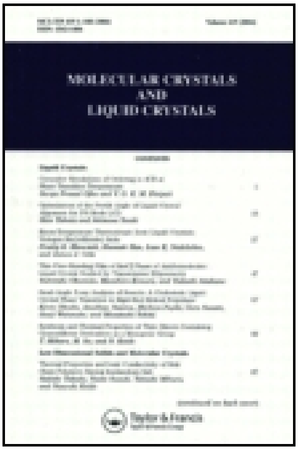

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Thermochromism of the Crystals of 2,3-Di(p-chlorophenylthio)-1,4-Naphthoquinone

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Abstract The crystals of 2,3-di(p-chlorophenylthio)-1,4-naphthoquinone have the dimorphs of red and dark red forms. The crystal structure of red form has been determined by the X-ray diffraction method. The red form changes to the dark red form upon heating. Such thermochromism was studied by measuring the solid state CP/MAS and temperature variable IR absoption spectra, and the DSC of the red form of 2,3-di(p-chlorophenylthio)-1,4-naphthoquinone.

INTRODUCTION

A number of organic compounds undergo reversible color changes by the alternation of the molecular structure with temperature. However, a few organic compounds in the solid phase can undergo chemical changes which are in many respects unparalleled for the same molecules in solution. For example, p-anisylquinone crystallizes as both yellow and red solids, and the yellow solid undergoes a thermal reaction to give the red form.[1] The irreversible thermochromism of the crystal of 2,3-di(phenylthio)-1,4-naphthoquinone (DPNQ) changes the violet form to the red form upon heating.[2] Such thermochromism in the solid phase occurs due to the alternation of the change transfer interaction in the crystals. In this paper, we report the irreversible thermochromism of the crystals of 2,3-di(p-chlorophenylthio)-1,4-naphthoquinone (DCPNQ) and discuss its mechanism based on the results of the X-ray analysis and the measurement of the CP/MAS NMR and IR absorption spectra.

EXPERIMENTAL

Synthesis. DCPNQ was prepared by the methods of Miyaki and Ikeda[3] and Fieser and Brown.[4] DCPNQ gave two kinds of crystals, red and dark red forms, according to the conditions of recrystallization.

Measurements. The ^{13}C NMR solution spectra were taken by the JNM-EX 270 MHz H NMR and 400MHz PC NMR spectrometers and the solid state CP/MAS NMR spectra by the JEOL CMX300, respectively. Thermal analyses were carried out using a Shimadzu DSC. The temperature variable IR absorption spectra of the single crystal were recorded using a JASCO FT-IR VALOR III with the hotplate FP82HT.

X-Ray structure analysis. A red crystal used had dimensions of $0.50 \times 0.23 \times 0.23$ mm. The reflection data were measured on a Rigaku AFC-5R four circle diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073Å) at 50 kV and 200 mA. Lattice parameters were determined with 25 reflections in the range $21° < 2\theta < 22°$. Crystal data: $C_{22}H_{11}O_2S_2Cl_2$, Mw=443.36, triclinic, space group $P\bar{1}$, a=10.890(6), b=11.525(5), c=9.43(1) Å, α=111.01(5)°, β=113.43(6)°, γ=88.91(4)°, V=1003(1) Å^3, Z=2, Dx=1.468 g cm^{-3}; μ(Mo Kα) =0.54 mm^{-1}. Intensities were measured up to sin θ/λ 0.5946Å^{-1} by using ω-2θ scan technique where scan speed was 6° min^{-1} in ω and scan range (1.78+0.30tan 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 3771 reflections were measured ranging h=−11 to 11, k=−13 to 12, l=0 to 11, and 3537 reflections were unique (Rint=0.012). For refinement 2272 reflections with Io larger than 3 σ(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[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). The non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. Extinction correction was performed according to Icorr=Io(1+2.17$\times$10^{-6}Ic). The final values of R and Rw were 0.041 and 0.033, respectively (S=1.70). In the last cycle of least-squares refinement $(\Delta/\sigma)_{max}$ was 0.86. In a final difference Fourier map maximum and minimum $\Delta\rho$ were 0.32 and -0.30 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 red crystal are listed in Table 1. The displacement ellipsoids and the numbering of atoms are shown in firure 1.[8] Projections of the crystal structure along c axis is shown in firure 2. Firure 3 shows that the DCPNQ molecule in the red form has the structure in which two phenylthio groups are located on the same side of the plane of 1,4-naphthoquinone (NQ) ring. The dihedral angle between the benzene ring and the quinoid group is 11.8(1) ° . The carbonyl oxygens deviate slightly from the quinoid ring: O(1) 0.420Å, and O(2) 0.610(4)Å. The DCPNQ molecule dose not have the Cs symmetry in the red form.

