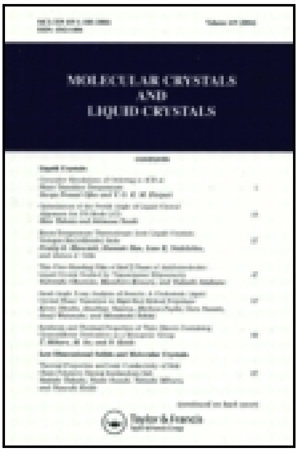

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TWO-MOLECULE CRYSTALS BETWEEN NITROANILINES AND NITROPHENOLS

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Abstract--Slow evaporation of a 1 : 1 or 1 : 2 molar solution of p-nitroaniline and p-nitrophenol in a mixture of dichloromethane and n-hexane deposited two kinds of single crystals which were mechanically separated: 2 : 1 molecular crystal **A** and 1 : 3 molecular crystal **B**. In a similar manner a 1 : 1 or 2 : 1 molar solution of m-nitroaniline and m-nitrophenol in a mixture of chloroform and petroleum ether deposited the single crystals of 2 : 1 molecular crystal **C**. The crystal structures of **A**, **B** and **C** were found to be isomorphic to those of p-nitroaniline, p-nitrophenol (b form) and m-nitroaniline, respectively. The characteristics of the crystal structures of **A**, **B** and **C** are discussed.

INTRODUCTION

In the course of our study on the nonlinear optical property of mixed crystals between two different organic compounds, we have reported on the preparation of two-component mixed crystals (1 : 1 molar ratio) from p-, m- and o-nitroanilines and p-, m- and o-nitrophenols using melting-resolidification process and on their SHG (second harmonic generation) activity. Among the fifteen mixed crystals prepared, at least eight mixed crystals, p-NA/o-NA,* p-NA/p-NP, m-NA/o-NA, m-NA/m-NP, o-NA/m-NP, o-NA/o-NP, p-NP/m-NP and p-NP/o-NP, were found to form a molecular compound between the two components.[1] This type of study for altering the SHG activity of certain nitroaniline derivatives by the mixed crystal formation is recently reported.[2-8] However further studies might be necessary for obtaining the single crystals of such molecular compounds using

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* Abbreviation: NA = nitroanilines; NP = nitrophenol.

crystallization process from a solution of two components. It is now generally accepted that hydrogen bonding interactions are one of the most important factors for the preparation of a crystalline molecular compound from two different organic compounds.

In attempts to obtain the single crystals of molecular compounds for the mixed crystal of nitroaniline-nitrophenol series by the crystallization from a solution of two components, we succeeded to obtain the single crystals of molecular crystals between p-NA and p-NP and between m-NA and m-NP. This paper describes the isolation and characterization of these molecular crystals and their X-ray crystallographic analysis.

MATERIALS AND METHODS

General procedure. Melting points were determined with a JANACO MP-500D apparatus and were uncorrected. 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 differential scanning calorimetry (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.

Preparation of molecular crystals. (i) Molecular crystals **A** and **B** from p-NA and p-NP.

In a typical run, a solution of p-NA (0.276 g; 2.0 mmol) and p-NP (0.278 g, 2.0 mmol) in a mixture of dichloromethane and n-hexane (2 : 1, v/v; 20 mL) was spntaneously evaporated at room temperature to deposit yellow prisms (**A**) and yellow needles (**B**) which were mechanically separated. **A**, m.p. 103-109°C, and **B**, m.p. 120-138°C. The same crystals **A** and **B** were also obtained from a 1 : 2 molar solution of p-NA and p-NP by a similar procedure. In the latter case, the formation of crystal **B** was predominant over **A**. The microanalytical results for several samples obtained from different batches are listed in Table 1.

(ii) Molecular crystal **C** from m-NA and m-NP.

In a typical run, a solution of m-NA (0.276 g; 2.0 mmole) and m-NP (0.278 g; 2.0 mmole) in a mixture of chloroform and petroleum ether (2 : 1, v/v; 20 mL) was spontaneously evaporated at room temperature to deposit **C** as yellow needles, m.p. 88-94°C. The molecular crystal **C** was also prepared from a 2 : 1 molar solution of m-NA and m-NP in a similar procedure. The microanalytical results for three samples obtained from different batches are listed in Table 1.

X-ray crystallographic analysis.

Detailed experimental and crystallographic data including atomic coordinates, bond distances and angles, torsion angles and non-bonded contacts have been deposited at the Cambridge Crystallographic Data Center.

A yellow prismatic crystal of **A** having approximate dimensions of 1.00 x 0.50 x 0.40 mm (**B**, 0.30 x 0.30 x 0.10; **C**, 0.20 x 0.30 x 0.80) was mounted on a glass fiber. Intensity measurements were made on a Rigaku AFC6A diffractometer for **A** and **B** (**C**, a Rigaku AFC7R diffractometer with a 18 kW rotating anode generator) with graphite monochromated Mo-$K\alpha$ radiation. Cell constants and an orientation matrix for data collection, were obtained from a least-squares refinement using the setting angles of 25 (**B**, 20; **C**, 25) carefully centered reflections in the range $28.08 < 2\theta < 31.92°$ (**B**, $12.99 < 2\theta < 16.71°$; **C**, $24.21 < 2\theta < 36.10°$).

