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Perylene-Hexacyanobutadiene (HCBD) Complex

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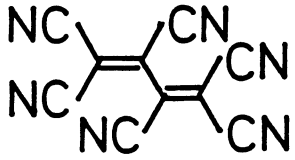
Hexacyanobutadiene (HCBD) gives dark red single crystals with equimolar perylene. The crystal structure analysis shows that the complex has mixed regular stacks. The physical properties of the single crystals indicate that the complex is an insulator with neutral ground state and close to neutral-ionic boundary.

Up to now only a few solid CT-complexes of HCBD have been reported on their physical and structural properties since the first synthesis of this strong acceptor in 1964.1) Pyrene,1) hexamethylbenzene,1) TTF,2) and TMTTF3,4) give 2:1 CT-complexes but only the complex with the last donor was studied precisely in its physical and structural features among them. The 2:1 TMTTF complex was identified as an ionic insulator of segregated type with dimerized TMTTF while HCBD stacks perpendicularly to the donor stacks. TMTTF also gives 1:1 insulating morphology in which both the ionic component molecules form segregated columns,4) and the complex shows three characteristic phase transitions by lowering temperature. The 1:1 molecular ratio was also found in TTMTTF5) complex which has partial CT ground state with segregated columns.4) In the present investigation, a search was made for the complexes with rather weak donors i.e., aromatic hydrocarbons to get the systematic information of this acceptor. This paper describes the perylene complex, of which the ΔE_{redox} value is slightly larger (0.39 V) than the required range for partial CT of $-0.02 \leq \Delta E_{redox} \leq 0.34$ V (for TTF-TCNQ system),6) and is expected to give a neutral ground state, where the ΔE_{redox} means the difference between the donor oxidation potential and the acceptor reduction potential ($E_{ox}^{1/2}$[perylene] = 1.08 V, $E_{red}^{1/2}$[HCBD] = 0.69 V).7)



HCBD

Microcrystals of the complex were accessible by slow cooling of the dry 1,2-dichloroethane (DCE) solution containing equimolar perylene and HCBD. Upon recrystallization of these microcrystals from dry DCE, larger crystals were available. Diffusion method in dry DCE also afforded the single crystals. The two methods gave the single crystals of the same type, which were dark red long

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Table 1. Crystallographic data of perylene-HCBD

Formula	$C_{30}H_{12}N_6$	
Formal Weight	456.47	
Crystal System	Monoclinic	
Space Group	$P2_1/a$	
Cell Constants	a= 16.2513(10) Å	
	b= 8.3811(5)	β= 91.583(4)°
	c= 7.8109(4)	
Volume	V= 1063.5(1) Å^3	
Number of Complexes in One Unit Cell		Z= 2
Density	obsd 1.39 g/cm^3	
	calcd 1.426	

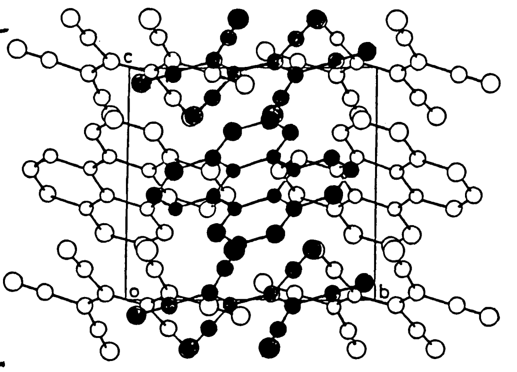

Fig.1. Projection along the a-axis. The molecules stacking along the axis of x=1, y=0.5 are painted.

prisms with flat hexagonal cut ends. From the crystal structure analysis, as will be described below, it was found that the most developped face is (100) and the axis of the crystal growth is the c-axis (stacking axis).

