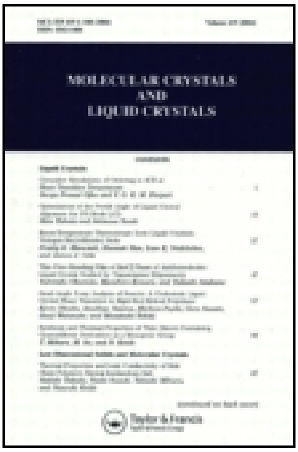

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Proton Transfer and Thermochromism of the Crystals of the Picric Acid CT Complexe

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PROTON TRANSFER AND THERMOCHROMISM OF THE CRYSTALS OF THE PICRIC ACID CT COMPLEXES

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Abstract The picric acid formed picrate salts or charge-transfer (CT) complexes with hexamethylbenzene(HMB), 2-iodoaniline(IAn), and 1-aminoanthracene(AAt). The crystals of these salts or complexes showed the thermochromism upon heating. The mechanism of the thermochromism was discussed by the temperature-variable FTIR absorption spectral data and the DSC thermal analysis data together with the results of the X-ray crystal structure analysis.

INTRODUCTION

It is well known that picric acid forms salts or charge-transfer(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, the stable polymorphs of picrate salts and CT complexes were found out and some crystals of them showed the thermochromism.[4,5]

In this paper, we report the temperature variable FTIR absorption spectral data and the thermal analysis data together with the results of the X-ray crystal structure analysis and discuss the mechanism of the thermochromism.

THERMOCHROMISM OF 2-IODOANILINIUM PICRATE

The crystals of 2-iodoanilinium picrate have the stable dimorphs of the monoclinic form (FORM I :yellow needle like crystal) and the triclinic form (FORM II : green plate like crystal). In these crystal, 2-iodoanilinium cation and picrate anion form a nearly planar pair of these ions with similar geometry of N-H···O hydrogen bond. Fig. 1 shows that the pairs in FORM I are stacked to form the segregated columns, while Fig. 2 shows that the anions and cations in FORM II are alternately stacked to form the continuous columns. The 2-iodoanilinium cation and picrate anion chosen as an asymmetric unit form a hydrogen-bonded pair in both forms.

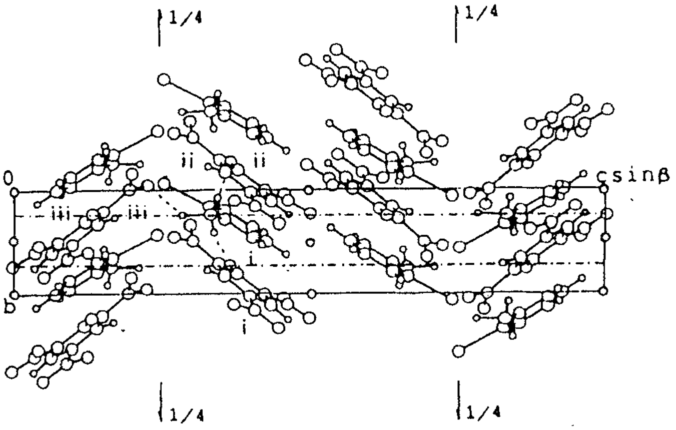

Fig. 1 Projection of the crystal structure of the FORM I of the 2-iodoanilinium picrate crystal viewed down the a axis.[4]

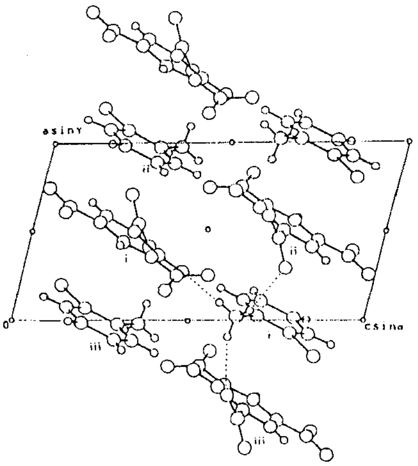

Fig. 2 Projection of the crystal structure of the FORM II of the 2-iodoanilinium picrate crystal viewed down the b axis.[4]

The polarized FTIR absorption spectra of the FORM I crystal are shown in Fig. 3. the sharp band at 3082 cm^{-1} can be assigned to the C-H stretching mode of the aromatic rings and three intense peaks in the region from 2400 to 3000 cm^{-1} are assigned to the overlap of the N-H symmetric and antisymmetric stretching modes of the NH_3^+ group and the intense band at 2000 cm^{-1} to the overtones and combinations of the NH_3^+ bending modes.[6] These assignments are in good agreement with the results of the X-ray crystal analysis. The polarized FTIR absorption spectra of the FORM II crystal are shown in Fig. 4. Each observed peak can be assigned in the same way as the FORM I.

