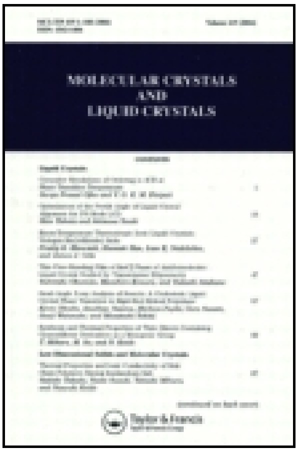

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Two-Component Mixed Crystals Consisting of Nitroanilines and Nitrophenols and Their Nonlinear Optical Property

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Two-Component Mixed Crystals Consisting of Nitroanilines and Nitrophenols and Their Nonlinear Optical Property

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Using *p*-, *m*- and *o*-nitroanilines and *p*-, *m*- and *o*-nitrophenols, fifteen mixed crystals of 1:1 molar ratio have been prepared by a melting-resolidification process and characterized by powder X-ray diffraction, differential scanning calorimetry, IR spectroscopy and phase diagram. Among them eight mixed crystals have been assigned to form molecular compounds and others to be simple mixtures of the component crystals. The second harmonic generation (SHG) activity was measured.

Keywords: Mixed crystals, nitroanilines, nitrophenols, molecular compounds, second harmonic generation

1. INTRODUCTION

Although the formation of crystalline molecular compounds from two different organic molecules through hydrogen bonding has recently been reported by Etter's group[1] and other workers,[2] it is still difficult to predict how such two compounds undergo molecular recognition in the crystal state.[3] In the course of our studies on the photochemistry of mixed crystals prepared from two different organic crystalline compounds by a melting-resolidification process or a crystallization process from solutions, we have shown that there are two principal cases for the nature of the mixed crystals.[4] One is the formation of a crystalline molecular compound between the components, and the other is the formation of a simple crystalline mixture of the components. One can discriminate between these two cases by the characterization of the mixed crystals by powder X-ray diffractometry (PXD), differential scanning calorimetry (DSC), infrared spectroscopy (IR) and the drawing of phase diagrams.

In order to throw further light on the problem about molecular recognition between two different molecules in crystals, we have carried out the preparation and characterization of two-component mixed crystals using *p*-(**1**), *m*-(**2**) and *o*-(**3**) nitroanilines and *p*-(**4**), *m*-(**5**) and *o*-(**6**) nitrophenols as the components. The second harmonic generation (SHG) activities of the mixed crystals were measured. While *m*-nitroaniline (**2**) has SHG activity, *p*-nitroaniline is known to show no SHG activity because of a centrosymmetric arrangement in its crystal structure.[5] We were interested to know whether the molecular compound formation with such compounds alters their nonlinear optical property or not.

2. EXPERIMENTAL SECTION

General Procedure: Melting Points (mp) are uncorrected and were measured with a YANACO MP-500D apparatus. IR spectra were taken on a Shimadzu IR-470 spectrophotometer. Powder X-ray diffractograms (PXD) were taken on a Rigaku Geigerflux by using a Cu-target X-ray tube equipped with RAD-C system. Differential scanning calorimetry (DSC) was done on a Rigaku Thermoflex TAS-200 DSC8230D. Second harmonic generation (SHG) activities were measured on a LEONIX LNT-0200 with a MINI-Q YAG laser (1064 nm) using urea crystals as a standard substance.

Preparation of mixed crystals from two different organic compounds: In a typical run, a mixture of *p*-nitroaniline (**1**) (0.276 g; 2.0 mmole) and *p*-nitrophenol (**4**) (0.278 g; 2.0 mmol) was heated in a vial to a homogeneous melt, which was then cooled at room temperature or in a refrigerator if necessary to resolidify. The solid is usually polycrystalline and pulverized before characterization.

Phase diagrams: phase diagrams were constructed by plotting the DSC results obtained at various ratios of the two components of a mixed crystal.

3. RESULTS AND DISCUSSION

Mixed crystals were prepared by melting a 1:1 molar mixture of two compounds followed by cooling the homogenous melt to resolidify into polycrystalline solid and they were characterized by PXD, DSC and IR and in some cases by the drawing of phase diagrams using DSC data obtained with mixed crystals of various molar ratios. Among these methods PXD data were most informative for proving the formation of a molecular compound. We concluded that at least eight mixed crystals among fifteen combinations formed molecular compounds as shown in Table 1.