The X-ray diffraction data were collected and the crystal structure was solved in the same way as described elsewhere.[4b,8] The final R-value was 0.041 and the obtained crystallographic data were summarized in Table 1. This complex is composed of equimolar donor and acceptor. Two characteristic features were found. First, although in all HCBD complexes, of which the crystal structures were determined, the donors and HCBD formed segregated columns,[4] this CT solid crystallizes in mixed stacks along the c-axis. And in this complex, perylene and HCBD alternately form unicomponent sheets parallel to the ab-plane (Fig.1). Second, while the forementioned segregated stacked complexes have the orientational disorder of HCBD (pseudo D_{2h} symmetry is generated), no disorder was observed for perylene-HCBD complex. In order to realize these traits, a pair of the donor and the acceptor was projected onto the perylene plane in Fig.2a. The interplanar separation evaluated as the averaged distances from the perylene best plane to the HCBD atoms is 3.16 Å, or from the HCBD best plane to the perylene carbon atoms is 3.26 Å, with a dihedral angle of 2.88°. The molecular centers of the donor and acceptor do not directly coincide with each other; if we pay attention to a half part of HCBD, i.e., the tricyanoethylene moiety, it locates just like as the TCNE molecule in perylene-TCNE complex.[9] Further, the interplanar spacing and the dihedral angle between the donor and the acceptor in these two complexes are almost similar (for perylene-TCNE, the mean distance is 3.186 Å, and the dihedral angle is 1.7°), in spite of the big difference of acceptor strength ($E^{1/2}_{red}$[TCNE] = 0.27 V[7]). Figure 2b is the schematic representation of the donor-HOMO and the acceptor-LUMO

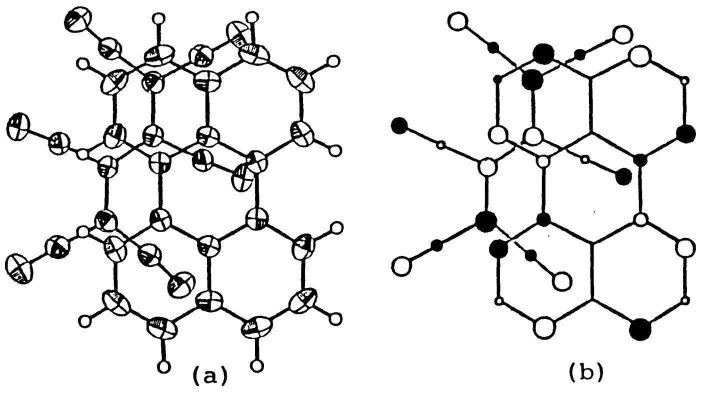

Fig.2. Molecular overlapping. (a) Projection onto the perylene plane and (b) Perylene-HOMO and HCBD-LUMO.

from the Hückel MO calculations. This figure shows that the orientation is convenient to gain the CT stabilization energy. So, this crystal structure may be regarded as a close-packing one in which the CT-force (orbital interaction) and the steric interaction between the neutral components are reasonably balanced.10)

As is expected from the crystal structure of this complex, the semiconductive behavior was observed. The resisitivity measured along the stacking axis by two probe dc method is 1.47×10^{4} Ω cm at room temperature with an activation energy of 0.19 eV.

The reflection spectra were measured for the polarized light parallel and perpendicular to the stacking axis on the (100) plane and the conductivity spectra were obtained by the Kramers-Kronig transformation as shown in Fig.3. The peak observed in the near infra-red region (5.6×10^{3} cm^{-1}) is exclusively polarized along the stacking axis (c-axis) and is not found in the spectra of either perylene or HCBD. So it can be assigned to the CT-transition between them. The energy difference between the peak and the hump at its higher energy side, 1.4×10^{3} cm^{-1}, suggests that the hump would be a vibrational structure, because the infra-red spectra of this complex (KBr disk) shows several absorption bands around 1400 cm^{-1} and in dry DCE this complex reveals only one broad absorption band at 8.2×10^{3} cm^{-1}. The peaks about 20×10^{3} cm^{-1} observed for both //c and ⊥c spectra correspond to the lowest energy transition of the neutral perylene molecule.11) However, no peaks corresponding to the perylene cation radical12) were observed. So we can conclude this complex has a neutral ground state.

