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MIXED CRYSTALS CONTAINING METHYL-SUBSTITUTED NITROANILINES AND THEIR SECOND HARMONIC GENERATION ACTIVITY

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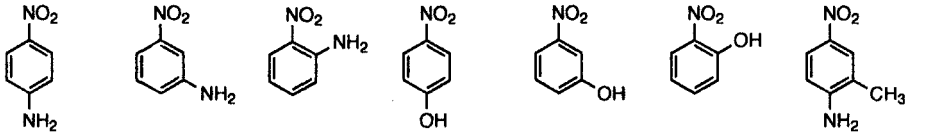
Abstract - Using a melting-resolidification process, mixed crystals of 1 : 1 molar ratio were prepared by the combination of various methyl-substituted nitroanilines **7** - **14** and unsubstituted nitroanilines **1** - **3** and nitrophenols **4** - **6**. The mixed crystals were characterized by powder X-ray diffractometry (PXD), IR spectroscopy and differential scanning calorimetry. Among seventy six mixed crystals prepared, twenty one mixed crystals showed new PXD and IR peaks which are different from those of the components, suggesting the formation of a molecular compound. The second harmonic generation (SHG) activities were measured.

INTRODUCTION

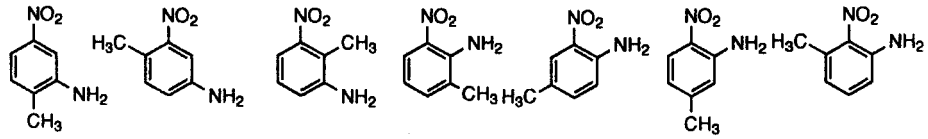
We have recently reported on the preparation of two-component mixed crystals of the 1 : 1 molar ratio using p- (**1**), m- (**2**) and o- (**3**) nitroanilines and p- (**4**), m- (**5**) and o- (**6**) nitrophenols and their SHG (second harmonic generation) property.[1] These mixed crystals were prepared from two different substrates by a melting-resolidification process and characterized by powder X-ray diffractometry (PXD), differential scanning calorimetry (DSC) and IR spectroscopy. Among the fifteen mixed crystals obtained, eight mixed crystals, **1/3**, **1/4**, **2/3**, **2/5**, **3/5**, **3/6**, **4/5** and **4/6** were assigned to form a molecular compound (Table 2, asterisked (*) part). We also found that the mixed crystal **1/5** showed SHG activity, although both **1** and **5** have no activity.

In addition to the above work, the various effects of the formation of mixed crystals to the SHG activity of certain nitroaniline derivatives have been reported by other workers.[2-8] In order to throw further light on the relationship between SHG activity and mixed crystal formation, we have further investigated on the

Table 1. Components of 1 : 1 mixed crystals. Their melting points and (SHG_{urea})



1	2	3	4	5	6	7
mp 148.3℃	mp 113.4℃	mp 73.1℃	mp 114.0℃	mp 97.7℃	mp 46.0℃	mp 131.5℃
(0)	(23.4)	(0)	(0)	(0)	(0)	(42.8)



8	9	10	11	12	13	14
mp 108.0℃	mp 78.2℃	mp 89.9℃	mp 93.7℃	mp 115.1℃	mp 110.6℃	mp 106.6℃
(0)	(0)	(6.8)	(0)	(0)	(0)	(0.24)

preparation of the mixed crystals consisting of methyl-substituted nitroanilines **7** - **14** and their SHG activities. Table 1 shows the melting points and the SHG activities of substrates.

MATERIALS AND METHODS

General procedure. Melting points were determined with a JANACO MP-500D apparatus and were uncorrected. Melting points listed in Table 1 were obtained by differential scanning calorimetry (DSC). IR spectra were recorded on a Shimadzu IR-470 spectrometer. Powder X-ray diffractometry (PXD) were taken on a Rigaku Geigerflex by using Cu-target X-ray tube equipped with RAD-C system and DSC was carried out on a Rigaku Thermoflex TAS-200 DSC8230D. Microanalyses were done with a Yanaco CHN Corder MT-5. All the compounds were reagent grade and commercially available.

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. Observed values are designated as SHG_{urea}.

