The Electronic Spectra of Diphenylacetylene and 1,3-Butadiyne

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The electronic absorption spectra of 2,4-hexadiyne-1,6-diol, diphenylacetylene, and diphenyldiacetylene were measured in a single crystalline state with a polarized light. The results of the polarization measurement and the theoretical calculations gave confirmative assignments of the electronic transitions of these molecules.

The electronic structures and electronic spectra of acetylene and poly-acetylenes have previously been investigated and have attracted considerable attention because of the simple molecular structures and the diveristy of electronic energy levels. Earlier extensive investigations of acetylene by Ingold *et al.*[1] and Innes[2] have revealed that the shape of the molecule in the excited state is not linear. The assignments of the electronic transitions of acetylene and poly-acetylenes have been discussed by many people.[3–9] The electronic spectra of diacetylene were studied by Woo and Chu[7] and by Price and Walsh,[8] and the bending of the excited state was suggested. Beer[9] investigated poly-acetylenes and classified the excited levels on the basis of the intensities of the electronic bands and the phosphorescence spectra. The polarization of band was measured on the crystal of dimethyldiacetylene, but the details of the analysis have not appeared. In this paper the polarization measurements in the near UV region of the derivatives of diacetylene, 2,4-hexadiyne-1,6-diol, diphenylacetylene and diphenyldiacetylene will be reported. The theoretical calculations of the energy levels of diacetylene and diphenylacetylene will also be presented in order to explain the observed spectra.

Experimental

2,4-Hexadiyne-1,6-diol was synthesized from propargyl alcohol.[10] The crystal for spectral measurements was obtained from a chloroform solution, and it was developed on the ac plane. The crystalline data will be reported in the Appendix. The projection of the molecules on the ac plane is shown in Fig. 1. The diphenylacetylene was obtained from the Tokyo Kasei Co. and was purified by recrystallization from methanol. The thin crystals for spectral measurement were obtained by sublimation; they were developed on the ab plane. The crystal structure was analyzed by Robertson and Woodward.[11] The diphenyldiacetylene was synthesized from phenylacetylene and was recrystallized from acetic acid. The crystal structure was analyzed by Wiebenga.[13] The crystalline absorption measurements were done with a microspectrophotometer.

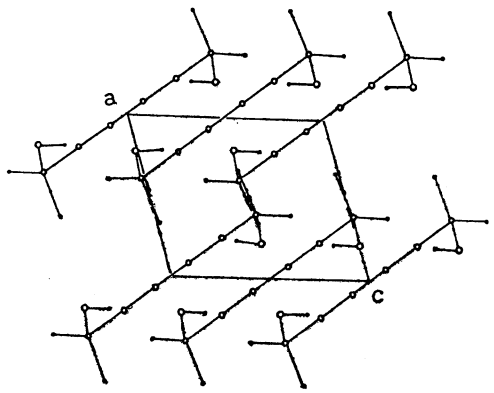


Fig. 1. Projection of 2,4-hexadiyne-1,6-diol crystal onto the ac plane.

Theoretical Calculations

The electronic energy levels of the diacetylene group and diphenylacetylene were calculated by a modification of the Pariser-Parr-Pople method, in which all the π and $\bar{\pi}$ electrons in the triple bonds are considered. The orthogonal MO sets, composed of $2p\pi$ and $2p\bar{\pi}$ atomic orbitals of carbon atoms, are calculated by the SCF method. The Hartree-Fock matrix elements are given as;

$$\begin{aligned}(\pi_\mu|\mathbf{F}|\pi_\mu) &= W_\mu + (\pi_\mu\pi_\mu|\pi_\mu\pi_{\mu'}) - \sum_{\nu}^{m}(\pi_\nu\pi_\nu|\pi_\mu\pi_{\mu'}) \\ &\quad - \sum_{\eta}^{n}(\bar{\pi}_\eta\bar{\pi}_\eta|\pi_\mu\pi_\mu) \\ &\quad + \sum_{\nu}^{m}\sum_{j}^{m}\{2C^*_{j\nu}C_{j\nu}(\pi_\nu\pi_\nu|\pi_\mu\pi_\mu) - C^*_{j\mu}C_{j\mu}(\pi_\mu\pi_\nu|\pi_\mu\pi_\nu)\} \\ &\quad + \sum_{\eta}^{n}\sum_{j}^{m}\{2C^*_{j\eta}C_{j\eta}(\bar{\pi}_\eta\bar{\pi}_\eta|\pi_\mu\pi_\mu) - C^*_{j\mu}C_{j\mu}(\bar{\pi}_\eta\pi_\mu|\bar{\pi}_\eta\pi_\mu)\} \\ (\pi_\mu|\mathbf{F}|\pi_\nu) &= \beta_{\mu\nu} - \sum_{j}^{m}C^*_{j\mu}C_{j\nu}(\pi_\mu\pi_\mu|\pi_\nu\pi_\nu) \\ (\pi_\mu|\mathbf{F}|\bar{\pi}_\eta) &= 0 \end{aligned} \quad (1)$$

