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Electronic States of the 4,4′-Dinitrobiphenyl-Benzidine Complex

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Synopsis. The charge transfer complex composed of 4,4′-dinitrobiphenyl and benzidine was studied by measuring and analyzing the UV crystalline spectra. The deep coloration of this complex was found to be due to the charge transfer bands appearing at 21000 and 25000 cm^{-1}, while the long axes of the component molecules are known to be perpendicular to each other.

Common electron donor-acceptor complexes crystallize in the plane-to-plane stacking of the molecules and are much more deeply colored than the component compounds. Nevertheless, 4,4′-dinitrobiphenyl has been known to form a complex with benzidine in a stack in which the 4,4′-dinitrobiphenyl molecules is arranged at right angles to each benzidine molecule and the complex becomes deeply red in color while the component molecules are light yellow.[1,2] Therefore, it is very interesting to determine whether or not the deep coloration of this complex is due to the appearance of broad, weak charge-transfer absorption. The author measured the polarized reflection and absorption spectra of the complex crystal and analyzed them theoretically.

Experimental and Theoretical

Single crystals of the complex were kindly supplied by the Research Institute for Polymers and Textiles. The crystals showed developed planes of (100) and (101). These planes were identified by X-ray examination. The reflection spectra at normal incidence and the transmission spectra were measured with spectrophotometers constructed in this laboratory. The absorption spectra obtained by the Kramers-Kronig[3] transformation of the reflection spectra are shown in Fig. 2 and the polarized transmission spectra in Fig. 3.

As Davydov splitting was not observed in these spectra, exciton treatment was not developed in this study and the electronic energy levels of the complex were calculated assuming a 1:1 dimer type complex of 4,4′-dinitrobiphenyl and benzidine molecules, although the actual composition is 4:1. The calculation of the dimer were made by taking into account the configuration interaction between the ground (Φ_0), locally-excited (LE; $\Phi_{at\to aj}$) and charge-transfer (CT; $\Phi_{at\to bj}$) configurations. These matrix elements were estimated in the zero differential overlap approximation, except for the elements between the Φ_0 and $\Phi_{at\to bj}$ configurations,[4]

$$(\Phi_0|H|\Phi_{at\to bj}) = -\sqrt{2}K(\phi_a{}^i|\phi_b{}^j)$$

where K is a constant and was taken to be 10.0. The atomic Coulomb integrals were estimated by the Nishimoto-Mataga method.

The molecular orbitals ϕ_a^i and the orbital energies were given using the PPP approximation. The results of the calculation are shown in Table 1.

The computation was carried out on the Facom 230-60 computer at the Nagoya University Computation Center.

Results and Discussion

Crystals of the 4,4′-dinitrobiphenyl–benzidine complex belong to the C_c space group.[5] The unit cell contains four of the complex groups $[O_2N\cdot C_6H_4\cdot C_6H_4\cdot NO_2]_4\cdot[H_2N\cdot C_6H_4\cdot C_6H_4\cdot NH_2]$. Figure 1 shows a projection of the unit cell along b on to the ac plane. The benzidine molecules lie along b and are thus seen end-on. Each dinitrobiphenyl molecule shown on the projection represents four molecules lying parallel to one another and separated by $(1/4)b$ or 3.7 Å. These dinitrobiphenyl molecules must all lie with their long axes very nearly on the $(40\bar{2})$ planes, while the benzidine molecules must lie almost wholly on these planes.

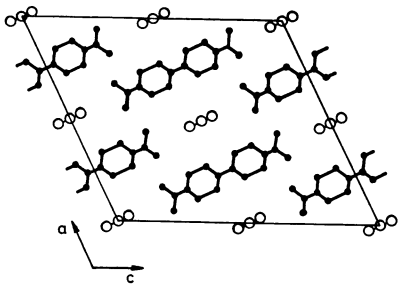

Fig. 1. A projection of the unit cell along b on to the ac plane.

Figure 2 shows the polarized absorption spectra of the crystal obtained by K-K analysis of the reflection spectra. In the b-axis spectrum, the long-axis polarized state of benzidine is located at about 32000 cm^{-1}. The long-axis state of 4,4′-dinitrobiphenyl is observed at

Table 1. Calculated transition energies, intensities and wavefunctions of the 4,4′-dinitrobiphenyl–benzidine complex

