, $\Phi_{ai\to aj}$ and $\Phi_{bi\to aj}$ are given in the zero-differential overlap approximation as follows:

$$\begin{aligned}
(\Phi_{ai\to aj}|\mathscr{H}|\Phi_{ai\to aj}) &= E_0 + \varepsilon_{aj} - \varepsilon_{ai} - (\phi_{ai}\phi_{ai}|\phi_{aj}\phi_{aj}) + 2(\phi_{ai}\phi_{aj}|\phi_{ai}\phi_{aj})\\
(\Phi_{bi\to aj}|\mathscr{H}|\Phi_{bi\to aj}) &= E_0 + \varepsilon_{aj} - \varepsilon_{bi} - (\phi_{bi}\phi_{bi}|\phi_{aj}\phi_{aj})\\
(\Phi_{ai\to aj}|\mathscr{H}|\Phi_{ak\to al}) &= 2(\phi_{ai}\phi_{aj}|\phi_{ak}\phi_{al}) - (\phi_{ai}\phi_{ak}|\phi_{aj}\phi_{al})\\
(\Phi_{ai\to aj}|\mathscr{H}|\Phi_{bk\to bl}) &= 2(\phi_{ai}\phi_{aj}|\phi_{bk}\phi_{bl})\\
(\Phi_{ai\to bj}|\mathscr{H}|\Phi_{ak\to bl}) &= -(\phi_{ai}\phi_{ak}|\phi_{bj}\phi_{bl})\\
(\Phi_{bi\to aj}|\mathscr{H}|\Phi_0) &= -\sqrt{2}\left(\phi_{bi}\left|-\frac{\hbar^2}{2\mu}\nabla^2\right|\phi_{aj}\right)\\
(\Phi_{ai\to aj}|\mathscr{H}|\Phi_{ai\to bl}) &= -\left(\phi_{aj}\left|-\frac{\hbar^2}{2\mu}\nabla^2\right|\phi_{bl}\right)\\
(\Phi_{ai\to aj}|\mathscr{H}|\Phi_{bk\to aj}) &= \left(\phi_{ai}\left|-\frac{\hbar^2}{2\mu}\nabla^2\right|\phi_{bk}\right)\\
(\Phi_0|\mathscr{H}|\Phi_{ai\to aj}) &= (\Phi_{ai\to aj}|\mathscr{H}|\Phi_{ak\to bl}) = (\Phi_{ai\to bj}|\mathscr{H}|\Phi_{bk\to al}) = 0
\end{aligned} \quad (4)$$

Here, the intermolecular kinetic and Coulomb integrals

are exactly calculated; the molecular orbitals, $\phi_{ai}$, and the orbital energies, $\varepsilon_{ai}$, were given in a previous paper.[6] The results of the calculation are shown in Tables 1 and 2, where the polarization directions are described by the coordinates shown in Fig. 1.

It may be seen from Table 2 that the lower CT transitions are mostly of the $\phi_{bi}\rightarrow\phi_{aj}$ type, which implies that the donor property of the benzene ring exceeds that of the diacetylene group.

TABLE 1. OBSERVED AND CALCULATED TRANSITIONS OF [3,3]-PARACYCLOPHADIYNE

| State (polarization) | Calculated | | Observed | |
|---|---|---|---|---|
| | Transition energy(eV) | Oscillator strength $f$ | Transition energy(eV) | Oscillator strength $f$ |
| $A_2$ | 4.22 | forbidden | 4.10 | — |
| $B_2(y)$ | 4.34 | $2\times10^{-4}$ | 4.20 | $3\times10^{-3}$ |
| $B_1(x)$ | 4.49 | $1\times10^{-4}$ | | |
| $B_1(x)$ | 4.80 | $1\times10^{-4}$ | | |
| $B_2(y)$ | 4.88 | $1\times10^{-3}$ | | |
| $B_2(y)$ | 5.69 | $6\times10^{-3}$ | 5.27 | $3\times10^{-2}$ |
| $B_1(x)$ | 5.75 | $2\times10^{-2}$ | | |
| $B_2(y)$ | 5.78 | $3\times10^{-2}$ | | |
| $A_1(z)$ | 5.97 | $1\times10^{-3}$ | | |

