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Optical Properties, Thermochromism and Crystal Structure of Picric Acid-1,5-Diaminonaphthalene Salt

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ABSTRACT The crystal structure of the 2:1 salt of picric acid with 1,5-diaminonaphthalene has been determined by the X-ray diffraction method. The crystals of the salt have the yellow green form. The crystals exhibit the thermochromism at about 110°C. This phenomenon was studied by measuring the temperature dependence of the IR absorption spectra of the crystals of the salt of picric acid with 1,5-diaminonaphthalene and the deutrated salt.

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 temperature variable IR absorption spectra and the X-ray crystal structure of the complex of picric acid with 1,5-diaminonaphthalene (15DANP). Furthermore, we discuss the mechanism of the thermochromism based on the spectral data and the DSC analysis data of the salt of PIC-OH with 15DANP and the deuterated salt.

EXPERIMENTAL

Optical and Thermal Measurement of the 2:1 Salt of PIC-OH with 15DANP Commercially available PIC-OH and 15DANP were used without further purification. Crystals were obtained by slow evaporation of a solution of the

2:1 components in methanol. The prismatic crystals show the yellow green color. The partially deuterated salt was obtained by slow evaporation of a 2:1 solution of deuterated picric acid (PIC-OD) and deuterated 15DANP in CH_3OD. 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 polarized IR absorption spectra of the single crystal were recorded using a JASCO FTIR VALOR III with a hotplate FP82HT.

X-Ray Structure Analysis of the 2:1 Salt of PIC-OH with 15DANP

A crystal used had dimensions of $0.28 \times 0.33 \times 0.50$ mm . The reflection data were measured on a Rigaku AFC-5R four circle diffractometer with graphite monochromated Mo Kα radiation (λ =0.71073 Å) at 50 kV and 200 mA. Lattice parameters were determined with 25 reflections in the range $21 < 2\theta < 22°$. Crystal data: $C_{23}H_{20}N_8O_{15}$, Mr=648.46, triclinic, space group $P\bar{1}$, a=10.135(4), b=15.644(5), c=9.056(8) Å, α =97.46(5), β =94.30(5), γ =107.06(3)° , V=1351(3)Å^3, Z=2, Dx=1.593 g cm^{-3}; μ (Mo Kα) = 0.128 mm^{-1}. Intensities were measured up to $\sin\theta/\lambda$ 0.6168 $Å^{-1}$ by using ω-2θ scan technique where the scan speed was 6° min^{-1} in ω and the scan range (1.68+0.30 tan θ)° 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 5748 reflectins were measured ranging h=-12 to 12, k=-17 to 17, l=0 to 11, and 4597 reflections were unique (Rint=0.016). For refinement 3404 reflections with Io larger than 3σ(Io) were used. Correction for Lorentz and polarization effects were applied, but no correction was applied for absorption. The structure was solved by a direct method MITHRIL[5] and refined by a full-matrix least-squares: the quantity minimized was $\Sigma w(|Fo| - |Fc|)^2$ where w refers to weights, σ^{-2}(Fo). Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms isotropically. Correction for the extinction effect was performed according to Icorr=Io(1+1.45 $\times 10^{-6}$Ic). The final values of R and Rw were 0.040 and 0.038, respectively (S=1.72). In the last cycle of least-squares refinement (Δ/σ)max was 0.69. In a final difference Fourier map maximum and minimum $\Delta\rho$ were 0.20 and -0.20 e $Å^{-3}$, respectively. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[6] Computations were carried out by using TEXAN[7] at the X-Ray Laboratory of Okayama University.

RESULTS and DISCUSSION

Crystal and Molecular Structure Final atomic parameters for the yellow green crystal are listed in Table 1. The displacement ellipsoids and the numbering of atoms are shown in Fig.1.[8] Projection of the crystal structure along an a axis is shown in Fig.2.