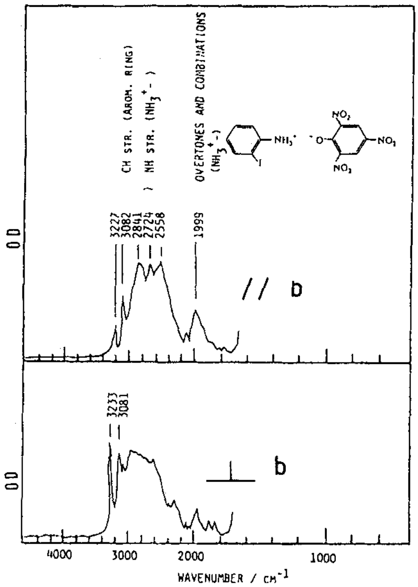

Fig. 3 The polarized FTIR absorption spectra of the FORM I crystal.

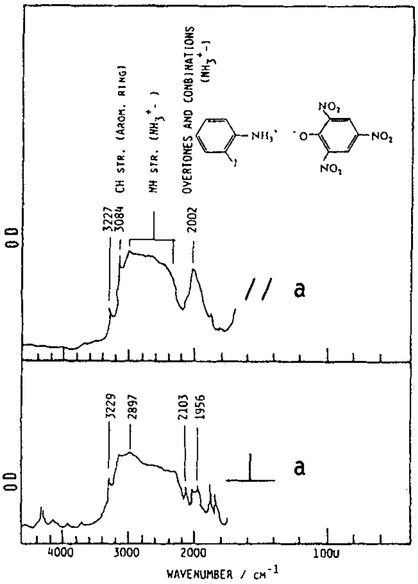

Fig. 4 The polarized FTIR absorption spectra of the FORM II crystal.

Fig. 5 shows the dfferential scanning calorimetiry (DSC) curves of the forms I and II crystals of the 2-iodoanilinium picrate. In the form I system, three endothermic peaks (62.8, 92.7, 118.3℃) were observed for the DSC curve. The yellow needle crystal of the form I changed to the red crystal at 92℃ and to the red solution at 119℃. Fig. 6 is the temperature-variable unpolarized FTIR absorption spectra of the 2-iodoanilinium picrate. The broad band due to the hydrogen-bonded system in the region from 2400 to 3000 cm^{-1} disappeared suddenly at about 95°C.

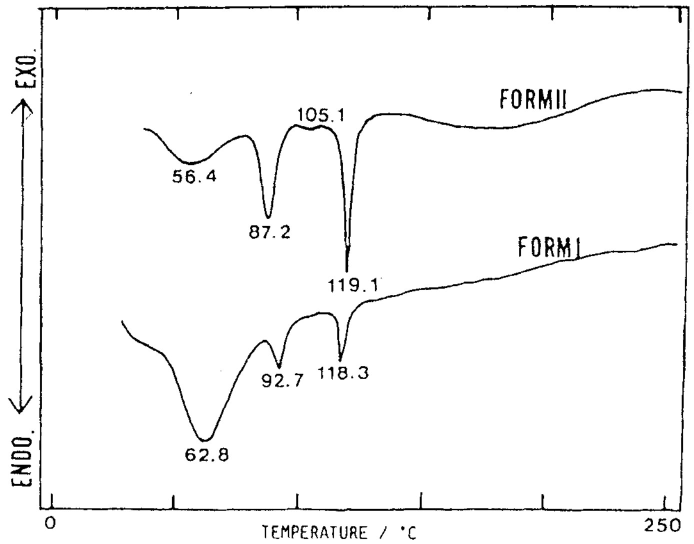

Fig. 5 DSC curves of the FORMs I and II crystals of the iodoanilinium picrate.

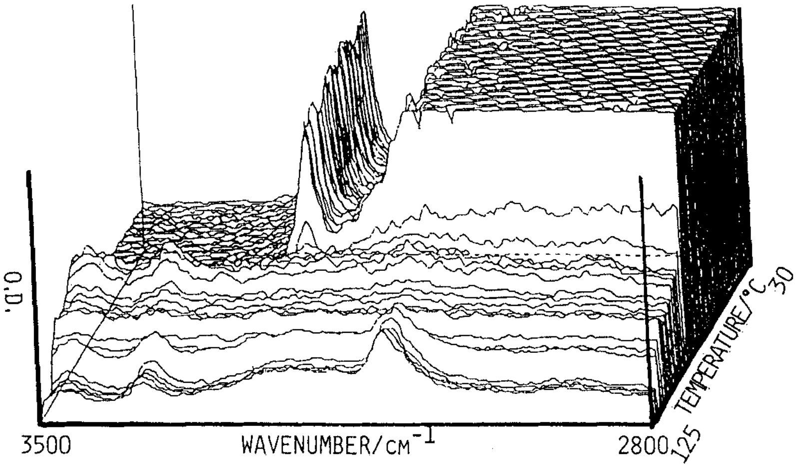

Fig. 6 Temperature variable unpolarized FTIR absorption absorption spectra of the crystal of the FORM I of 2-iodoanilinium picrate.