where the subscript j denotes the filled MO, which varies from 1 to m, and where μ, ν, and η designate carbon atoms with orthogonal $2p\pi$ orbitals, π and $\bar{\pi}$. The one-electron Coulomb integrals are taken as:

$$(\pi_\mu\pi_\mu|\pi_\mu\pi_\mu) = (\bar{\pi}_\mu\bar{\pi}_\mu|\bar{\pi}_\mu\bar{\pi}_\mu) = 10.53\ \text{eV}$$

and

$$(\pi_\mu\pi_\mu|\bar{\pi}_\mu\bar{\pi}_\mu) = (\pi_\mu\pi_\mu|\pi_\mu\pi_\mu) - 1/2(\pi_\mu\bar{\pi}_\mu|\pi_\mu\bar{\pi}_\mu)$$

where

$$(\pi_\mu\bar{\pi}_\mu|\pi_\mu\bar{\pi}_\mu) = 0.91\ \text{eV}.$$

The valence-state ionization potential, W_p, is taken as -11.24 eV for the sp hybridized state and as -11.22 eV for the sp^2 hybridized state. The resonance integrals, β, were taken only for nearest neighbors; they were calculated by

$$\beta = -2.38\exp(2.375 - 1.7r)\ \text{eV}.$$

All the calculations were based on the structure data determined by the X-ray crystal analysis. The configurational interaction of one-electron excited states were calculated with the SCF MO. The calculation for diphenylacetylene was performed similarly. The

Table 1. Transition energies of diacetylene

State	Calculated values			Experimental values		
	Transition energy (eV)	Oscillator strength f	Dichroic ratio $I_{//c}/I_{\perp c}$	Transition energy (eV)	Oscillator strength f	Dichroic ratio $I_{//c}/I_{\perp c}$
$^1A_{1u}$	4.41	forbidden		4.25	2×10^{-5}	1.1
$^1E_{2u}$	4.73	forbidden	1.63 (long-axis)	4.77	1×10^{-3}	1.5
$^1A_{2u}$	9.44	2.93		—	—	—
$^3A_{2u}$	3.42	forbidden		3.39[9]	—	—

Table 2. Molecular orbitals and state function of diacetylene

ε (eV)	j, j'	$c_{j\mu}=c_{j\mu'}$	
		$\mu=1$	2
−14.06	1	0.4236	0.5662
−11.32	2	0.5662	0.4236
−1.56	3	0.5662	−0.4236
1.18	4	0.4236	−0.5662

$^1A_{1u}$: $1/\sqrt{2}\{\psi_{2\to3'}-\psi_{2'\to3}\}$
$^1E_{2u}$: $1/2\{\psi_{2\to3'}+\psi_{2'\to3}+\psi_{2\to3}-\psi_{2'\to3'}\}$
$1/2\{\psi_{2\to3'}+\psi_{2'\to3}-\psi_{2\to3}+\psi_{2'\to3'}\}$
$^1A_{2u}$: $1/\sqrt{2}\{\psi_{2\to3}+\psi_{2'\to3'}\}$

Table 3. Transition energies of diphenylacetylene

State	Sym-metry	Calculated values		Experimental values	
		Transition energy (eV)	Oscillator strength f	Transition energy (eV)	Oscillator strength f
$^1B_{2u}$	y	4.20	1.50	4.21	0.66
$^1B_{3u}$	x	6.10	0.93	5.66	0.40
$^1B_{2u}$	y	6.40	0.82	6.30	—

results gave the transition energies and oscillator strengths shown in Tables 1 and 2. The observed spectral data are also shown there.

Results and Discussion

2,4-Hexadiyne-1,6-diol. The electronic absorption spectra in an ethanol solution are shown in Fig. 2. Two different series of absorption bands have been observed, one with a very weak intensity in the 30000—37000 cm^{-1} region and another with a medium intensity in the 37000—48000 cm^{-1} region. Both series are accompanied by vibrational progressions of 2200—2300 cm^{-1}, which can reasonably be correlated with the total symmetric vibration of the triple bonds. Because the intensities of these bands are rather weak, both series may be regarded as having a forbidden character.