Table 2. Mixed crystals of 1 : 1 molar ratio from compounds **1 – 14**.

'YES': New peaks appeared in PXD and IR suggesting the formation of a molecular compound,
'NO': The PXD and IR patterns are virtually the same as the sum of those of the two components.
SHG_{urea} values are shown in parentheses.
(* Results of a previous report[1].)

1														
2 (0)	NO* (10.4)													
3 (0)	YES* (0)	YES* (3.3)												
4 (0)	YES* (0)	?* (16.5)	NO* (0)											
5 (0)	?* (4.0)	YES* (14.8)	YES* (0)	YES* (0)										
6 (0)	NO* (0)	NO* (15.9)	YES* (0)	YES* (0)	?* (0)									
7 (42.8)	YES (51.6)	YES (37.6)	? (20.4)	YES (52.0)	YES (0.36)	? (44.4)								
8 (0)	YES (0)	YES (10.8)	? (0)	YES (0)	? (0)	? (0)	? (23.2)							
9 (0)	YES (0)	YES (4.4)	? (0)	YES (0)	? (0)	YES (0)	NO (25.2)	? (0)						
10 (6.8)	YES (4.0)	NO (16.0)	NO (0)	? (1.52)	YES (0)	NO (2.48)	? (41.2)	NO (1.16)	YES (0.04)					
11 (0)	NO (0)	? (3.8)	YES (0)	YES (0)	? (0)	YES (0)	NO (20.0)	NO (0)	NO (0)	YES (0)				
12 (0)	NO (0)	NO (0.8)	NO (0)	NO (0)	NO (0)	NO (0)	NO (10.4)	NO (0)	? (0)	NO (0)	NO (0)			
13 (0)	YES (1.6)	? (6.6)	? (0)	YES (0)	NO (0)	NO (0)	NO (26.4)	? (0)	? (0)	? (0.88)	NO (0)	? (0)		
14 (0.24)	NO (0)	NO (5.2)	NO (0)	YES (0)	NO (0)	NO (0)	NO (24.0)	NO (0)	NO (0)	NO (0.52)	NO (0)	NO (0)	NO (0)	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14

Preparation of mixed crystals.

A mixture of two crystalline compounds (1 : 1 molar ratio; 2 mmol each) was heated in a vial to a homogeneous melt, which was then cooled at room temperature or in a refrigerator, if necessary, to resolidify giving a mixed crystal. The mixed crystal was usually polycrystalline and pulverized before characterization.

RESULTS AND DISCUSSION

Mixed crystals were prepared by melting a 1 : 1 molar mixture of two compounds followed by cooling the homogeneous melt to resolidify into polycrystalline solid and they were characterized by PXD, IR and DSC. Among the newly prepared seventy six mixed crystals, twenty one, which are designated as 'YES' in Table 2, showed new peaks in their PXD patterns and IR spectra different from those of the components. Typical examples are given in Figure 1 (PXD patterns of mixed crystals **4/11** and **5/7** in comparison with those of the components) and Figure 2 (IR spectrum of mixed crystal **5/10** in comparison with those of **5** and **10**). There are, however, a few exceptions for mixed crystals **9/10**, **4/13** and **4/14**. These mixed crystals showed new PXD peaks but their IR spectra were virtually the same as the sum of those of the components. The appearance of new peaks in the PXD patterns and the IR spectra suggests the formation of a molecular compound between two substrates.

Comparing with the unsubstituted series of nitroanilines **1** - **3** and nitrophenols **4** - **6**, for which eight mixed crystals form molecular compounds among fifteen combinations, the probability of molecular compound formation for the methyl-substituted series of nitroanilines is considerably lower. This is most probably due to the steric repulsion caused by the methyl group which prevents an intimate hydrogen bonding interaction between two component molecules.