Table 1. Fractional Atomic Coordinates and Equivalent Displacement Parameters of Non-Hydrogen Atoms

$$Beq = (8\pi^2/3)\,\Sigma ij Uij ai^* aj^* ai \cdot aj$$

	x	y	z	Beq / Å²		x	y	z	Beq / Å²
O(1)	0.1702(2)	0.0488(1)	0.0763(2)	3.29(7)	C(11)	0.1986(3)	0.4585(2)	0.5870(3)	3.1(1)
O(2)	0.2568(2)	-0.0977(1)	0.1093(2)	4.65(9)	C(12)	0.1067(3)	0.3841(2)	0.6269(3)	2.8(1)
O(3)	0.4809(2)	-0.0419(1)	0.1466(3)	5.8(1)	C(13)	0.0645(3)	0.0345(2)	0.7034(3)	2.6(1)
O(4)	0.6201(2)	0.1595(2)	0.6284(2)	6.1(1)	C(14)	0.1492(3)	-0.0163(2)	0.7242(3)	3.5(1)
O(5)	0.5098(3)	0.2547(2)	0.6891(2)	6.1(1)	C(15)	0.1671(3)	-0.0759(2)	0.6021(3)	4.0(1)
O(6)	0.1260(3)	0.2622(2)	0.3566(3)	7.8(1)	C(16)	0.0991(3)	-0.0829(2)	0.4633(3)	3.2(1)
O(7)	0.0902(3)	0.1972(2)	0.1326(2)	6.5(1)	C(17)	-0.0100(3)	0.0306(2)	0.5614(3)	2.4(1)
O(8)	0.0570(2)	0.2691(1)	0.7839(2)	3.20(7)	C(18)	0.8592(3)	0.3998(2)	0.9002(3)	2.6(1)
O(9)	0.2946(2)	0.2435(2)	0.9008(3)	7.1(1)	C(19)	0.7804(3)	0.4377(2)	0.8200(3)	3.5(1)
O(10)	0.4422(3)	0.3702(2)	0.9975(3)	7.7(1)	C(20)	0.8186(3)	0.5316(2)	0.8290(3)	3.6(1)
O(11)	0.5540(2)	0.5864(2)	0.6557(3)	5.8(1)	C(21)	0.9353(3)	0.5856(2)	0.9180(3)	3.1(1)
O(12)	0.3863(2)	0.6089(2)	0.5236(3)	6.0(1)	C(22)	0.9813(3)	0.4522(2)	0.9964(3)	2.33(9)
O(13)	-0.0484(2)	0.3889(1)	0.4299(2)	4.32(9)	C(23)	0.6332(7)	0.2340(5)	0.1829(8)	9.7(3)
O(14)	-0.1241(2)	0.2931(1)	0.5767(2)	4.49(9)	H(3)	0.509(3)	0.054(2)	0.399(3)	3.0(6)
O(15)	0.7651(4)	0.2776(3)	0.1685(4)	9.1(2)	H(5)	0.329(2)	0.243(2)	0.481(3)	3.0(6)