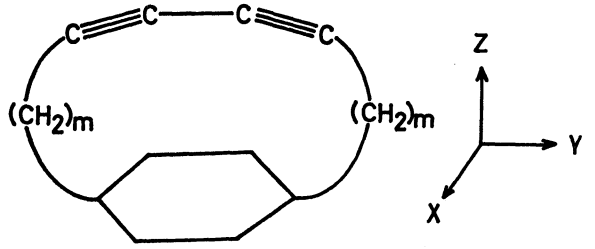


Fig. 1. The shape of [*m*,*m*]-paracyclophadiyne and the coordinate axes.

## Results and Discussion

*[4,4]-Paracyclophadiyne.* The electronic absorption spectrum in solution is shown in Fig. 2, while that in a crystal is shown in Fig. 3. The spectra are considered to be superpositions of those of the two chromophores, the benzene and diacetylene groups, and a red shift of the $^1E_{1u}$-type band of benzene is observed. In the crystalline spectra, the weakest $^1A_{1u}$-type band of the diacetylene group is observed in the 33500—35500 $cm^{-1}$ region, and the second transition, starting at 36700 $cm^{-1}$, may be reasonably correlated with the band at 38500 $cm^{-1}$ of the diacetylene group, because it shows the vibrational progressions characteristic of the diacetylene group. Overlapping with this band series, the $^1B_{2u}$ parentage band of the benzene ring may exist in this region. Since the crystal structure is not known for this molecule, an extensive argument on the polarization and assignment can not be developed, but the band at 44500 $cm^{-1}$ may be regarded as originating from the $^1E_{1u}$ level of the benzene group. The red shift of this band as compared to that of benzene may be caused by the CT-type interaction, which indicates that the level may be located in the higher energy region. The

TABLE 2. WAVE FUNCTIONS FOR THE SINGLET ELECTRONIC STATES OF [3,3]-PARACYCLOPHADIYNE

$A_1$ type state

| Energy(eV) | $\Phi_0$ | $\Phi_{b_3\rightarrow a_3^*}$ | $\Phi_{a_2^*\rightarrow b_4}$ |
|---|---|---|---|
| 0.00 | 0.9999 | 0.0053 | −0.0141 |
| 5.01 | −0.0052 | 0.9999 | 0.0009 |
| 5.97 | −0.0141 | 0.0008 | −0.0141 |

$A_2$ type state

| Energy(eV) | $\Phi_{a_2\rightarrow a_3^*}$ | $\Phi_{a_2^*\rightarrow a_3}$ | $\Phi_{b_2\rightarrow a_3^*}$ | $\Phi_{a_2^*\rightarrow b_5}$ |
|---|---|---|---|---|
| 4.22 | 0.7332 | −0.6605 | 0.1611 | 0.0104 |
| 4.70 | 0.6188 | 0.7463 | 0.2445 | 0.0170 |
| 5.37 | −0.2818 | −0.0795 | 0.9562 | 0.0048 |
| 5.78 | 0.0042 | 0.0199 | −0.0021 | 0.9998 |

$B_1$ type state

| Energy(eV) | $\Phi_{b_2\rightarrow b_4}$ | $\Phi_{b_3\rightarrow b_5}$ | $\Phi_{b_3\rightarrow a_3}$ | $\Phi_{a_2\rightarrow b_4}$ |
|---|---|---|---|---|
| 4.49 | 0.7069 | 0.6874 | −0·0306 | 0.1639 |
| 4.80 | 0.0299 | 0.0101 | 0.9994 | 0.0150 |
| 5.75 | −0.0062 | 0.2384 | 0.0123 | −0.9711 |
| 6.48 | 0.7067 | −0.6859 | −0.0116 | −0.1731 |

