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Thermochromism of the Crystal of the N-Salicylidene-2-Aminopyrazine – Hydroquinone Complex

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N-Salicylidene-2-aminopyrazine (NSAPZ) and hydroquinone (HQ) form a crystalline complex consisting of two NSAPZs and one HQ in a molar ratio. The structure of this crystal was determined by the x-ray analysis and the thermochromism of the crystal was studied based on the temperature dependence of the visible and IR absorption spectra .

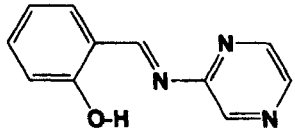
Keywords: N-Salicylidene-2-aminopyrazine; Hydroquinone; X-ray structure analysis; Visible absorption spectra; IR absorption spectra

INTRODUCTION

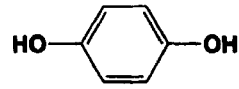
The reversible solid state photochromism of N-salicylidene-anilines (aniles) was first observed by Senier and co-workers.[1] Cohen and co-workers undertook a more systematic study of crystalline anils and confirmed that many anils are dimorphic and that two forms occasionally differ in color.[2] Hadjoudis and co-workers

extended the structural studies in the series of heterocyclic anil like N-salicylidene-2-aminopyridine (NSAP).[3] Inabe and coworkers prepared many compounds of the anils family and studied the structural and optical properties in the crystalline state.[4] On the other hand, Tanaka and coworkers studied the reversible thermochromism of the crystal of the charge transfer complex of NSAP with 1,3,5-tribitrobenzene (TNB) by the x-ray analysis and the measurement of the variable temperature visible absorption spectra.[5] In this paper, we report the reversible thermochromism and the crystal structures of the complex of NSAPZ with HQ.

N-Salicylidene-2-aminopyridine NSAPZ



Hydroquinone HQ



EXPERIMENTAL

Synthesis. NSAPZ was prepared by a well-known method.[6] The crystal of the complex of NSAP with HQ were obtained as the red orange prism from the solution of aceton and ethylacetate. The color of the crystal changes from red-orange to yellowish white upon cooling.

Measurements. The temperature dependence of the visible absorption spectra of the single crystals of the NSAPZ/HQ complex was measured using an absorption microphtometer made in our laboratory with the cooling plate of LINKAM.

X-Ray structure analysis. The reflection data of the crystal of NSAPZ2-HQ complex were measured on a Rigaku AFC-5R four circle diffractometer with MoKa radiation up to $2\theta = 56.0^\circ$. Lattice parameters were determined with 25 reflections in the range $21.5^\circ < 2\theta < 21.9^\circ$. Crystal data: $C_{28}H_{24}N_6O_4$, Mw=508.54, triclinic, space group $P\bar{1}$, a=12.039(4), b=15.146(4), c=7.170(4) Å, α=99.67(3)°, β=106.94(4)°, γ=79.45(2)°, V=1220(2) Å^3, Z=2, Dx=1.384 g/cm^3, μ(Mo Kα)=0.089 mm^{-1}. Intensities were measured up to $\sin\theta/\lambda$ by using ω-2θ sacn technique where scan speed was 6.0° min^{-1} in ω and scan range $(1.73+0.30\tan\theta)^\circ$ in ω. In total 6350 reflections were measured and 5883 reflections were unique. For refinement 4806 reflections with Io larger than 0.50 σ(Io) were used.The structure was solved by the direct method MITHRIL[7] and refined by a full-matrix least-squares: the quantity minimized was $\Sigma w(|Fo| - |Fc|)^2$ where w refers to weights $4Fo^2/\sigma^2(Fo^2)$. The final values of R and Rw were 0.062 and 0.056, respectively. In a final difference Fourier map maximum and minimum $\Delta\rho$ were 0.23 and -0.26 e Å^{-3},respectively. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[8] Computations were carried out by using TEXAN[9] at the X-Ray Laboratory of Okayama University.

RESULTS and DISCUSSION

Crystal structure. Final atomic parameters for the red orange crystal are listed in Table 1. The displacement ellipsoids and the numbering of atoms are shown in Figure 1. A crystal view of the molecular arrangement in the NSAPZ2-HQ crystal is shown in Figure 2. Figure 2 shows that two independent NSAPZs are stacked along the c axis and the complex is formed by the O-H ···N hydrogen bonds connecting one HQ and these NSAPZs molecules. Two planar NSAPZ molecules are located at the trans position around one HQ molecule.