The crystalline absorption spectra on the ac plane are presented in Fig. 3. Although the 0-0 band origin was not confirmed for this spectra, nevertheless the spectral pattern was clearly resolved, showing some vibrational progressions. The weakest and lowest transition starts at 30400 cm^{-1} and extends to 37000 cm^{-1}. The two band maxima at 33900 and 36100 cm^{-1} are separated by 2200 cm^{-1}, which is regarded as the total

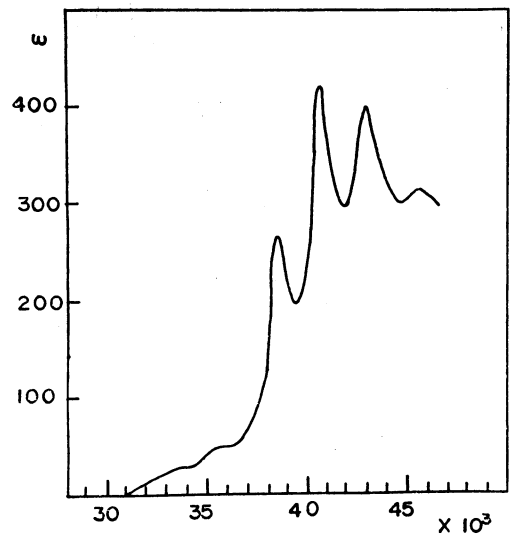


Fig. 2. Electronic absorption spectrum of 2,4-hexadiyne-1,6-diol in ethanol solution measured with Carl Zeiss spectrophotometer PMQ-II.

symmetric stretching vibration of the carbon-carbon triple bond. Taking the 0-0 band origin of the series as at 30400 cm^{-1}, one may suppose the presence of a coupled asymmetric mode which makes the forbidden transition active. For instance, the first vibronic allowed level may be assumed at 31700 cm^{-1}; therefore, a coupled frequency must be about 1300 cm^{-1} at its maximum.

The second, stronger series starts at 38500 cm^{-1}, followed by the vibrational progressions given by $38500+2200n$ cm^{-1} ($n=1,2,\cdots$). The dichroic intensity ratios for these two band series are estimated by taking the intensity ratio from the areas of these observed bands; they are tabulated in Table 1. The calculated value (1.63) is obtained from the crystal structure data by assuming that the electronic transitions are polarized parallel to the long axis of the molecule. With the second stronger transition, the observed value (1.5) is in good agreement with the predicted value of the long-axis polarization. For the first band, the polarization seems to be along the short-axis, because the observed intensity ratio (1.1) deviates from the value of the long-axis. As regards the transition polarized perpendicular to the long-axis, the direction could not be determined in $D_{\infty h}$ symmetry, but the dissimilar polarization ratio may be considered as proof of a different polarization character.

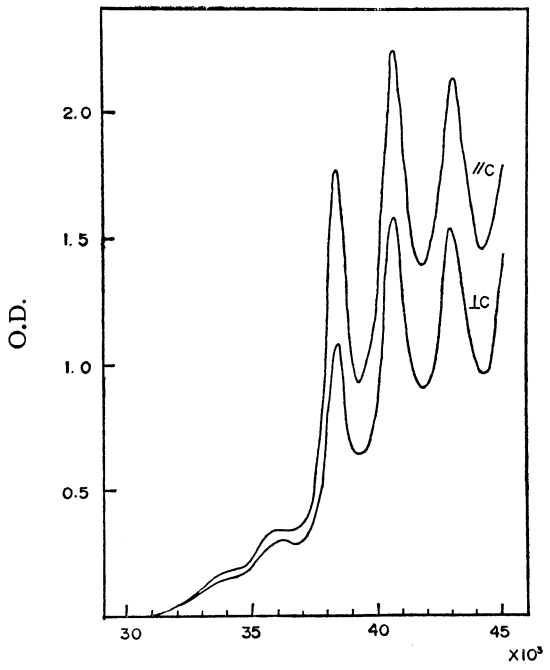


Fig. 3. Crystalline absorption spectra of 2,4-hexadiyne-1,6-diol for ac plane with the light polarized parallel and perpendicular to the c-axis.

Following the results of the theoretical calculations, the first forbidden band is assigned to the $^1A_{1u}$ state; it is shown that the transition is a $\pi \rightarrow \bar{\pi}^*$ type and is strictly forbidden. In the symmetry of the $D_{\infty h}$ of the linear system, the band is not active and it should appear when the excited state is deformed to the *trans*-form and/or when the molecule is coupled with the e_{1g}-type vibration. The vibronic analysis suggests that the observed vibronic excited state may be bent by a coupling with an asymmetric vibrational mode.