$B_2$ type state

| Energy(eV) | $\Phi_{b_2\rightarrow b_5}$ | $\Phi_{b_3\rightarrow b_4}$ | $\Phi_{a_2\rightarrow a_3}$ | $\Phi_{a_2^*\rightarrow a_3^*}$ | $\Phi_{b_2\rightarrow a_3}$ | $\Phi_{a_2\rightarrow b_5}$ |
|---|---|---|---|---|---|---|
| 4.34 | 0.0072 | 0.0003 | −0.6957 | 0.6839 | −0.2192 | 0.0152 |
| 4.88 | 0.0513 | −0.0025 | 0.1229 | −0.1878 | −0.9729 | 0.0206 |
| 5.69 | 0.4789 | −0.2983 | −0.0162 | −0.0249 | 0.0462 | 0.8238 |
| 5.78 | −0.4779 | 0.6992 | −0.0122 | −0.0236 | −0.0128 | 0.5308 |
| 6.44 | 0.7147 | 0.6309 | −0.1625 | −0.1555 | 0.0414 | −0.1973 |
| 9.37 | 0.1696 | 0.1550 | 0.6885 | 0.6868 | −0.0372 | −0.0062 |

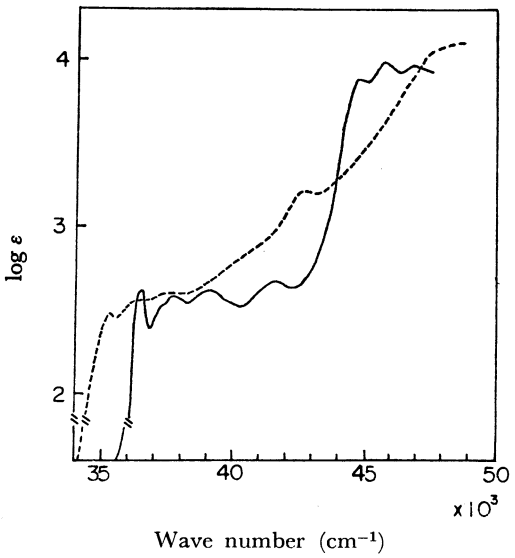


Fig. 2. The UV absorption spectra of
---- [3,3]-paracyclophadiyne and
—— [4,4]-paracyclophadiyne.

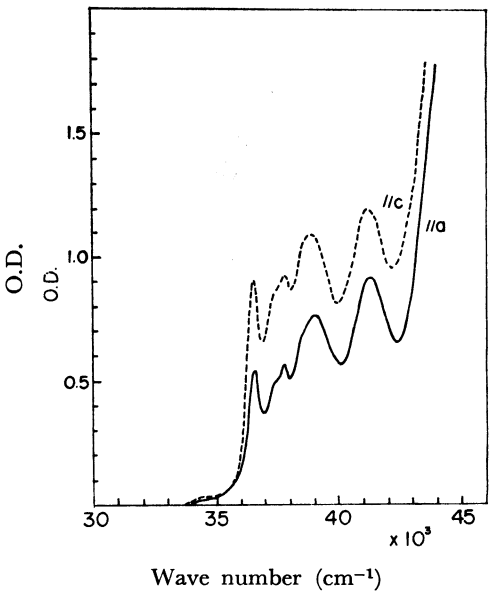


Fig. 3. The crystalline UV absorption spectra of [4,4]-paracyclophadiyne with (010) plane.

inter-group distance, separated by four methylene groups, will be larger than 3.3 Å, and the electronic overlap between the groups is not so effective that the CT transition may not appear at lower energies with a noticeable intensity.