Torrance et al. plotted $h\nu_{CT}$ (the CT transition energy) against the ΔE_{redox} of 26 solid CT complexes which have mixed stack.13) The plotted points were on the V-shaped line which was derived from the simple consideration regarding the ΔE_{redox} and the Madelung energy. According to this treatment, ionic complexes locate in the low ΔE_{redox} region and neutral complexes in the high ΔE_{redox} region. The neutral-ionic boundary (ΔE_{redox} = 0.2 V, where calculated $h\nu_{CT} = 5.65 \times 10^{3}$ cm^{-1} from the equation and the parameters in reference 13) actually tends to separate the neutral from the ionic complexes. The neutral-ionic transition is detected in the complex, TTF-p-chloranil which locates near the boundary (ΔE_{redox} = 0.29 V,7) $h\nu_{CT} = 5.32 \times 10^{3}$ cm^{-1} 13c)). Although the ΔE_{redox} of the perylene-HCBD complex (0.39 V) is apart from the boundary, the $h\nu_{CT}$ value is almost the same as that of TTF-p-chloranil complex.

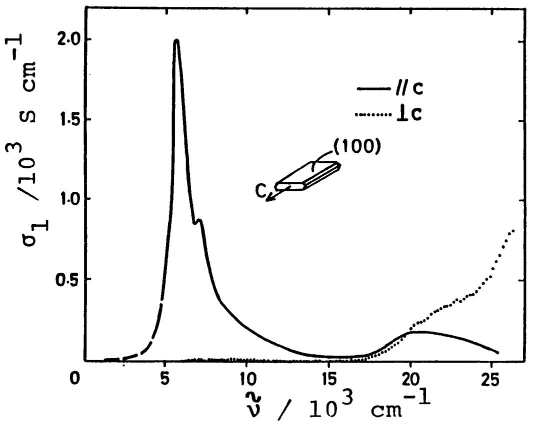

Fig.3. Conductivity spectra on the (100) face. In the region below 5.0×10^{3} cm^{-1}, the //c spectrum was extrapolated by assuming that the 5.6×10^{3} cm^{-1} band is a Lorentzian.

In conclusion, perylene-HCBD is a neutral solid CT-complex with mixed 1:1 regular stacks. Conformity to the treatment by Torrance, this complex locates close to the neutral-ionic boundary. So it may be expected that this complex will exhibit neutral-ionic transition, provided that the transition is exclusively governed by the electronic properties. On the other hand, in the planes perpendicular to the stacking axis, the surroundings are different in these two complexes. In the TTF-p-chloranil complex, the nearest neighboring molecules of a component are two foreign molecules and two kindred molecules, although, in the perylene-HCBD complex, each component forms the sheet exclusively. The effect of such structural difference and of the consequent difference in Madelung energy on the occurrence of this transition is interesting.

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7) This work. (vs. SCE, 0.1 M $(TBA)BF_4$, in CH_3CN, Pt electrodes)

8) The structure was solved by direct method of Monte-Carlo MULTAN 78 and refined by full-matrix least-squares calculations with 1718 reflections.

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11) This assignment is also supported from the dichroism. Resolving the $\perp c$ reflectance spectrum into Lorentzian absorptions, there are three overlapped peaks at 20.3, 22.3, and 24.8 x 10^3 cm^{-1} in the 20 x 10^3 cm^{-1} band. After transformed to the conductivity spectra, the evaluated oscillator strength $f_\perp$ was 0.458. On the other hand, from the integration of the $/\!/c$ conductivity spectra, the values of $f_{/\!/} = 0.253$ was obtained. This dichroic ratio ($f_\perp : f_{/\!/} = 1:1.81$) is close to the ratio of $f_\perp : f_{/\!/} = 1:3.24$ that was calculated from the direction cosine of the long axis of perylene.

12) In Ph-NO_2, perylene cation radical shows two absorption bands at 13.7 and 18.0 x 10^3 cm^{-1}. See, W. Ij. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, J. Chem. Soc., 1959, 3055.

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