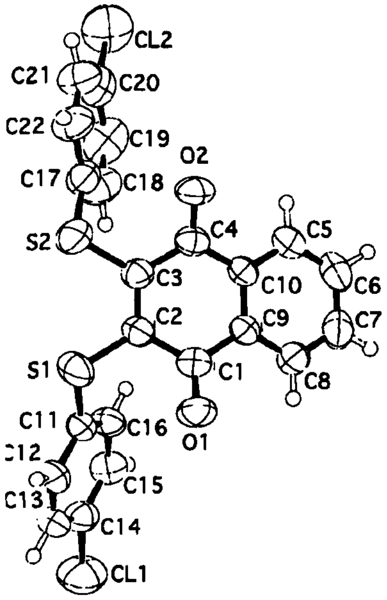

FIGURE. 1 The numbering of atoms of DCPNQ.

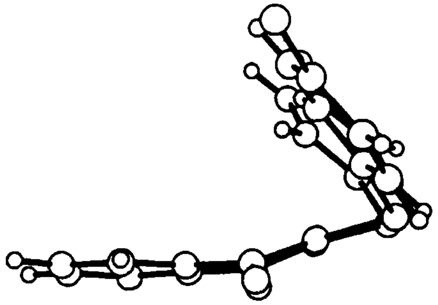

FIGURE. 3 DCPNQ molecule in the red form.

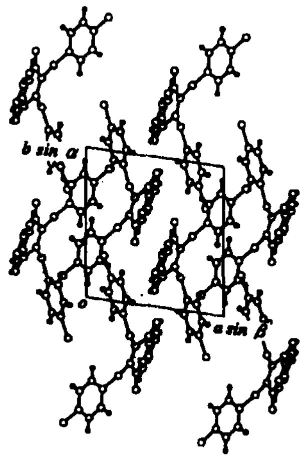

FIGURE. 2 Projections of the crystal along c axis.