N(1)	0.3646(3)	-0.0371(2)	0.1614(3)	3.7(1)	H(9)	0.473(3)	0.464(2)	0.806(3)	3.7(6)
N(2)	0.5255(3)	0.1917(2)	0.6040(3)	4.6(1)	H(11)	0.173(2)	0.487(2)	0.514(3)	3.2(6)
N(3)	0.1475(3)	0.2101(2)	0.2583(3)	3.8(1)	H(14)	0.208(3)	-0.011(2)	0.824(3)	4.7(7)
N(4)	0.3437(3)	0.3249(2)	0.9085(3)	4.7(1)	H(15)	0.232(3)	-0.115(2)	0.619(3)	4.8(7)
N(5)	0.4313(3)	0.5665(2)	0.6087(3)	4.1(1)	H(16)	0.115(2)	-0.126(2)	0.382(3)	3.6(6)
N(6)	-0.0312(2)	0.3534(2)	0.5403(3)	3.1(1)	H(19)	0.701(3)	0.399(2)	0.755(3)	4.0(6)
N(7)	0.0446(3)	0.0947(2)	0.8334(2)	2.65(9)	H(20)	0.761(3)	0.555(2)	0.775(3)	3.9(7)
N(8)	0.8204(3)	0.3009(2)	0.8886(3)	3.2(1)	H(21)	0.961(2)	0.649(2)	0.919(3)	3.4(6)
C(1)	0.2487(3)	0.0832(2)	0.1964(3)	2.6(1)	H(71N)	-0.049(3)	0.078(2)	0.855(3)	5.1(8)
C(2)	0.3520(3)	0.0447(2)	0.2501(3)	2.8(1)	H(72N)	0.070(3)	0.163(2)	0.822(3)	6.9(9)
C(3)	0.4412(3)	0.0793(2)	0.3786(3)	3.2(1)	H(73N)	0.105(3)	0.090(2)	0.922(4)	6.0(8)
C(4)	0.4297(3)	0.1542(2)	0.4685(3)	3.3(1)	H(81N)	0.883(3)	0.283(2)	0.853(3)	3.8(8)
C(5)	0.3330(3)	0.1954(2)	0.4286(3)	3.3(1)	H(82N)	0.725(4)	0.272(2)	0.826(4)	8(1)
C(6)	0.2469(3)	0.1626(2)	0.2958(3)	2.7(1)	H(83N)	0.808(3)	0.283(2)	0.998(4)	6.7(9)
C(7)	0.1418(3)	0.3345(2)	0.7386(3)	2.8(1)	H(150)	0.793(5)	0.295(3)	0.230(5)	9(2)
C(8)	0.2877(3)	0.3698(2)	0.7987(3)	3.2(1)	H(231)	0.609(5)	0.244(3)	0.263(5)	10(2)
C(9)	0.3789(3)	0.4448(2)	0.7605(3)	3.5(1)	H(232)	0.616(7)	0.271(4)	0.119(6)	14(2)
C(10)	0.3340(3)	0.4888(2)	0.6546(3)	3.1(1)	H(233)	0.591(8)	0.171(5)	0.098(9)	26(2)

