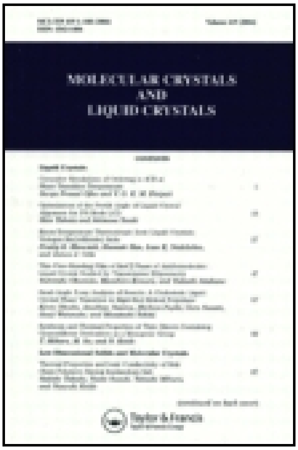

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Optical Properties, Thermochromism and Crystal Structure of Picric Acid-Hexamethylbenzene Complex

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Abstract The crystal structure of the picric acid-hexamethylbenzene 1:2 complex has been determined by the X-ray diffraction method. The crystals of the complex have the orange form and the yellow form. This orange crystal exhibits the thermochromism at about 116℃. This phenomenon was studied by measuring the temperature dependence of the IR and visible absorption spectra of the crystals of the picric acid-hexamethylbenzene complex and the deuterated complex.

INTRODUCTION

It is well known that picric acid (PIC-OH) forms salts or CT complexes with many organic compounds.[1] That is, the crystals of picrate salts are formed with aromatic amines and aliphatic amines,[2] while CT complexes of picric acid are formed with aromatic hydrocarbons.[3] In these complexes, two stable dimorphs of picrate salts with 2-iodoaniline showed the thermochromism and changed to CT complexes upon heating.[4] In the present paper, we report the polarized visible and IR absorption spectra and the X-ray crystal structure of the picric acid-hexamethylbenzene (PIC-OH-HMB) CT complex. Furthermore, we discuss the mechanism of the thermochromism based on the spectral data and the DSC analysis data of the PIC-OH-HMB complex and its deuterated complex.

EXPERIMENTAL

Optical and Thermal Measurement of the Crystal of PIC-OH-HMB Complex

Commercially available PIC-OH and HMB were used without further purification. Crystals were obtained by the slow evaporation of an equimolar solution of the components in acetone or ethyl acetate. The platelike crystals have two kinds of crystals of the orange and the yellow forms. The partially deuterated (PIC-OD-HMB) complex was obtained by the slow evaporation of an equimolar solution of the deuterated picric acid (PIC-OD) and HMB in $CDCl_3$. The thermal analyses were carried out using a Shimadzu DSC-50 (TGA-50) at a heating rate of 10 ℃ min^{-1} under N_2 gas. The IR absorption spectra of the single crystal were recorded using a JASCO FTIR VALOR III with a hot plate FP82HT. The visible absorption spectra of the single crystal were taken using a polarized absorption microspectrophotometer made in our laboratory.[5]

X-Ray Structure Analysis of PIC-OH-HMB 1:2 Complex

A crystal used had dimensions of 0.25 × 0.25 × 0.55 mm. The reflection data were measured on a Rigaku AFC-5R four circle diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 50 kV and 200 mA. Lattice parameters were determined with 25 reflections in the range $21 < 2\theta < 22^\circ$. Crystal data: $C_{18}H_{21}N_3O_7$, Mr=391.38, triclinic, space group $P\bar{1}$, a= 8.953(2), b=14.207(5), c=8.951(2) Å, $\alpha = 108.38(3)$, $\beta = 120.01(2)$, $\gamma = 88.91(3)^\circ$, V=922(1) Å^3, Z=2, Dx=1.409 g cm^{-3}; μ (Mo $K\alpha$)=0.10 mm^{-1}. Intensities were measured up to $\sin\theta/\lambda$ 0.5722 Å^{-1} by using ω-2θ scan technique where scan speed was 6° min^{-1} in ω and scan range $(1.52+0.30 \tan\theta)^\circ$ in ω. Background was measured for 4 s on either side of the peak. Three standard reflections were monitored during the data collection for every 97 reflections with a fluctuation within 1.2% in F. In total 3100 reflections were measured ranging h=-9 to 8, k=-16 to 15, l=0 to 10, and 2889 reflections were unique (Rint=0.012). For refinement 1413 reflections with Io larger than $3\sigma(Io)$ were used. Correction for Lorentz and polarization effects were applied, but no correction was applied for absorption effect. The structure was solved by a direct method MITHRIL[6] and refined by a full-matrix least-squares: the quantity minimized was $\Sigma w(|Fo| - |Fc|)^2$ where w refers to weights, $\sigma^{-2}(Fo)$. The molecule of picric acid was disordered to have a pseudo three-fold axis. One of the nitro groups of picric acid was also disordered around the C-N bond. The occupancy factors of disordered O atoms of the hydroxyl and the nitro group were estimated by a difference Fourier map and the least-squares refinement. One O atom of the hydroxyl groups and two O atoms of the nitro group, which had the low occupancy factor, were refined isotropically. The other non-H atoms were refined anisotropically. The H atoms of the hydroxyl groups were not found in the difference Fourier map, and they were not included in the refinement. The positional parameters of the other H atoms were estimated by assuming usual geometry, and included in the Fc calculation. The isotropic displacement parameters of these H atoms were assumed to be 1.2 times of equivalent displacement parameters of the atoms to which they were attached. Extinction correction was performed according to $Icorr=Io(1+2.82\times10^{-6}Ic)$. The final values of R and Rw were 0.067 and 0.055, respectively (S=2.07). In the last cycle of least-squares refinement $(\Delta/\sigma)_{max}$ was 0.69. In a final difference Fourier map maximum and minimum $\Delta\rho$ were 0.19 and -0.17e Å^{-3}, respectively. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[7] Computations were carried out by using TEXAN[8] at the X-Ray Laboratory of Okayama University.