Table 1. Fractional Atomic Coordinates of red form

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

atom	x	y	z	B(eq)	atom	x	y	z	B(eq)
Cl(1)	0.8673(1)	-0.29620(8)	0.2265(1)	9.08(5)	C(15)	0.8377(3)	-0.0576(3)	0.3769(4)	5.4(1)
Cl(2)	1.1665(1)	0.8772(1)	1.1581(1)	9.94(5)	C(16)	0.7973(3)	0.0563(3)	0.3785(4)	4.9(1)
S(1)	0.6816(1)	0.21938(7)	0.2226(1)	6.45(4)	C(17)	0.8833(3)	0.6100(3)	0.6469(4)	5.5(1)
S(2)	0.7701(1)	0.50566(8)	0.4449(1)	7.28(4)	C(18)	0.9629(4)	0.5660(4)	0.7639(6)	7.4(2)
O(1)	0.4910(2)	0.1069(2)	0.3161(2)	6.28(8)	C(19)	1.0498(4)	0.6463(4)	0.9203(7)	7.8(2)
O(2)	0.6414(2)	0.5830(2)	0.6901(2)	5.86(8)	C(20)	1.0580(3)	0.7738(4)	0.9598(4)	6.4(1)
C(1)	0.5526(3)	0.2088(3)	0.4225(3)	4.5(1)	C(21)	0.9828(4)	0.8192(4)	0.8427(5)	7.0(2)
C(2)	0.6434(3)	0.2860(2)	0.3946(3)	4.4(1)	C(22)	0.8947(4)	0.7376(3)	0.6871(5)	6.7(2)
C(3)	0.6827(3)	0.4101(2)	0.4923(3)	4.6(1)	H(5)	0.625(2)	0.514(2)	0.911(3)	5.3(7)
C(4)	0.6395(3)	0.4698(3)	0.6304(3)	4.4(1)	H(6)	0.557(3)	0.379(2)	1.014(3)	5.9(7)
C(5)	0.5947(3)	0.4286(3)	0.8477(4)	5.3(1)	H(7)	0.471(3)	0.173(2)	0.835(3)	5.7(8)
C(6)	0.5511(4)	0.3491(4)	0.9025(5)	6.1(2)	H(8)	0.465(2)	0.096(2)	0.567(3)	5.2(7)
C(7)	0.5017(4)	0.2257(4)	0.7980(5)	6.0(2)	H(12)	0.660(2)	-0.010(2)	-0.017(3)	4.2(6)
C(8)	0.4973(3)	0.1810(3)	0.6409(4)	5.1(1)	H(13)	0.736(3)	-0.201(2)	-0.025(3)	5.7(7)
C(9)	0.5459(3)	0.2586(2)	0.5863(3)	4.0(1)	H(15)	0.881(2)	-0.070(2)	0.478(3)	5.0(7)
C(10)	0.5934(3)	0.3843(2)	0.6901(3)	4.1(1)	H(16)	0.814(2)	0.121(2)	0.479(3)	5.1(7)
C(11)	0.7303(3)	0.0740(2)	0.2306(3)	4.4(1)	H(18)	0.957(3)	0.477(3)	0.737(4)	10(1)
C(12)	0.7072(3)	-0.0241(3)	0.0807(4)	5.2(1)	H(19)	1.100(3)	0.621(3)	1.002(4)	8(1)
C(13)	0.7521(3)	-0.1368(3)	0.0797(4)	5.6(1)	H(21)	0.992(3)	0.907(3)	0.867(4)	8(1)
C(14)	0.8157(3)	-0.1520(3)	0.2272(5)	5.4(1)	H(22)	0.838(3)	0.767(3)	0.608(3)	6.7(8)

Thermal studies. DPNQ gives two kinds of crystals according to the conditions of recrystallization, one of red prism (red form) and the other of dark red form. The red form changes slowly and irreversibly to the dark red form at the vicinity of about 145 °C . DSC under nitrogen gas, presented in firure 4, shows the exothermic peaks over the wide temperature range from 145°C to 170°C and the phase transition energy is estimated to be 7.8 kJ/mol. The melting point is observed at 179.6°C. The cooling curve shows no endothermic peak.

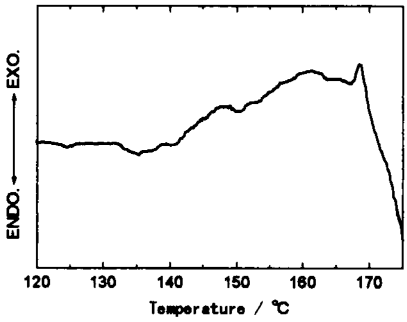

FIGURE. 4 DSC curve of the red form.

NMR studies. Figure 5 shows the ^{13}C NMR spectra of the red solution of DCPNQ in $CDCl_3$. Figure 6 (A) and (B) show the solid state ^{13}C NMR spectra of the red and dark red forms. The solution spectrum has a peak at 178.5 ppm of carbonyl carbons and a peak at 148.0 ppm of C(2) and C(3) carbons. That is, DCPNQ molecules in the solution have the symmetry of Cs.[2] On the other hand, figure 6 shows the solid state CP/MAS spectra of the red and dark red forms. The spectrum of the red form has the doublet at 179.0 ppm and 176.8 ppm due to the carbons at carbonyl groups of NQ. The similar spectrum is obtained for the dark red form with the doublet at 177.9 ppm and 165.7 ppm. The broad peaks at 130 ppm can be assingned to the carbons in the benzene rings of NQ and two phenylthio groups. The other peaks at 65 ppm and 200 ppm are the spinning side bands.