Figure 1 and 2 show typical examples of the characterization. The PXD pattern of the mixed crystal **1/4** shows a number of new peaks which are not seen in that of each component (Figure 1), indicating the formation of a molecular compound. The PXD patterns of the mixed crystals **1/3**, **2/3**, **2/5**, **3/5**, **3/6**, **4/5** and **4/6** also showed similar features to that of **1/4**. On the other hand the PXD patterns of seven other mixed crystals were virtually the same as the sum of those of the components, indicating that they are the simple mixtures of component crystallites.

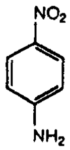
In the cases of the mixed crystals **1/5**, **2/4** and **2/6** (Figures 2a, 2b and 2d, respectively), their phase diagrams (Figure 2a–ad) were drawn by using the DSC curves obtained at the various ratios of the components. In accordance with the PXD results, the phase diagrams of **1/5**, **2/4** and **2/6** showing an eutectic point at 75.2, 73.5 and 40.4°C respectively, indicate that these mixed crystals are eutectic mixtures,[6] namely simple mixtures of the component crystallites. On the other hand, the phase diagram of **2/5** (Figure 2c) shows an eutectic point (74.5°C) in the range of the lower ratio of **2** to **5**, but shows no eutectic point in the range of the higher ratio of **2** to **5**. This is

TABLE I

The formation of molecular compounds for the mixed crystals and their SHG activity

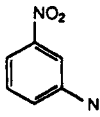
Mixed crystals	**1/2**	**1/3**	**1/4**	**1/5**	**1/6**	**2/3**	**2/4**
Molecular compound formation	No	Yes	Yes	No	No	Yes	No
SHG activity (rel. to urea)	10.4	0	0	4.0	0	3.3	16.5

Mixed crystals	**2/5**	**2/6**	**3/4**	**3/5**	**3/6**	**4/5**	**4/6**	**5/6**
Mol. Compd. form.	Yes	No	No	Yes	Yes	Yes	Yes	No
SHG activity	14.8	15.9	0	0	0	0	0	0



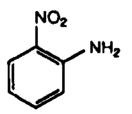
1

mp 148.3°C



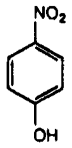
2

113.4°C



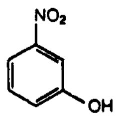
3

73.1°C



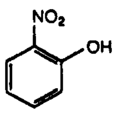
4

114.0°C



5

97.7°C



6

46.0°C

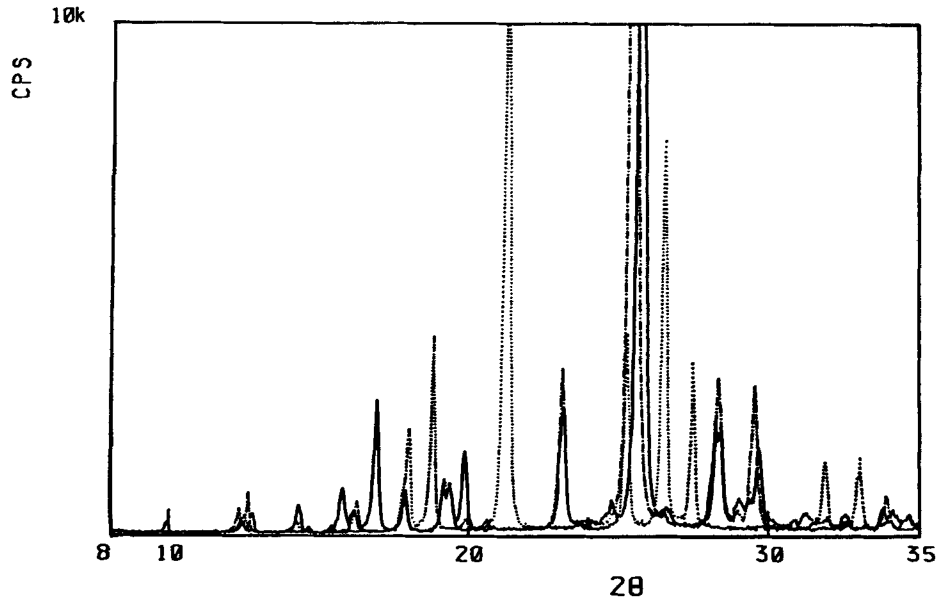


FIGURE 1 PXD patterns of *p*-nitroaniline (**1**) (—··—··—), *p*-nitrophenol (**4**) (··········)and the mixed crystal **1/4** (————).

interpreted as an indication of the formation of a molecular compound at least partially.