Obsd ΔE (cm^{-1})	Obsd ΔE (cm^{-1})	Obsd f	Calcd Wave functions[a]
21000	21870	0.00	$0.9968\ \Phi(\phi_2{}^8\to\phi_1{}^{11}) + 0.0711\ \Phi(\phi_2{}^8\to\phi_1{}^{13})+\cdots$
25000	24700	0.00	$0.9994\ \Phi(\phi_2{}^8\to\phi_1{}^{12}) - 0.0275\ \Phi(\phi_2{}^6\to\phi_1{}^{12})+\cdots$
29000	29200	0.27	$0.7532\ \Phi(\phi_1{}^{10}\to\phi_1{}^{11}) + 0.6528\ \Phi(\phi_2{}^7\to\phi_1{}^{11})+\cdots$
	30300	0.21	$0.6561\ \Phi(\phi_1{}^{10}\to\phi_1{}^{11}) - 0.7368\ \Phi(\phi_2{}^7\to\phi_1{}^{11})+\cdots$
32000	32400	0.52	$0.9199\ \Phi(\phi_2{}^8\to\phi_2{}^9) + 0.2789\ \Phi(\phi_2{}^6\to\phi_1{}^{12}) - 0.1874\ \Phi(\phi_1{}^8\to\phi_1{}^{12})+\cdots$

a) $\phi_1{}^i$ indicates the i-th MO of the 4,4′-dinitrobiphenyl molecule and $\phi_2{}^j$ the j-th MO of the benzidine molecule.

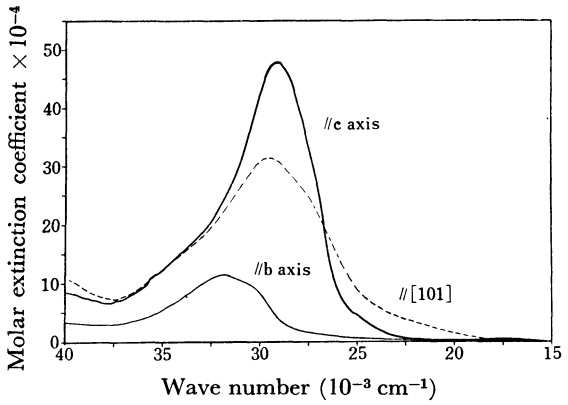

Fig. 2. The polarized absorption spectra of the crystal obtained by the Kramers-Kronig analysis of the reflection spectra.

29000 cm^{-1} in the c- and [101]-axis spectra. Two broad, weak shoulders occur in the vicinity of 17500 to 25000 cm^{-1} in the [101]-axis spectrum.

Figure 3 shows the polarized absorption spectra of the crystal obtained by the transmission method. Two peaks are observed at 21000 and 25000 cm^{-1} in the [101]-axis spectrum.

Table 1 shows that the first and second bands at about 21000 and 25000 cm^{-1} are assigned to the CT bands from the occupied MO of the benzidine molecule

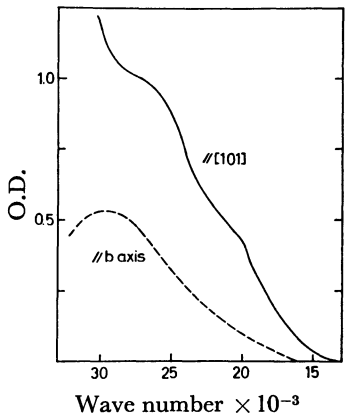

Fig. 3. The polarized absorption spectra of the crystal obtained by the transmission method.

to the vacant MO of the dinitrobiphenyl molecule. As these CT configurations do not mix strongly with the ground and LE configurations, the absorption intensities to these CT states are nearly forbidden and weak, as is shown in Figs. 2 and 3. In the third and fourth states, the large mixing between the LE configuration $\Phi(\phi_1^{10} \rightarrow \phi_1^{11})$ of the dinitrobiphenyl molecule and the CT configuration $\Phi(\phi_2^{7} \rightarrow \phi_1^{10})$ from the occupied MO of benzidine to the vacant MO of dinitrobiphenyl is due to the nearly degenerate configuration energies and the transition moments of these states depend mainly on the transition moments of the LE configuration $\Phi(\phi_1^{10} \rightarrow \phi_1^{11})$ of the dinitrobiphenyl molecule. The LE configuration $\Phi(\phi_1^{10} \rightarrow \phi_1^{11})$ is polarized parallel to the long axis of the dinitrobiphenyl molecule. Therefore, the 29000-cm^{-1} band observed in the c- and [101]-axis spectra may be assigned to the long-axis state of dinitrobiphenyl. The fifth state consists of the LE configuration $\Phi(\phi_2^{8} \rightarrow \phi_2^{9})$ polarized parallel to the long axis of the benzidine molecule and the 32000-cm^{-1} band in the c-axis spectrum can be assigned to the long-axis state of benzidine.

In the ground state, mixing with the charge-transfer configurations is small and the stabilization of the ground state appears to be due to the quadrupole interaction rather than to the charge-transfer and polarization effects. Accordingly, this dinitrobiphenyl–benzidine complex forms an inclusion compound and can be crystallized in various molecular ratios.

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