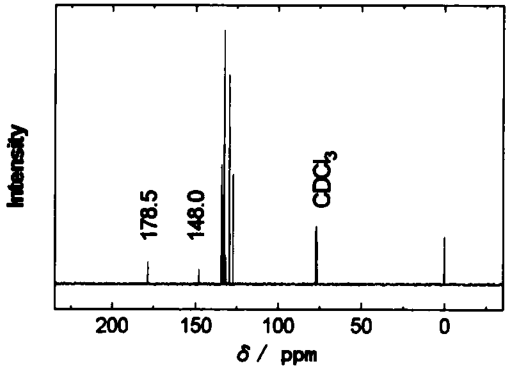

FIGURE. 5 The ^{13}C NMR spectra of the red solution of DCPNQ in $CDCl_3$ together with the assignment of each peak.

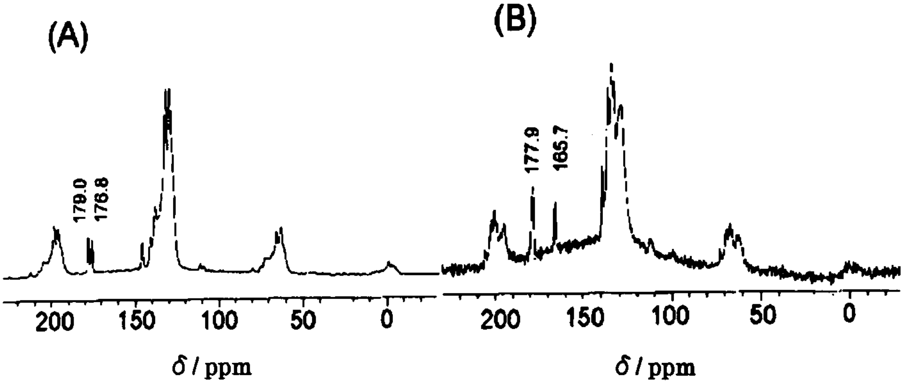

FIGURE. 6 The solid state CP/MAS spectra of (A) red and (B) dark red forms.

IR absorption studies. The CCl_4 solution IR spectrum has one C=O peak at 1672 cm^{-1} as expected in figure 5. On the other hand, figure 7 shows the temperature variable FT-IR absorption spectra of DCPNQ crystals. Many peaks of the DCPNQ molecules in the red form do not change upon heating, except for the C=O stretching band at 1669 cm^{-1}. This C=O band splits into two peaks at 1671 cm^{-1} and 1655 cm^{-1} with the promotion of the temperature upon heating. This behavior is consistent with that of the DSC curve of the red form as shown in figure 4.

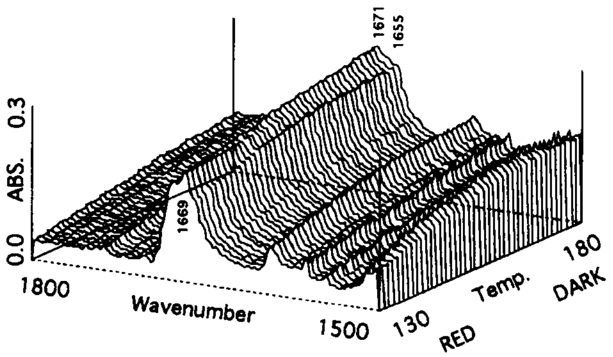

FIGURE. 7 Temperature variable FT-IR spectra of the red form of DCPNQ.

REFERENCES

1 G.R.Desiraju, I,C.Paul, and D.Y.Curtin, *J.Am.Chem.Soc.*,99,1594(1977).

2 M.Tanaka, H.Hayashi, S.Matsumoto, S.Kashino, and K.Mogi, to be submitted

3 K.Miyaki and N.Ikeda, *Japanese Yakugaku Zasshi*,73,964(1953).

4 L.H.Fieser and R.H.Brown, *J.Am.Chem.Soc.*, 71,3609(1949).

5 G.J.Gilmore, *J.Appl.Crystallogr.*,17,42(1984).

6 "International Tables for X-Ray Crystallogrphy,"Kynoch Press, Birmingham. (Present distributor Kluwer Academic Publisher, Dordrecht) (1974), Vol.IV, pp. 22-98.

7 TEXAN. Single Crystal Structure Analysis Software, Version 5.0,"Molecular Corpration, The Woodlands,Texas (1989).

8 C.K.Johnson,"ORTEP II,Report ORNL-5138",Oak Ridge National Laboratory, Tennessee (1976).