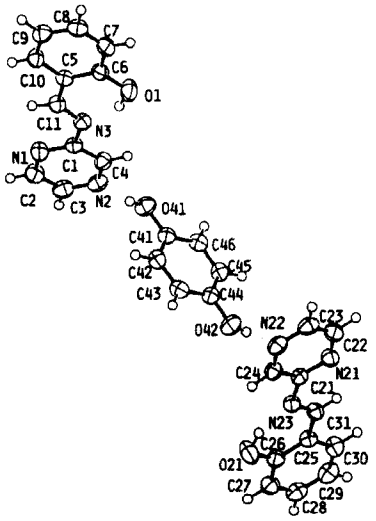


Figure 1. The numbering of the atoms of NSAPZ2-HQ complex.

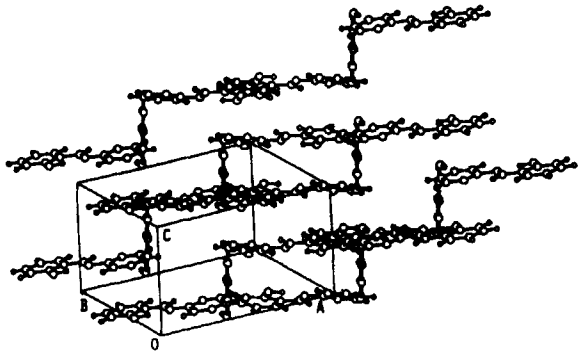


Figure 2. A view of the molecular arrangement in the NSAPZ2-HQ crystal

Table 1. Fractional Atomic Coordinates of NSAPZ2-HQ Crystal.

$$B(eq) = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}\, a_i^* a_j^* a_i \cdot a_j$$

atom	x	y	z	B(eq)
O(1)	0.8090(1)	1.0688(1)	0.1081(2)	5.23(7)
O(21)	0.6899(1)	-0.0734(1)	0.2323(2)	4.64(6)
O(41)	0.8425(1)	0.55521(9)	-0.0548(2)	4.20(6)
O(42)	0.6590(1)	0.44381(9)	0.4749(2)	4.27(6)
N(1)	1.1331(1)	0.8188(1)	0.3087(2)	3.59(6)
N(2)	0.9766(1)	0.6961(1)	0.1166(2)	3.68(7)
N(3)	0.9794(1)	0.93857(9)	0.2071(2)	3.10(6)
N(21)	0.3643(1)	0.1813(1)	0.2614(2)	3.63(6)
N(22)	0.5239(1)	0.3028(1)	0.3239(2)	3.78(7)
N(23)	0.5210(1)	0.06025(9)	0.2542(2)	3.14(6)
C(1)	1.0225(1)	0.8459(1)	0.2132(2)	2.84(6)
C(2)	1.1637(2)	0.7297(1)	0.3061(3)	3.92(8)
C(3)	1.0870(2)	0.6687(1)	0.2119(3)	3.83(8)
C(4)	0.9448(2)	0.7849(1)	0.1174(3)	3.30(7)
C(5)	1.0058(1)	1.0936(1)	0.2851(2)	2.97(7)
C(6)	0.8886(2)	1.1256(1)	0.1941(2)	3.35(7)
C(7)	0.8522(2)	1.2182(1)	0.1909(3)	3.94(8)
C(8)	0.9304(2)	1.2780(1)	0.2787(3)	4.03(9)
C(9)	1.0459(2)	1.2476(1)	0.3717(3)	4.22(9)
C(10)	1.0835(2)	1.1564(1)	0.3742(3)	3.79(3)
C(11)	1.0476(2)	0.9979(1)	0.2885(2)	3.09(7)
C(21)	0.4769(1)	0.1532(1)	0.2714(2)	2.92(7)
C(22)	0.3327(2)	0.2708(1)	0.2819(3)	3.94(8)
C(23)	0.4112(2)	0.3311(1)	0.3146(3)	3.87(8)
C(24)	0.5565(2)	0.2138(1)	0.3008(3)	3.53(8)
C(25)	0.4959(1)	-0.0942(1)	0.2303(2)	2.88(6)
C(26)	0.6120(1)	-0.1284(1)	0.2260(2)	3.18(7)
C(27)	0.6488(2)	-0.2212(1)	0.2153(3)	3.77(8)
C(28)	0.5726(2)	-0.2796(1)	0.2074(3)	3.66(8)
C(29)	0.4597(2)	-0.2471(1)	0.2115(3)	3.69(8)