RESULTS and DISCUSSION

Crystal and Molecular Structure

Final atomic parameters for the orange crystal are listed in Table 1. The displacement ellipsoids and the numbering of atoms are show in Fig.1.[9]

Table 1. Fractional Atomic Coordinates and Equivalent Displacement Parameters of Non-Hydrogen Atoms, and Occupancy Factors of Disordered Atoms

$$B_{eq} = (8\pi^2/3)\Sigma_{ij}U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	x	y	z	Beq / Å^2	occu-pancy
O(1A)	0.247(3)	0.251(2)	0.953(3)	6.7(5)	0.22
O(1B)	0.539(1)	0.242(8)	0.639(2)	7.1(5)	0.39
O(1C)	-0.037(1)	0.2575(8)	0.356(1)	6.6(5)	0.39
O(2)	0.5529(7)	0.2315(4)	1.0946(6)	8.7(2)	
O(3)	0.6888(6)	0.2251(4)	0.9520(7)	9.0(3)	
O(4)	0.358(2)	0.207(1)	0.312(2)	12.3(7)	0.62
O(4D)	0.126(3)	0.213(1)	0.201(3)	11.7(7)	0.38
O(5)	0.141(2)	0.293(1)	0.247(2)	12.6(7)	0.62
O(5D)	0.374(3)	0.285(1)	0.363(3)	11.1(6)	0.38
O(6)	-0.1895(6)	0.2751(4)	0.5376(7)	8.7(3)	
O(7)	-0.0517(7)	0.2689(4)	0.8118(8)	8.9(3)	
N(1)	0.5596(8)	0.2329(4)	0.9646(8)	6.2(2)	
N(2)	0.248(1)	0.2507(7)	0.341(1)	8.5(3)	
N(3)	-0.0603(8)	0.2672(4)	0.6723(9)	6.2(3)	
C(1)	0.249(1)	0.2500(4)	0.8133(9)	4.7(2)	
C(2)	0.401(1)	0.2430(4)	0.8063(8)	4.5(3)	
C(3)	0.406(1)	0.2436(4)	0.654(1)	4.8(3)	
C(4)	0.249(1)	0.2500(5)	0.5079(9)	4.8(3)	
C(5)	0.0943(9)	0.2564(4)	0.5061(9)	4.7(3)	
C(6)	0.100(1)	0.2571(4)	0.664(1)	4.4(3)	
C(7)	0.586(1)	0.4992(4)	0.907(1)	5.1(3)	
C(8)	0.409(1)	0.5125(4)	0.8307(7)	5.0(3)	
C(9)	0.3265(8)	0.5135(4)	0.925(1)	4.8(2)	
C(10)	0.685(1)	0.4966(6)	0.808(1)	11.6(5)	
C(11)	0.323(1)	0.5262(5)	0.6434(9)	12.3(4)	
C(12)	0.1376(9)	0.5286(5)	0.833(1)	11.1(4)	
C(13)	-0.083(1)	0.0012(4)	0.3234(7)	4.7(3)	
C(14)	-0.1718(8)	0.0138(4)	0.417(1)	4.6(2)	
C(15)	-0.086(1)	0.0124(4)	0.594(1)	4.6(3)	
C(16)	-0.185(1)	0.0045(6)	0.130(1)	12.0(5)	
C(17)	-0.365(1)	0.0287(5)	0.331(1)	12.3(4)	
C(18)	-0.177(1)	0.0267(6)	0.703(1)	12.4(5)	