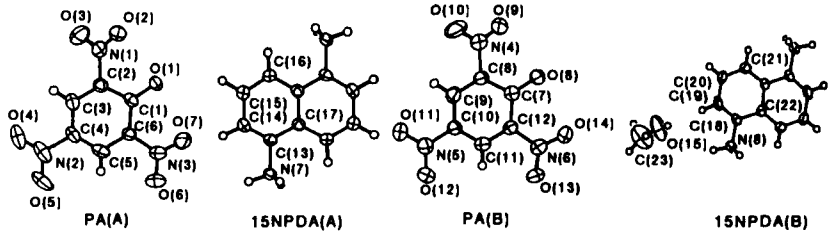

Fig. 1. The displacement ellipsoids with the numbering of atoms for PA, 15NPDA and methanol.

Two independent molecules of picrate (PA) anion and 1,5-naphthyl-diammonium (15NPDA) cation are referred to PA(A) and PA(B), and 15NPDA(A) and 15NPDA(B), respectively. The cations 15NPDA(A) and 15NPDA(B) occupy the centers of symmetry at (0, 0.5, 0) and (0, 0, 0.5), respectively. Each cation is sandwiched between two anions related by the centers of symmetry to form an ionic pair $(C_{10}H_{12}N_2)^{2+}$ $(C_6H_2N_3O_7)_2^{2-}$. Therefore, there are two ionic pairs and two methanol molecules in a unit cell. The molecular plane of each cation is overlapped with that of each anion. The dihedral angle between the overlapping molecular planes is 17.2(1)° for the pair of A, and 33.12(9)° for the pair of B. The hydrogen atoms of two ammonium groups in 15NPDA form intermolecular hydrogen bonds with the oxygen atoms O(1) and O(8) of PA: O(1)···N(7) 2.739(3), O(1)···H(73N) 1.78(3)Å; O(1)···N(7) 2.886(4), O(1)···H(71N) 2.20(3)Å; O(8)···N(7) 2.790(3), O(8)···H(72N) 1.78(3)Å; O(8)···N(8) 2.795(4), O(8)···H(81N) 1.98(3)Å, respectively. Furthermore, ammonium group in 15NPDA(A) donates hydrogen bond to O(15) of methanol: O(15)···N(8) 2.685(5), O(15)···H(83N) 1.64(4)Å. One of the nitro groups deviates from the benzene ring plane in PA: the torsion angle around the C-N bond is 137.1(1)° for PA(A) and 29.9(2)° for PA(B). The nitro group of PA accepts a hydrogen bond from the ammonium N atom of 15NPDA: for PA(A) O(9)···N(7) 2.855(4), O(9)···H(72N) 2.26(3)Å; for PA(B) O(14)···N(8) 2.915(4), O(14)···H(81N) 2.53(3)Å.

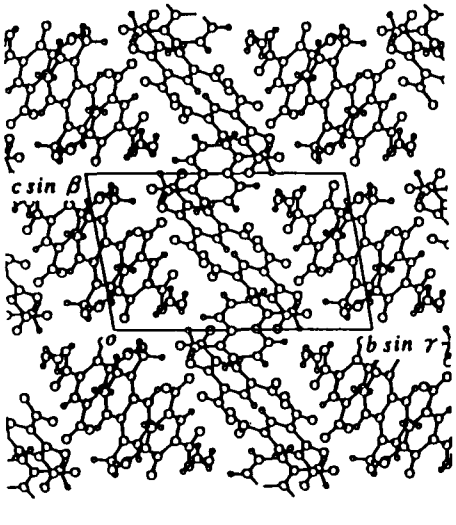

Fig. 2. Projection of the crystal structure along an a axis.

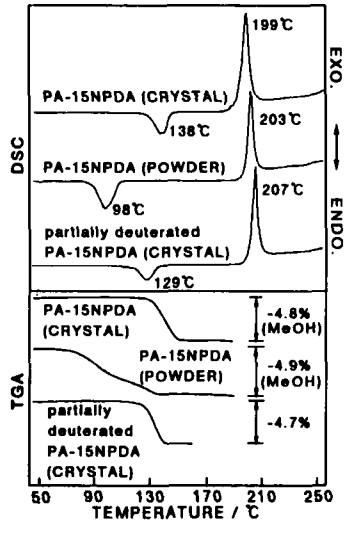

Fig. 3. DSC and TGA curves of the yellow green crystals of the PA-15NPDA salt and the partially deuterated PA-15NPDA crystals and the yellow powder of the PA-15NPDA.

Thermochromism of the Crystal Figure 3 shows the differential scanning calorimetory (DSC) and the thermo-gravimetry analysis (TGA) curves of the PA-15NPDA crystals and its powder and the partially deuterated crystals. There are one endothermic peak (138°C) and one exothermic peak (199°C) for the PA-15NPDA crystals and there are one endothermic peak (129°C) and one exothermic peak (207°C) for the deuterated crystals, while the DSC curve of the yellow powder of PA-15NPDA has one endothermic peak at 98°C and one exothermic peak at 203°C. On the other hand, the loss of mass is observed at the same temperature range as the endothermic point upon heating each sample. The values (about 5%) correspond to the loss of the solvated methanol molecules.

