Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Masashi Tanaka [a] & Hajime Tsunekawa [a]

[a] Department of Natural Science Informatics, School of Informatics and Science, Nagoya University, Chikusa-ku, Nagoya, 464-01, Japan

Version of record first published: 04 Oct 2006

To cite this article: Masashi Tanaka & Hajime Tsunekawa (1998): Spectral Study of the Phase Transition of the Crystal of the CT Complex between Picric Acid and 1-Bromo-2-aminonaphthalene, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 313:1, 355-360

To link to this article: http://dx.doi.org/10.1080/10587259808044299

Mol. Cryst. Liq. Cryst., 1998, Vol. 313, pp. 355-360
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Spectral Study of the Phase Transition of the Crystal of the CT Complex between Picric Acid and 1-Bromo-2-aminonaphthalene

MASASHI TANAKA and HAJIME TSUNEKAWA
Department of Natural Science Informatics, School of Informatics and Science, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

The phase transition of the crystals of the complex of picric acid with 1-bromo-2-aminonaphthalene(BAN) is studied by measuring the temperature variable IR absorption spectra and the differential scanning calorimetry (DSC).

Keywords: Thermochromism; Phase transition; Proton transfer

INTRODUCTION

A few organic compounds in the solid phase can undergo chemical changes which are in many respects unparallel for the same molecules in a solution. Such thermochromism in the solid phase occurs due to the variation of the charge transfer interaction in the crystal. In the present paper, we report such phase transition of the crystals of picric acid with BAN and discuss the mechanism of the thermochromism by the measurement of the variable temperature IR absorption spectra.

EXPERIMENTAL

Synthesis BAN was prepared by the method of Whitehurst[1].

The crystals of the complex of picric acid with BAN have four polymorphic forms. The red crystal (RED A) is obtained from the chloroform solution containing picric acid and BAN. This crystal changes to the yellow crystal (YELLOW B) in two months. Another yellow crystal (YELLOW C) is obtained from the 1-butanol solution contaning picric acid and BAN.

RESULTS AND DISCUSSION

Thermal Analysis Figure 1 shows the DSC heating curves of the phase transition of RED A, YELLOW B and YELLOW C. The DSC curve of RED A has the endo peak at 99.5℃ with the transition energy of 2.05 kJ/mol while the crystal color does not change. The DSC curve of YELLOW B has the endo peak with 26.0 kJ/mol when YELLOW B changes to the red crystal (RED D). The DSC curve of YELLOW C has the endo peak at 132.5℃ with 29.6 kJ/mol when YELLOW C changes to RED D. The peaks at about 182℃ are the melting point of RED D.

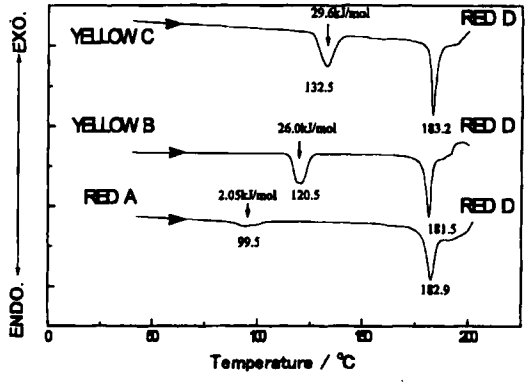

FIGURE 1 The DSC heating curves of RED A, YELLOW B and YELLOW C.

Figure 2 shows the DSC cooling curves of the heated crystals of RED A, YELLOW B, and YELLOW C. These curves have the exo peaks at about 78℃ with 2.1 kJ/mol. This absolute value (2.1 kJ/mol) is almost equal to the value of the endothermal energy of the phase transition from RED A to RED D.