DSC measurements were done with all of the 1 : 1 mixed crystals. The DSC curves obtained may be divided into three major categories as exemplified in Figure 3. (1) As seen in the DSC curve of mixed crystal **8/11** (Figure 3a), a sharp eutectic peak appears when the melting points of the components are close. Other typical

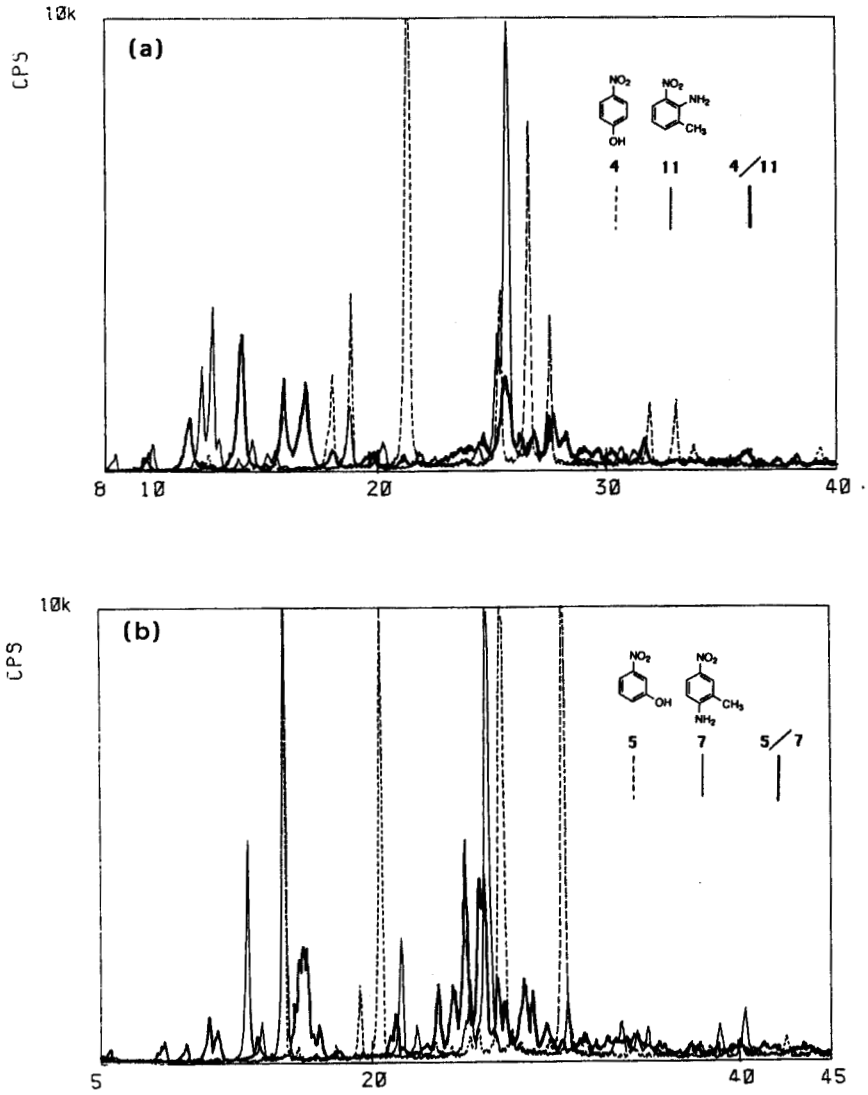


Figure 1. PXD patterns of (a) **4**, **11** and mixed crystal **4/11** and (b) **5**, **7** and mixed crystal **5/7**.