*[3,3]-Paracyclophadiyne.* In the solution spectra of [3,3]-paracyclophadiyne (Fig. 2), a bathochromic shift of the UV absorption is apparent. The first absorption band in the 34500—37500 $cm^{-1}$ region may be related to the diacetylene group,[6] but the transition to the $^1B_{2u}$ state of the benzene ring may overlap in this region. In the crystalline spectra (Fig. 4), a broad band with vibrational structures are observed in the 33500—37000 $cm^{-1}$ region, and the band intensities along the a- and b-axes are nearly the same throughout this spectral region. These results seem consistent with

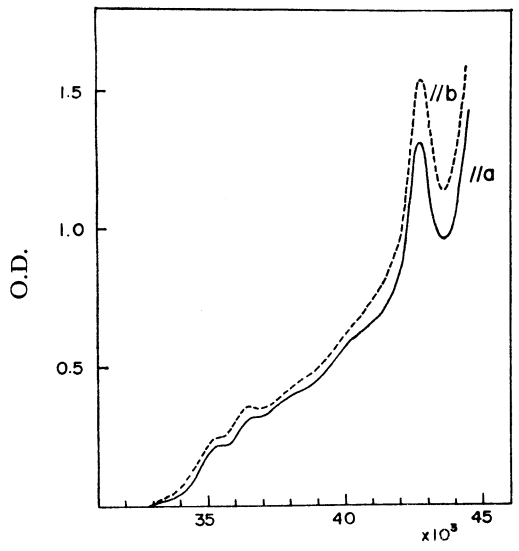


Fig. 4. The crystalline UV absorption spectra of [3,3]-paracyclophadiyne with (001) plane.

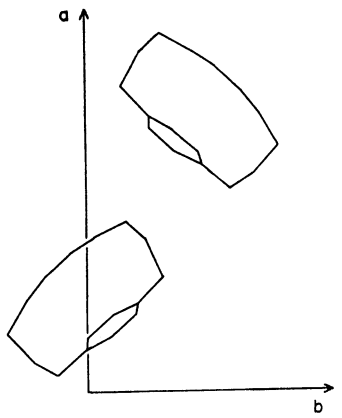


Fig. 5. The projection of [3,3]-paracyclophadiyne onto the (001) plane.

the assignment of the $^1B_2(y)$-type transition, since the crystal structure analysis shows that the y-polarized band should give a nearly equal intensity along the a- and b-axes. If the $^1B_{2u}$-type transition of the benzene ring dominates in this region, the intensity should be predominant along the b-axis rather than distributed equally between the two axes; hence, the contribution of the $^1B_{2u}$-type band may not be so significant in the 38500—40000 $cm^{-1}$ region.

Several CT transitions from the benzene ring to the diacetylene group are calculated to exist in this region, although they have weak intensities. In the shorter-wavelength region, a sharp prominent transition is observed at 42700 $cm^{-1}$; it is an extra band not belonging to either of the component chromophores. Following the theoretical calculation, a CT transition of the $^1B_2(y)$ type may be responsible for this transition, in which the charge transfer from the benzene ring to the diacetylene group is predominant. The polarization characteristic of this transition is that of the y-axis. However, the direction of the transition moment could

not unambiguously be determined by the observed polarization ratio ($I_b/I_a$), because the possibility of z polarization still remains to be solved.

According to the crystal-structure analysis, the inteatomic distances between the diacetylene group and the benzene-ring plane are in the range of 3.1—3.2 Å; a significant electronic interaction can be expected at such a short interatomic distance. Although the CT transition does not appear with strong intensities in the near UV region, the spectrum shows a bathochromic shift of the first band as large as 1300 $cm^{-1}$, in contrast to the case of [4,4]-paracyclophadiyne. The vibrational structure of the band is also blurred off. Moreover, the $^1E_{1u}$-type band of the benzene ring is blue-shifted in contrast to [4,4]-paracyclophadiyne because of the presence of the CT state at 42700 $cm^{-1}$, below the original position of the $^1E_{1u}$ level. The influence of the CT transition is thus shown to be important in determining the spectral properties of the system, with chromophores interacting through *trans*-annular interactions.

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