The IR spectra of the mixed crystals were also compared with those of the component crystals. While the IR spectra of **1/2**, **1/5**, **1/6**, **2/4**, **2/6**, **3/4** and **5/6**, were

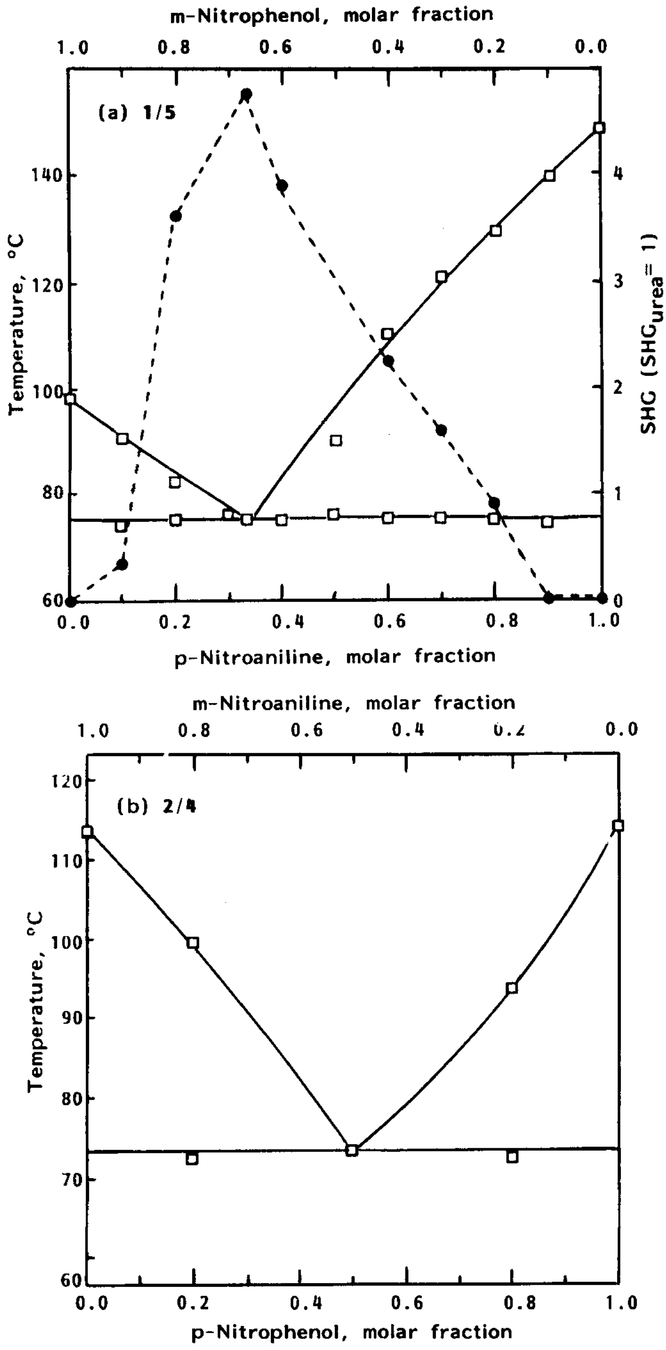


FIGURE 2 The phase diagrams of the mixed crystals **1/5** (a), **2/4** (b), **2/5** (c) and **2/6** (d) and the SHG activities of the mixed crystal **1/5** at various molar fractions of **1** and **5** (a; broken line).