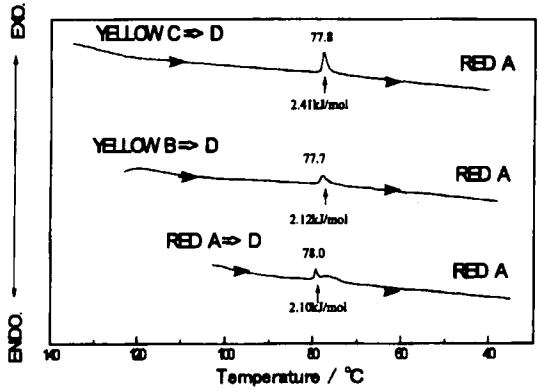

FIGURE 2 The DSC cooling curves of RED A, YELLOW B, and YELLOW C.

The Visible Crystal Absorption Spectra In the crystal of RED A, picric acid and BAN molecules are stacked alternately along the c axis to form the continuous columns and the moleular overlapping in the column is shown in Figure 3[2]. Picric acid and BAN molecules are plannar and each molecular planes are parallel to the ab plane which is the developed plane of the crystal of RED A.

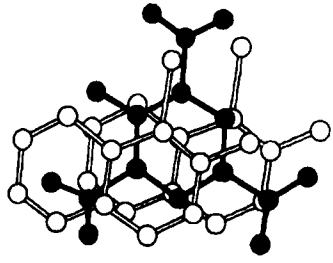

FIGURE 3 View of the crystal of RED A[2].

Figure 4 shows the polarized crystal spectra of RED A. The spectra have two peaks at about 400 and 600 nm. The 400nm band may be assigned to the original band of picric acid or picrate cation and the new band at 600 nm seems to be the CT band. Figure 5 shows the polarized crystal absorption spectra of YELLOW C. The spectra has the intense band at 400 nm of picric acir or picrate ion and the weak CT band at 600 nm.

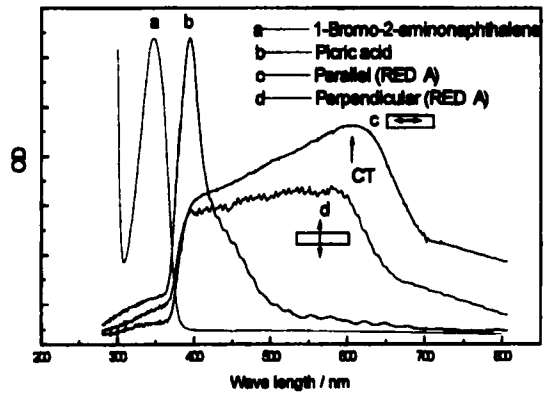

FIGURE 4 Polarized absorption spectra of RED A.

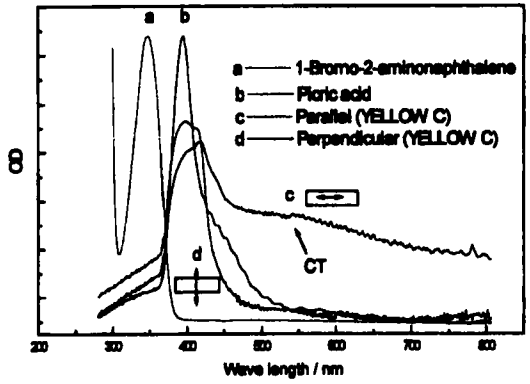

FIGURE 5 Polarized absorption spectra of YELLOW C.

The Temparature Variable IR Absorption Spectra Figure 6 shows the temperature variable absorption spectra of RED A. The 1628 cm^{-1} band of the N-H inplane bending mode becomes weak upon heating. Figure 7 shows the temperature vaiable IR absorption spectra of YELLOW B. YELLOW B has the N-H symmetric and antisymmetric stretching band of the NH_3^+ group in the wide region from 3100 to 2000 cm^{-1} and the overtone bands and combination bands of the NH_3^+ bending modes at 2030 cm^{-1}. In the higher temperature, these bands