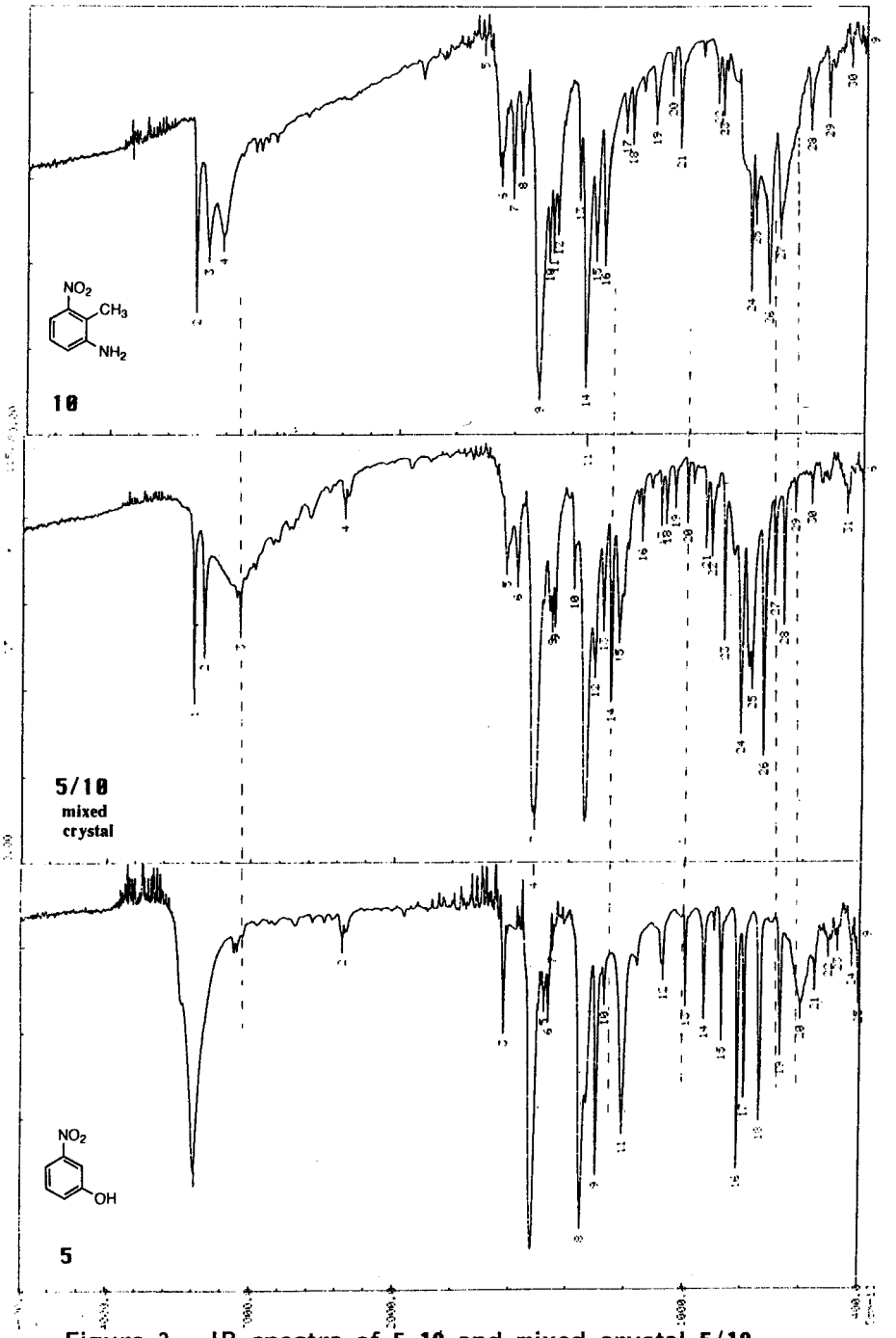


Figure 2. IR spectra of **5**, **10** and mixed crystal **5/10**. (Broken lines show new peaks appeared in the spectrum of mixed crystal **5/10**.

examples are mixed crystals **2/4**, **1/7**, **5/10**, **4/12** and **12/13**. (2) An eutectic peak and a broad peak appear as seen in the case of mixed crystal **6/7** (Figure 3b), when the melting points of the components are separated as mixed crystals **6/7**, **6/8**, **1/10** and **1/14**. (3) Two relatively sharp peaks appear near the eutectic point region as Figure 3c for mixed crystal **9/12**. Other examples are mixed crystals **2/10**, **3/11**, **6,11**, **3/12**, **6/12**, **7/12**, **9/12**, **6/13** and **7/14**. The more detailed interpretations for the above phenomena should wait further thermochemical analysis such as the construction of phase diagrams from the DSC mesurements of mixed crystals at various molar ratios.

The SHG activities were measured by a powder method using urea as a standard substance and the SHG_{urea} values are listed in Table 2. Since the crystals of compoundds **2** (SHG_{urea} 23.4), **7** (42.8), **10** (6.8) and **14** (0.24) are active, the mixed crystals containing these active compounds as a component are naturally SHG active, except that some of the mixed crystals containing **14** showed substantially no activity because of the low activity of **14**.