continued

atom	x	y	z	B(eq)
C(30)	0.4202(2)	-0.1555(1)	0.2229(3)	3.41(7)
C(31)	0.4535(2)	0.0019(1)	0.2432(2)	3.02(7)
C(41)	0.7989(1)	0.5283(1)	0.0799(2)	3.19(7)
C(42)	0.8468(2)	0.5455(1)	0.2805(3)	3.34(7)
C(43)	0.7988(2)	0.5176(1)	0.4111(3)	3.34(7)
C(44)	0.7036(1)	0.4705(1)	0.3409(2)	3.14(7)
C(45)	0.6561(2)	0.4527(1)	0.1405(3)	3.39(7)
C(46)	0.7036(2)	0.4810(1)	0.0104(3)	3.47(7)
H(1O)	0.855(2)	1.012(2)	0.133(3)	7.2(6)
H(2)	1.243(2)	0.709(1)	0.379(3)	4.3(4)
H(3)	1.112(2)	0.604(1)	0.217(2)	4.1(4)
H(4)	0.866(2)	0.810(1)	0.049(2)	3.3(4)
H(7)	0.770(2)	1.239(1)	0.121(3)	5.3(5)
H(8)	0.906(2)	1.341(1)	0.274(3)	5.5(5)
H(9)	1.102(2)	1.287(1)	0.432(3)	4.8(4)
H(10)	1.165(2)	1.133(1)	0.437(3)	4.5(4)
H(11)	1.124(2)	0.981(1)	0.355(3)	4.2(4)
H(21O)	0.648(2)	-0.012(2)	0.240(3)	8.4(7)
H(22)	0.254(2)	0.292(1)	0.277(3)	5.0(5)
H(23)	0.387(2)	0.396(1)	0.336(2)	4.2(4)
H(24)	0.637(2)	0.189(1)	0.304(3)	5.1(5)
H(27)	0.727(2)	-0.243(1)	0.212(3)	5.1(5)
H(28)	0.596(2)	-0.342(1)	0.202(3)	4.5(4)
H(29)	0.403(2)	-0.289(1)	0.208(2)	3.8(4)
H(30)	0.343(2)	-0.132(1)	0.225(2)	3.6(4)
H(31)	0.374(2)	0.020(1)	0.253(2)	4.2(4)
H(41O)	0.885(2)	0.601(2)	-0.002(3)	6.6(6)
H(42)	0.915(2)	0.576(1)	0.325(2)	3.8(4)
H(42O)	0.615(2)	0.395(2)	0.405(3)	7.0(6)
H(43)	0.828(1)	0.530(1)	0.546(3)	3.6(4)
H(45)	0.590(2)	0.419(1)	0.092(2)	3.7(4)
H(46)	0.670(1)	0.467(1)	-0.130(2)	3.0(3)

Thermal studies. Figure 3 shows the DSC curves of NSAPZ crystal, HQ crystal amd NSAPZ2-HQ crystal. The curve has the peak of the melting point at 115.5°C for NSAPZ, at 173.3 °C for HQ and 102.5°C for NSAPZ2-HQ. No peak is observed over the thermochromic region.

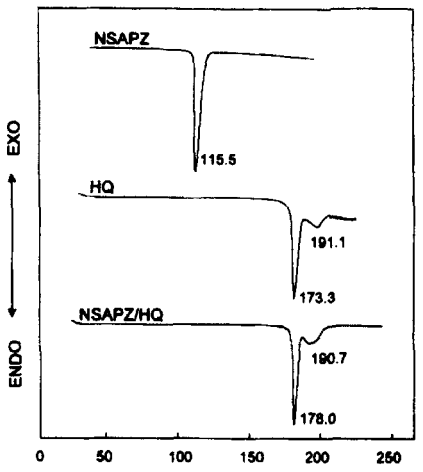


Figure.3 The DSC curves of NSAPZ, HQ and NSAPZ2-HQ.