In the form II system, four endopeaks (56.4, 87.2, 105.1, and 119.1℃) were observed for the DSC curve as is shown in Fig. 5. The dark green plate crystal changed to the pale red crystal at about 87℃ and to the red crystal suddenly at about 105℃. Fig. 7 shows the temperature-variable unpolarized FTIR absorption spectra of the form II. The broad band due to the hydrogen-bonding systen in the region from 2400 to 3000 cm^{-1} disappeared suddenly at about 90℃. On the other hand, the peaks assigned to the N-H stretching mode of the free NH_2 group appeared at 3470 and 3378cm^{-1} and the C-H stretching band of the aromatic ring became more intense at 3121cm^{-1} at the higher temperature. That is, the proton transfer occurs upon heating. Therefore, the mechanism of the thermochromism is shown by the reaction given in Fig. 8.

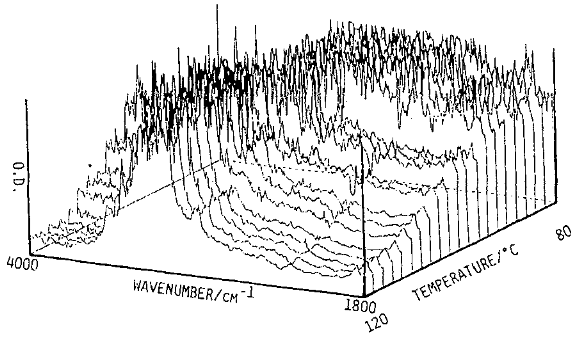

Fig. 7 The temperature variable unpolarized FTIR absorption spectra of the FORM II of the 2-iodoanilinium picrate.

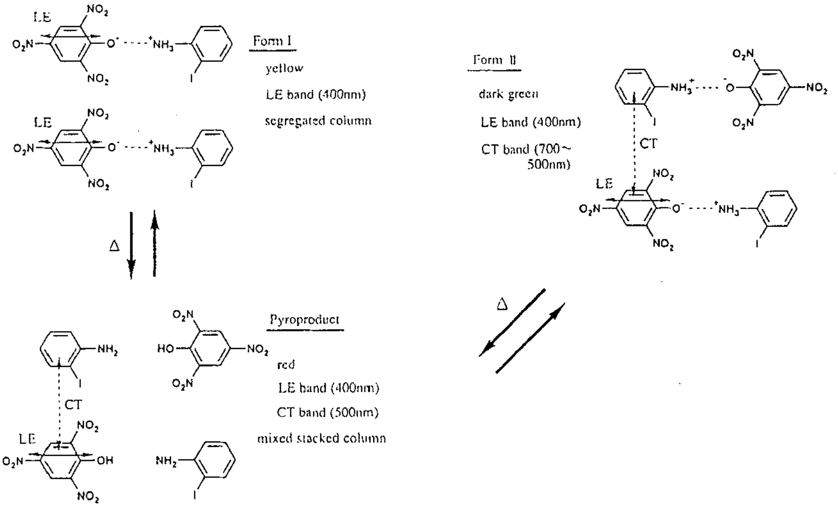

Fig. 8 The mechanism of the thermochromism of the crystal of 2-iodoanilinium picrate.

THERMOCHROMISM OF PICRIC ACID-HEXAMETHYLBENZENE CT COMPLEX

Picric acid forms the CT complex with hexamethylbenzene. The crystals of the complex have the orange and yellow forms.[5] The orange form is triclinic and the molecules of picric acid and hexamethylbenzene form a mixed stack column as is shown in Fig. 9. Two independent molecules of hexamethylbenzene lie on the crystallographic centers of the symmetry. The picric acid moiety is disordered as it has a pseudo three fold symmetry. Therefore, 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. Fig. 10 shows the DSC curves of the crystals of the orange and yellow forms. One endothermic peak(116℃) and one exothermic peak (179℃) are observed for the heating curve of the orange form, while the cooling curve under 150℃ has no peak. The orange platelike crystals change to the red crystal in the vicinity of 116℃, while the DSC curve for the yellow form does not show the thermochromism.