There are several features for the SHG activities of the mixed crystals. (1) Mixed crystal **1/13** is active despite that none of the components is active. (2) The activities of mixed crystals **1/7**, **4/7** and **6/7** prepared by a combination of SHG active and nonactive components are higher than that of the active component **7**. (3) Inversely, the activities of mixed crystals **2/3**, **5/7**, **2/11**, **2/12**, **9/10**, **3/10**, **5/10** and **10/11** having an SHG active component are much lower than that of each SHG active component.

The above results indicate that SHG activity can be modified by mixed crystal formation. Similar observations have been reported.[2-8] It is still difficult, at this moment, to provide a general rule for the relationship between the SHG activites and the nature of mixed crystals such as molecular compound formation. We have recently succeeded to obtain the single crystals of two molecular crystals of 2 : 1 and 1 : 3 molar ratios from p-nitroaniline and p-nitrophenol and also a molecular crystal of 2 : 1 molar ratio from m-nitroaniline and m-nitrophenol for X-ray structural analysis.[9] We are further attempting to obtain single crystals from the present series of mixed crystals composing of methyl-substituted nitroanilines.

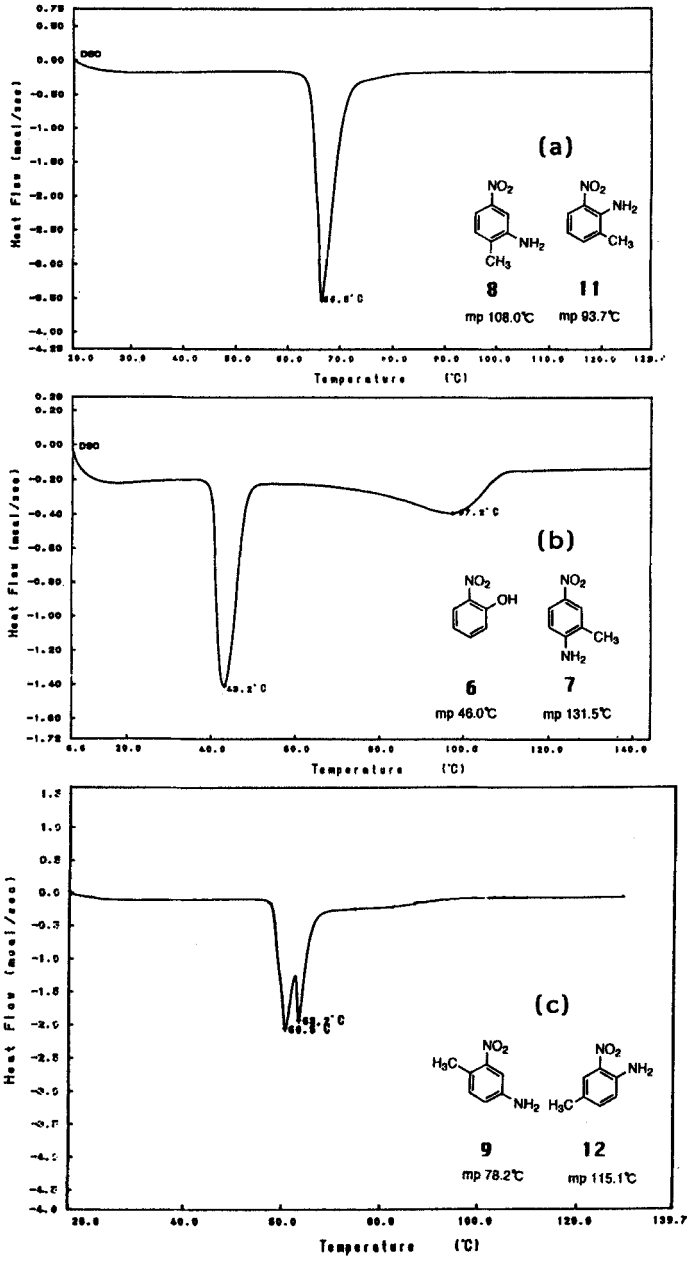


Figure 3. DSC curves of mixed crystals, (a) 8/11, (b) 6/7 and (c) 9/12.

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