Thermal Change of the IR Spectra of the Crystal Figure 4 shows the IR spectra of the crystals and the powder of the PA-15NPDA salt and the crystals of the partially deuterated PA-15NPDA salt. The crystalline spectra have the structural band in the higer wave number region than 3800 cm^{-1} and the broad band over the wide range from 2000 to 3500 cm^{-1}. The structural band seems to be due to the streching band of OH group and the broad band can be assigned to the streching N-H (N-D) band of the NH_3^+(ND_3^+) group. However, these bands are not observed for the powder spectrum. In the lower wave number region, the behavior of the spectra of the PA-15NPDA salt is similar to that of the partially deuterated salt, but is slightly different from those of the powder. The temperature variable IR spectra of the crystals of the PA-15NPDA salt and the partially deuterated salt show that the structural band in the higher wave number region than 3800 cm^{-1} disappears at 127°C and the background intensity increases suddenly.

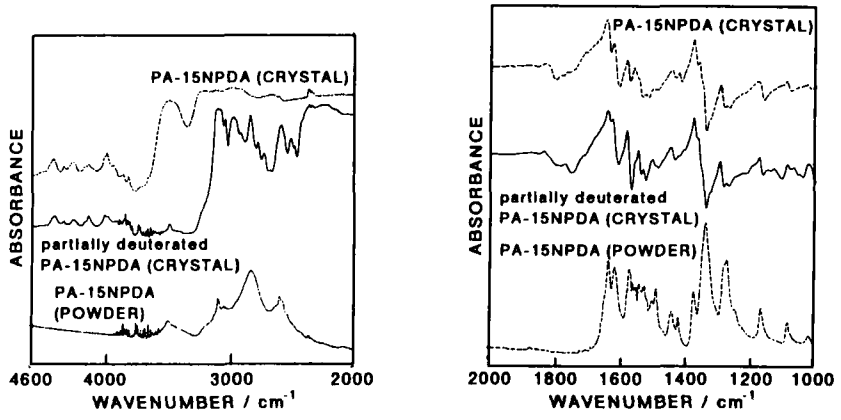

Fig. 4. The IR spectra of the crystals and the powder of the PA-15NPDA and the crystals of the partially deuterated PA-15NPDA salt.

Figure 5 shows the temperature variable IR spectra in the lower wave number region of the crystal of the partially deuterated salt. The N-H bending band of NH_3^+ at 1577 cm^{-1} and the N-D bending band of ND_3^+ at 1172 cm^{-1} become weaker in the region of 110°C, while the N-H bending band of NH_2 at 1635 cm^{-1} and the N-D

bending band of ND_2 at 1319 cm^{-1} become more intense. Another bands located in the region between 1000 to 1700 cm^{-1} change the absorption intensity at the temperature lower than the phase transition temperature. This fact shows that the proton transfer of the hydrogen bond system induces the thermochromism of PA-15NPDA crystals by the scheme shown in Fig. 6.

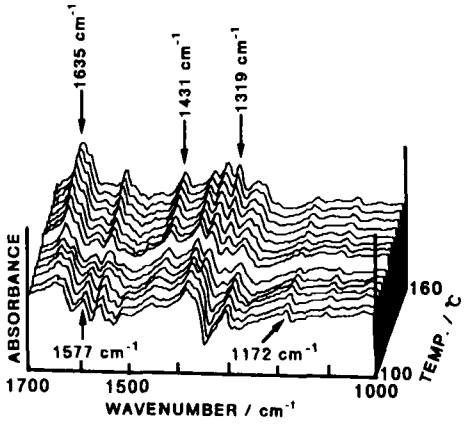

Fig. 5. The temperature variable IR absorption spectra of the partially deuterated PA-15NPDA salt.

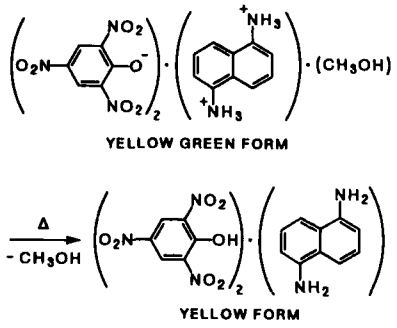

Fig. 6. The mechanism of the thermochromism .

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