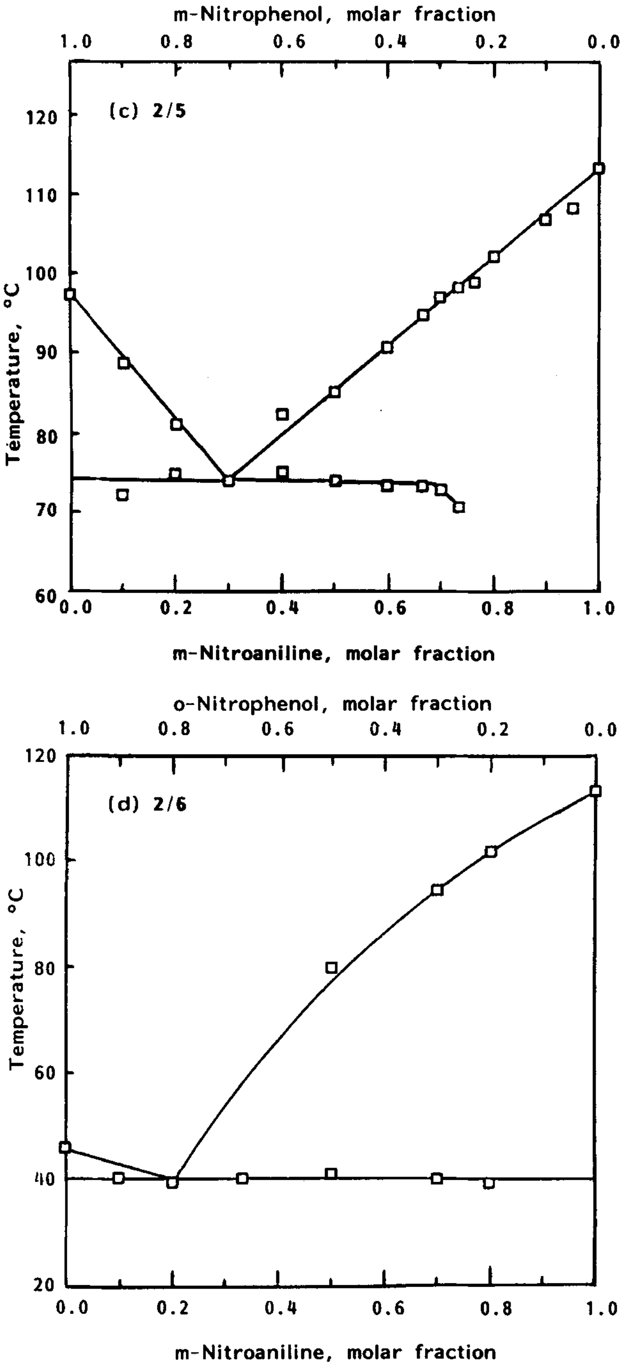


FIGURE 2 *(Continued.)*

approximately the same as the sum of those of the components, the spectra of other mixed crystals forming molecular compounds showed the appearance of new peaks and the disappearance of some of the component peaks. However, the difference between the spectrum of the mixed crystals and the sum of the component spectra is usually so small that it is not suitable for proving the formation of a molecular compound.

We measured the second harmonic generation (SHG) activities of all of the mixed crystals using a YAG laser. The results are listed in Table 1. Among the six starting compounds, only *m*-nitroaniline (**2**) has SHG activity as reported:[6] observed $\text{SHG}_{\text{urea}} = 23.4$. Accordingly, it is understandable that all of the mixed crystals containing *m*-nitroaniline (**2**) showed SHG activity. Interestingly, the mixed crystal **2/3** showed a considerably lower activity than **2** suggesting that the molecular arrangement of **2** responsible for the SHG activity might be modified by the formation of a molecular compound.

Another notable observation is that the mixed crystal **1/5** showed SHG activity, although both **1** and **5** have no activiy. For this phenomenon we first considered an interpretation that the centro-symmetrical arrangement in the crystal of **1** might be altered into non-centro-symmetrical one in the mixed crystal formation. The occurrence of SHG activity of **1** resulting from the inclusion into a non-centrosymmetrical host molecule, such as α-cyclodextrin[7] or polyoxyethylene,[8] appeared to be a similar phenomenon. However, the phase diagram (Figure 2a; solid line) as a simple eutectic mixture and the PXD pattern of the mixed crystal **1/5** indicate that the mixed crystal consists of a simple mixture of the components crystallites. We also measured the SHG activities of the mixed crystals **1/5** at different molar ratios (Figure 2a; dotted line) and found that the activity becomes maximum at the molar ratio of 3:7 which is close to the eutectic point. A possible interpretation may be the contamination of the eutectic mixture of **1/5** by a non-centro-symmetrical crystal modifications of **5** having SHG activity. In fact, *m*-nitrophenol (**5**) has two crystal modification, SHG inactive α-form and active β-form.[9] We are undertaking further studies for clarifying this point.

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Note added in the proof: The SHG activity of mixed crystals containing *p*-nitroaniline has been reported; (a) K. Wakita, N. Sonoda, T. Shimizu and S. Kaida, *SPIE*, Vol. 1337, Nonlinear Optical Properties of Organic Materials III (1990); (b) R. Matsushima, K. Hirayama and N. Okamoto, *J. Mater. Chem.*, **3**, 1045 (1993) and references cited therein.