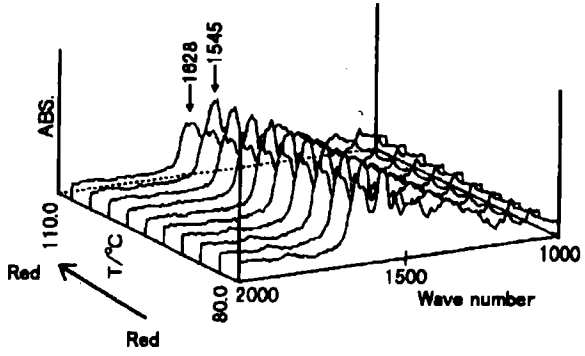

FIGURE 6 Temperature vaiable IR spectra of RED A.

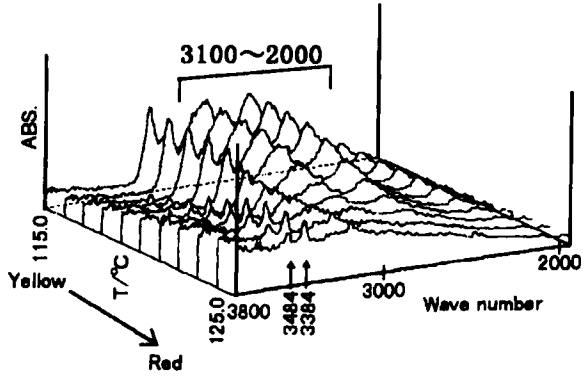

FIGURE 7 Temperature vaiable IR spectra of YELLOW B.

disappear and two peaks of the N-H stretching mode of the NH_2 group appear at 3484 and 3384 cm^{-1}. Figure 8 shows similar phenomenone for the thermochromism of YELLOW C. We conclude that the scheme of the thermochromism is shown in Figure 9.

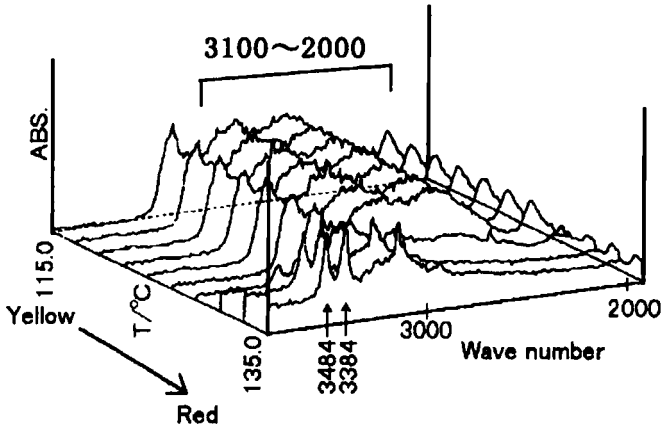

FIGURE 8 Temperature variable IR spectra of YELLOW C.

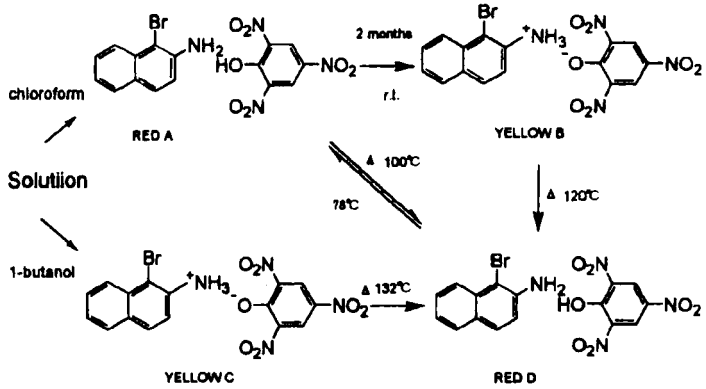

FIGURE 9 The scheme of the thermochromism.

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[2.] E.Carstensen-Oeser, S.Gottlicher, and G.Haberwell, Chem.Ber.,101,1648(1968).