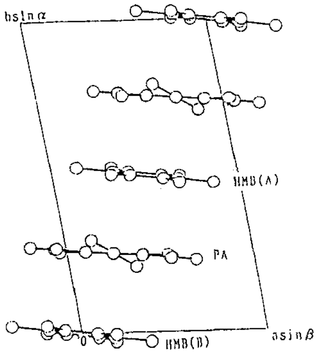

Fig. 9 Projection of the crystal structure of the picric acid-hexamethylbenzene CT complex along the c axis.[6]

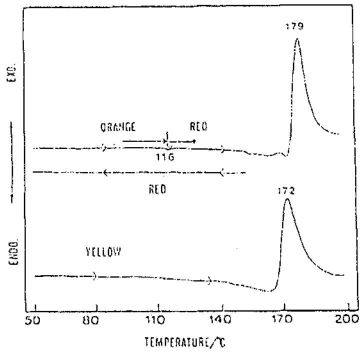

Fig. 10 DSC curves of the crystal of the orange and yellow forms of the piric acid-hexamethylbenzene CT complex.

Fig. 11 shows the temperature variable polarized FTIR absorption spectra of the crystal of the orange form of the picric acid-hexamethyl benzene complex. The broad and intense band located in the region from 2700 to 3200 cm^{-1} can be assigned to the overlap of the C-H stretching mode of the aromatic rings and the O-H stretching mode under the hydrogen bonding system. The shoulder at 3400 cm^{-1} may be assigned to the free O-H stretching mode . Two intense peaks at 4313 and 3985 cm^{-1} belong to the picric acid. In the higher temperature, a sharp peak of the C-H stretching modes appears at 3111 cm^{-1} and the shoulder of the free O-H stretching mode at 3400 cm^{-1} becomes intense. At 148℃, the shoulder becomes the peak and the broad and intense band seems to shift to the higher wavenumber side. Its peaks are located in the wide region from 2800 to 3400 cm^{-1} and the peak of the O-H stretching mode under the hydrogen bonding system separates at 2930 cm^{-1}. Two intense bands at 4313 and 3985 cm^{-1} disappear and a sharp peak appears at 2179 cm^{-1}. Thse facts mean that the hydrogen bonding system between the hydroxyl and nitro groups of the picric acid disappears slowly upon heating.

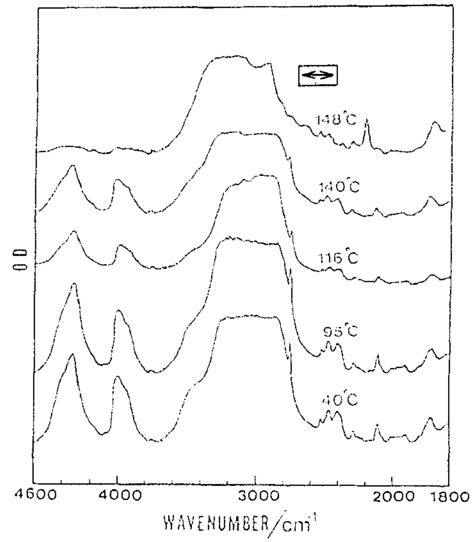

Fig. 11 The temperature variable polarized FTIR absorption spectra of the crystal of the orange form of the picric acid-hexamethylbenzene CT complex.

THERMOCHROMISM OF THE PICRIC ACID-1-AMINOANTHRACENE CT COMPLEX

Picric acid forms the red crystal with 1-aminoanthracene from the ethanol solution. The red crystal changes to the yellow crystal upon heating. Unfortunately, the X-ray analysis of the red crystal did not succeed because the crystal was poor. Fig. 12 shows the temperature variable polarized FTIR absorption spectra of the picric acid-hexamethyl benzene crystal. The free N-H stretching mode of the amino group in the 1-aminoanthracene molecule can be observed clearly. This fact means that the picric acid forms the CT complex with 1-aminoanthracene. Two sharp bands of the free N-H stretching mode becomes weaker upon heating and disappears at the thermochromism point. This mean that the CT complex of the picric acid-1-aminoanthracne changes to the picrate salt by the proton transfer mechanism although many picrate salts change to the CT complex upon heating.

ACKNOWLEDGEMENT

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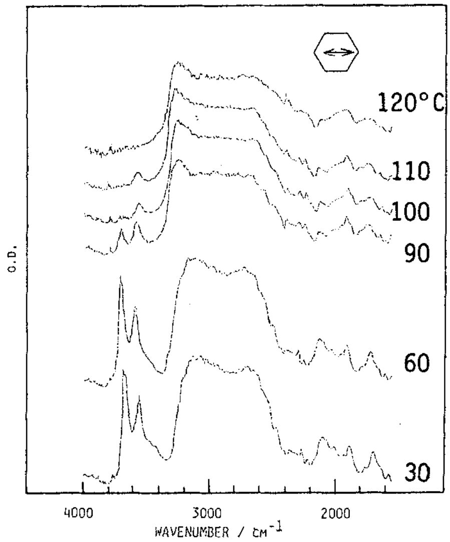

Fig. 12 The temperature variable polarized FTIR absorption spectra of the crystal of picric acid-1-aminoanthracene complex.

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