The second band is assigned to the transition to the $^1E_{2u}$ state, which is also forbidden but which has a mixed character of $\pi \rightarrow \pi^*$ and $\pi \rightarrow \bar{\pi}^*$-type transitions. The calculated energy values are in good agreement with the observed value. The $^1E_{2u}$ state of the linear system is changed to the ^1B_u state in the *trans*-form and to the $^1B_1$ state in the *cis*-form. The transition to these states will be allowed along the direction of the triple bond.[3-9] The presence of two band systems in the near UV region is in good agreement with the results of Woo and Chu,[7] who found a very weak system at 33700—37730 cm^{-1} and a diffuse and stronger band in the 38460 cm^{-1} region.

The results of polarization measurements on the crystalline spectra are in good agreement with the theoretical predictions of the transition directions. Thus, the assignments have been established for the first and second bands.

Diphenylacetylene. The UV spectrum in the ethanol solution is shown in Fig. 2. The first absorption band, starting at 33800 cm^{-1}, shows vibrational progressions of 2000 cm^{-1} and 950 cm^{-1}. The former is regarded as a totally symmetric vibration of the

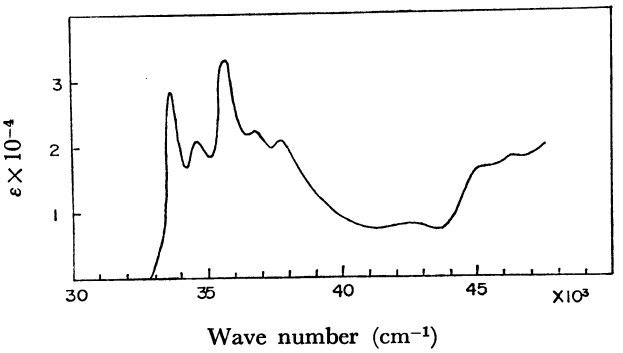


Fig. 4. Electronic absorption spectrum of diphenylacetylene in ethanol solution.

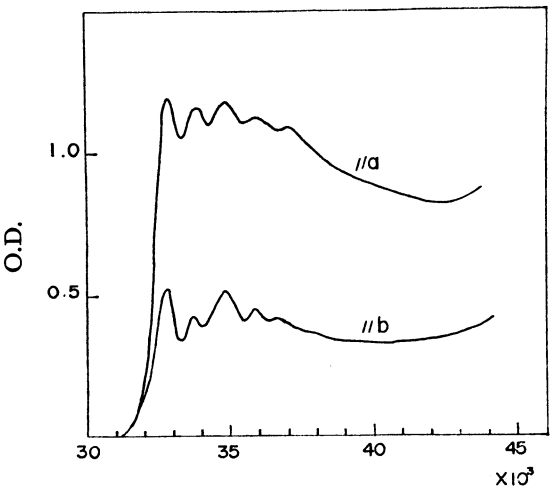


Fig. 5. Crystalline absorption spectra of diphenylacetylene for ab plane with the light polarized parallel to the a- and b-axes.

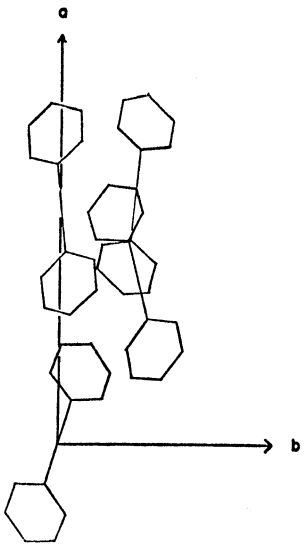
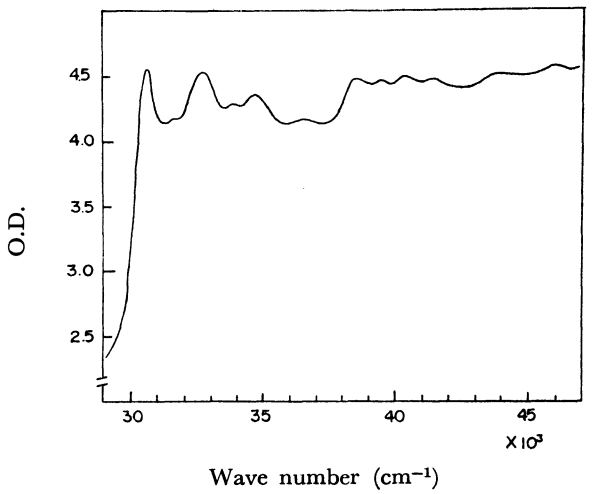


Fig. 6. Projection of diphenylacetylene in crystal onto the ab plane.