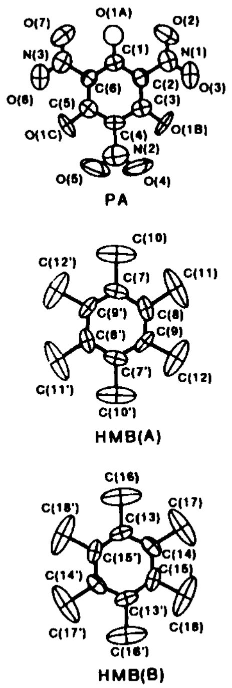

Fig.1. The displacement ellipsoids at 50% probability level with the numbering of non-H atoms for PA, HMB(A), and HMB(B). O(1A) of PA is represented as a sphere, and the disordered O atoms attached to N(2) are omitted for clarity. In HMB(A) and HMB(B) the atoms related by a center of symmetry are denoted with a prime.

Projections of the crystal structure along a c axis is shown in Fig.2. Because of disordering in the picric acid moiety (PA), detailed discussion on the molecular structure is out of the limit of the precision. However, meaningful results have been obtained for the crystal structure. There are two independent molecules of HMB in a unit cell, which are referred to HMB(A) and HMB(B) hereafter. As is shown in Fig.3, a characteristic feature of the molecular overlapping is that C(2) and C(6) of the PA lie on the center of the benzene rings of HMB(A) and HMB(B), respectively. Thus, molecules of PA and HMB form a mixed-stack column along the direction of $[1\ 1\ \bar{1}]$ as shown in Fig.2. In the planes of (0 1 0), (0 2 0) and (0 4 0), the molecules of HMB(B), HMB(A) and PA are hexagonally arranged, respectively. Accordingly, the PA is disordered in a manner as it has a pseudo three-fold symmetry. Furthermore, a nitro group at C(4) is disordered around C(4)-N(2) bond. The O atoms of this nitro group have large displacement parameters, and deviate significantly from the benznene-ring plane of PA in contrast with the nitro groups at C(2) and C(6) [C(1)-C(2)-N(1)-O(2) -0.2(8), C(5)-C(6)-N(3)-O(6) -0.5(7)° ; C(3)-C(4)-N(2)-O(4) 28(1), C(5)-C(4)-N(2)-O(4D) -34(2)°]. This is explained by the facts that the nitro groups at C(2) and C(6) overlap with some part of the HMB molecules[O(2)···C(11') 3.322(9), O(3)···C(12') 3.366(8), O(6)···C(17) 3.370(9), O(7)···C(18) 3.316(9) Å], while the disordered nitro group is not overlapped by any part of HMB(A) or HMB(B). As seen from Fig.1, both molecules of HMB show remarkable librational motion about the axes perpendicular to the respective molecular planes. The dihedral angles between the benzene-ring planes of the molecules overlapping in the column are 5.0(4)° . The position of the hydroxylic hydrogen atom was not located because of the disordering. However, it is suggested that weak intermolecular hydrogen bonds are formed between the hydroxyl and nitro groups; the O···O contacts ranging from 3.07(1) to 3.16(1)Å.

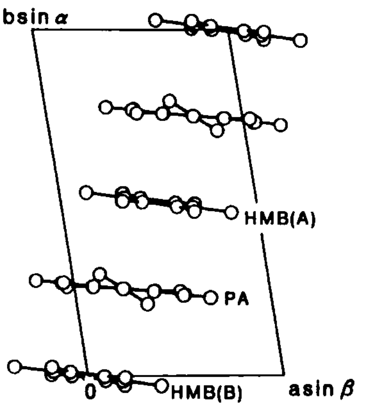

Fig. 2. Projection of the crystal structure along a c axis showing a mixed stack of the molecules of PA and HMB.

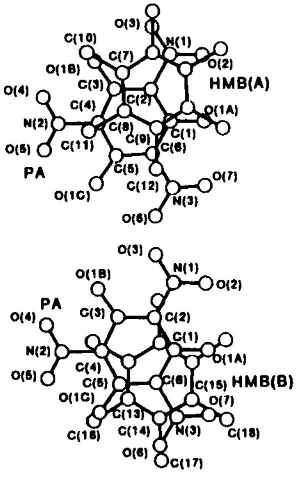

Fig. 3. Molecular overlapping of PA to HMB(B), and HMB(A) to PA. The H-atoms and the disordered O atoms of the nitro group are omitted.