Visible absorption spectra. Figure 4 shows the temperature dependence of the visible absorption spectra of the NSAPZ2-HQ crystal. The absorption spectra in the region of 400 nm to 550 nm has two bands. The 500 nm band disapears at low temperature and the 400 nm band does not change upon cooling. That is, the 400 nm band is the absorption band of the stable enole form and the 500 nm band is the absorption band of the less stable keto form. The energy difference between the enol and keto forms can be estimated by the plot of the log of the optical density at 500 nm against 1/T. The value of the energy difference is found to be 8.0 kJ/mol. This value is nearly equal to the value of the NSAP crystal.[3,5]

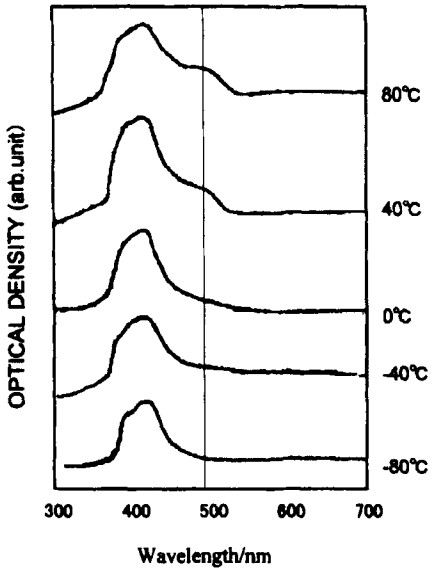


Figure 4. Temperature dependence of the visible absorption spectra of the NSAPZ2-HQ crystal.

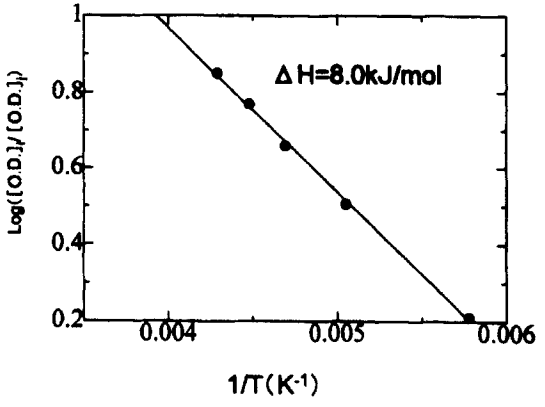


Figure 5. The plot of the logarism of the optical density at 500 nm against 1/T of the NSAPZ2-HQ crystal.

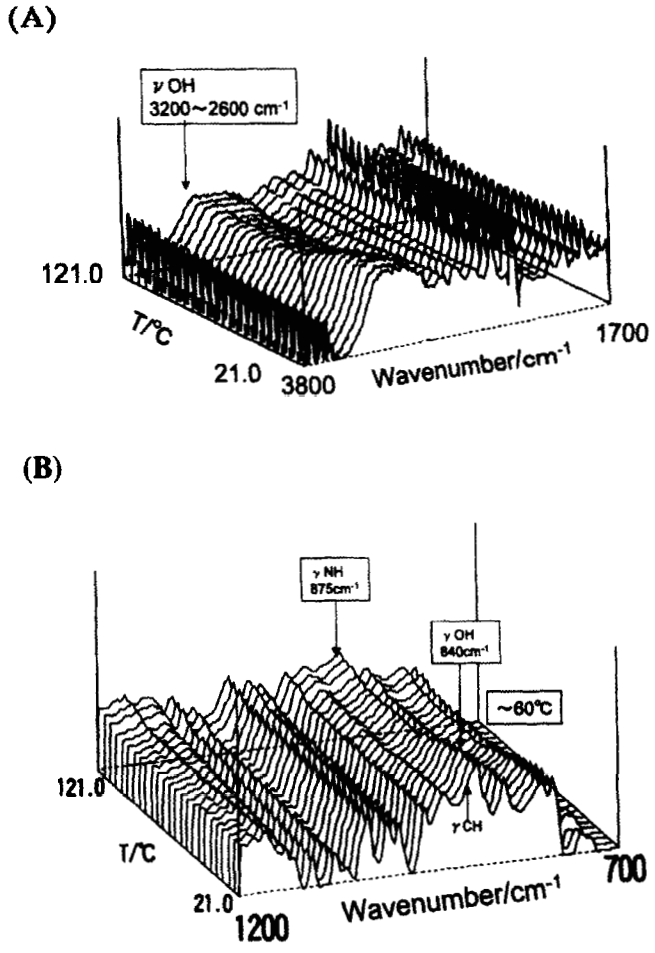


Figure 6. The temperature variable IR absorption spectra of the NSAPZ2-HQ crystal.

IR absorption studies. Figures 6(A) and (B) show the temperature variable IR absorption spectra of the NSAPZ2-HQ complex. The OH streching band at 3500 cm^{-1} shifts to the lower wavenumber region upon cooling and the intensity variation of the γ OH and γ NH out of plane bands at about 800 cm^{-1} is also observed.

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