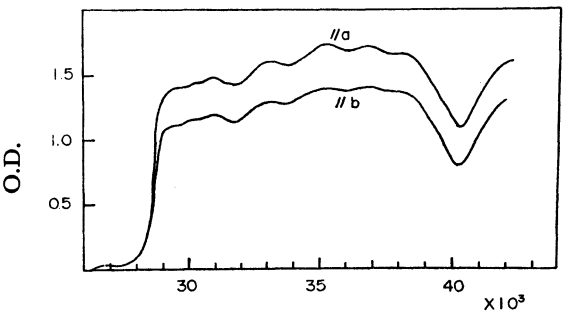
carbon-carbon triple bond, while the latter may be a vibration of the benzene ring. The results of the calculation show that the first band is the long-axis-polarized allowed transition. The crystalline absorption spectra are shown in Fig. 5. While the projection of molecules onto the developed ab plane is illustrated in Fig. 6. The intensity ratio observed on the crystalline spectra can reasonably be explained by the oriented gas model, and the first absorption band has been shown to be polarized parallel to the long-axis. These results support the earlier investigation by Mikailenko *et al.*[12] of the polarization study of the fluorescence.

Diphenyldiacetylene: The UV spectrum in the ethanol solution is shown in Fig. 7. The observed bands are very broad, and they seem to be composed of two or three band series starting at 30700 cm^{-1} and at 38500 cm^{-1}. The crystalline spectra are recorded with the ab plane, as is shown in Fig. 8. Following the crystalline structure data of Wiebenga,[13] the projection of molecules onto the ab plane is shown in Fig. 9. It will be easily found that the long-axis of the molecule is slightly more inclined to the a-axis than to the b-axis, and that the intensity ratio by the oriented gas model is $I_a/I_b=$ 1.4 : 1, while the observed value is 1.25 : 1 for both the first and second bands. Those results show that the polarization of the first and second bands are both along the long-axis.



Wave number (cm^{-1})

Fig. 7. Electronic absorption spectrum of diphenyldiacetylene in ethanol solution.



Wave number (cm^{-1})

Fig. 8. Crystalline absorption spectra of diphenyldiacetylene for ab plane with the light polarized parallel to the a- and b-axes.

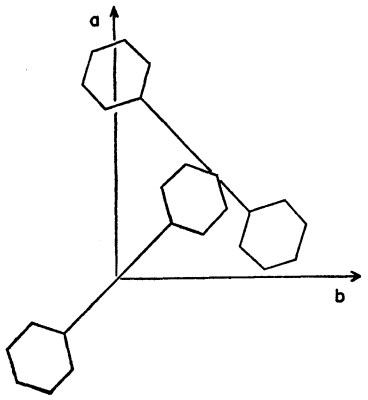


Fig. 9. Projection of diphenyldiacetylene molecules to the ab plane in the crystal.

Appendix

Crystalline Data of 2,4-Hexadiyne-1,6-diol. After the completion of our crystalline structure analysis, we found that an independent research has already been published.[14] However, the atomic coordinates were not given, and so we briefly describe our own results.

Crystal Data. From Weissenberg photographs and single-crystal diffractometry on a Hilger-Watt Four-circle diffractometer with Cu$K\alpha$, $\lambda=1.5418$ Å, $a=4.083(1)$, $b=16.000(1)$, $c=4.764(1)$ Å, $\beta=106.3°$, $Z=2$. $d_{obsd}=1.14$ g/cm³, and $d_{calcd}=1.19$ g/cm³. Space group $P2_1/c$. When the intensity data were collected on the diffractometer, 360 independent reflections were obtained. The data were corrected by the Lorentz and polarization factors. The absorption correction was not applied since the crystal size was so small as $0.1\times0.5\times$ 1 mm. The center of the molecule is coincident with the origin of the crystal for symmetry reasons. The molecule is linear, and the direction of the molecular axis can easily be found in the Patterson map. The refinement of the structure was performed by the block-diagonal least-squares method and by Fourier synthesis. A program of the UNICS written by Dr. Ashida was employed. The calculation was performed on the Hitac 5020 at Computer Centre, the University of Tokyo. The final R-index including hydrogen atoms was 0.107.

Atomic coordinates.

	x / a	y / b	z / c
C1	0.0814	0.0286	0.1083
C2	0.2235	0.0759	0.2883
C3	0.4094	0.1367	0.5144
O1	0.2133	0.2108	0.5057
H1	0.3970	0.1073	0.6755
H2	0.6669	0.1545	0.4664
H3	0.2178	0.2389	0.3716

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