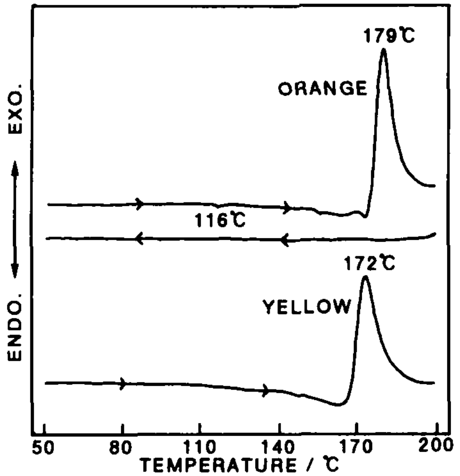

Fig. 4. DSC curves of the single crystals of the orange and yellow forms.

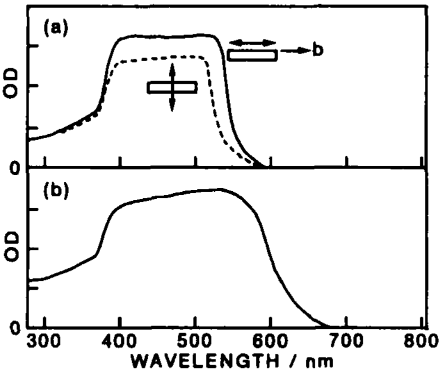

Fig. 5. The polarized visible absorption spectra of the orange crystal. (a) before and (b) after heating.

Thermochromism of the Crystal

Figure 4 shows the differential scanning calorimetry (DSC) curves of the single crystals of the orange and yellow forms. There are one endothermic peak (116°C) and one exothermic peak (179°C) for the heating curve of the orange form, while the cooling curve under 150°C has no peak. On the other hand, the melting points of picric acid and HMB crystals are 123 and 165°C, respectively. The orange platelike crystal changes to the red crystal in the vicinity of 116°C upon heating, but the red crystal does not change to the orange crystal at 116°C by cooling. The red crystal melts at about 150°C, but no endothermic peak appears at the melting point for the DSC curve. For the yellow form, the DSC curve has only one exothermic peak at 172°C and the thermochromism is not observed. Figure 5 shows the polarized visible absorption spectra of the single crystal of the orange form. The spectra at room temperature have the LE band at 400 nm and the CT band at 500 nm. The absorption spectrum of the red solution molten at the higher temperature than 150°C has the broad band with the peak at 550 nm.

Thermal Change of the Polarized IR Spectra of the Crystal

Figure 6(a) shows the temperature variable IR spectra of the crystal of the orange form of the PIC-OH-HMB complex. The intense 3000 cm^{-1} band consists of three peaks located at 3213, 3086 and 2901cm^{-1}. The 2901 cm^{-1} peak can be assigned to the O-H stretching mode under the hydrogen bond system between the hydroxyl and nitro groups. The peak at 3213 cm^{-1} assigned to the free O-H stretching mode becomes more intense and shifts to the higher wave number range upon heating. Furthermore, the 3086 cm^{-1} peak can be interpreted by the C-H stretching of the aromatic rings. For the crystal of the partially deuterated PIC-OD-HMB complex as shown in Figure 6(b), the broad and intense band located at 2365 cm^{-1} can be assigned to the O-D stretching mode under the hydrogen bond system and shifts to 2372 cm^{-1} upon heating. The shoulder at 2449 cm^{-1} may be assigned to the free O-D stretching mode and appears upon heating. These facts mean that the hydrogen bond system between the hydroxyl and nitro groups of the picric acid disappears upon heating.

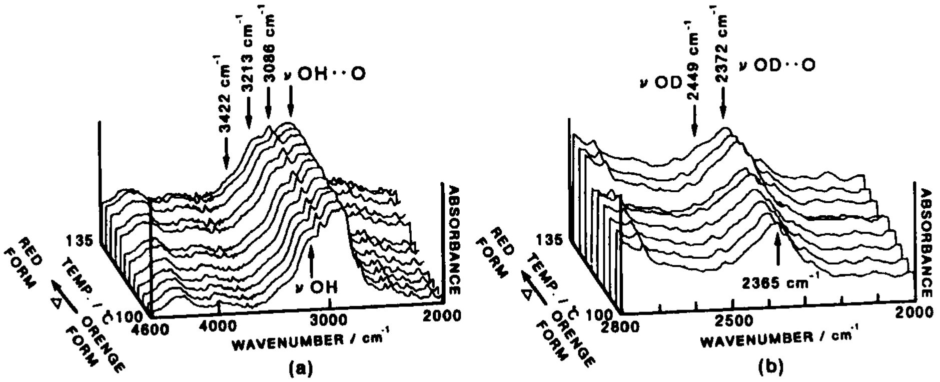

Fig. 6. The temperature variable IR absorption spectra of the orange form of (a) PIC-OH-HMB and (b) PIC-OD-HMB.

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