A, p-NA:p-NP=2:1	**B**, p-NA:p-NP=1:3	**C**, m-NA:m-NP=2:1
a = 8.508(3) Å	a = 14.990(6) Å	a = 19.347(4) Å
b = 6.056(1) Å	b = 11.130(3) Å	b = 6.595 Å
c = 12.252(4) Å	c = 3.774 Å	c = 4.970(2) Å
V = 631.0(6) Å	V = 616.9(7) $Å^3$	V = 634.2(3) $Å^3$
β = 91.73(3)°	β = 101.58(3)°	

For Z = 4 (**B**, Z = 4; **C**, Z = 4) and F.W. = 138.62 (**B**, 138.86; **C**, 138.45), the calculated density is 1.46 g/cm^3 (**B**, 1.50 g/cm^3; **C**, 1.45 g/cm^3). The systematic absence uniquely determine the space group to be:

A, $P2_1/n$ (#14) **B**, $P2_1/a$(#14) **C**, $Pca2_1$ (#29)

The data were collected at a temperature of 25 ± 1°C (**B**, 25 ± 1°C; **C**, 25 ± 1°C) using the w-20 scan technique to a maximum 20 value of 60.1° (**B**, 60.1°; **C**, 120.1°). Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.41° (B, 0.38°; C, 0.31°)with a take-off angle of 6.0. Scans of (1.30 ± 0.50 tan θ)° (B, (1.20 ± 0.50 tan θ)°; C, (1.52 ± 0.30 tan θ)°) were made at a speed of 4.0°/mon (in omega) (B, 4.0°/min; C, 16.0°/min). The weak reflections ($1 \leq 10.0\sigma(I)$) were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statics. (In the case of C, stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2 : 1.

Of the 2061 (B, 2188; C, 1090) reflections which were collected, 1947 (B, 1896; C, 666) were unique (R_{int} = 0.035 (B, 0.066; C, 0.027)). The intensities of three representative reflection were measured after every 200 reflections. No decay correction was applied. The linear absorption coefficient, μ, for Mo-Kα radiation is 1.2 cm^{-1} (B, 1.2 cm^{-1} for Mo-Kα radiation ; C, 9.7 cm^{-1} for Cu-Kα radiation). Azimuthal scana of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[9] and expanded using Fourier techniques.[10] The non-hydrogen atoms were refined aniso-tropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinements was based on 1258 (B, 1126; C, 558) observed reflections ($I - 3.00\sigma(I)$) and 116 (B, 112; C, 115) variable parameters and converged with unweighed and weighed agreement factors of:

A, R = 0.060	B, R = 0.066	C, R = 0.041
R_w = 0.077.	R_w = 0.083	R_w = 0.068

The weighting scheme was based on counting statics and included a factor (p = 0.045) (B, p = 0.045; C, p = 0.050) to downweight the intense reflections. The maximum and minimum peaks on the final defference Fourier map corresponded to 0.73 and -0.25 $e^-/Å^3$ (B, 0.64 and -0.27 $e^-/Å^3$; C, 0.13 and -0.12 $e^-/Å^3$), respectively. Neutral atom scattering factors were taken from Cromer and Waber.[11] Anomalous dispersion effects were included in Fcalc; the values for Δf' and Δf" were those of Creagh and McAuley.[12] All calculations were performed using the teXsan[13] crystallographic software package of Molecular Structure Corporation.

RESULTS AND DISCUSSION

The two-molecule crystals were obtained by the crystallization from solutions. When a 1 : 1 or 1 : 2 molar solution of p-NA and p-NP in a mixture of dichloromethane and n-hexane was slowly evaporated at room temperature, two kinds of single crystals deposited which could be mechanically separated: crystal **A**, yellow prisms, m.p. 120-138°C and crystal **B**, yellow needles, m.p. 103-109°C. In a similar manner, slow evaporation of a 1 : 1 or 2 : 1 molar solution of m-NA and m-NP in a mixture of chloroform and petroleum ether deposited crystal **B** as yellow prismatic crystals, m.p. 88-94°C. The microanalytical data are listed in Table I which indicated that **A**, **B** and **C** were 2 : 1 p-NA/p-NP, 1 : 3 p-NA/p-NP and 2 : 1 m-NA/m-NP, respectively. The analytical data were the same within experimental errors for the molecular crystals obtained from several different batches. These results show that each molecular crystal has a definite stoichiometrical ratio of components, and that the elemental compositions of **A** and **B** were independent on the concentrations of p-NA and p-NP in the solution, suggesting the formation of a molecular compound, although the possibility of the formation of a solid solution with a limited solubility[14] is not eliminated at this stage.

The X-ray structural analysis of **A**, **B** and **C** showed that their amino and hydroxyl group cannot be discriminated in the crystal structures, possibly due to the disorder between two components. Only two amino hydrogens for **A** and **C** appeared on each d-map, while only a hydroxyl hydrogen for **B** appeared on the d-map. Therefore, the refinements for **A**, **B** and **C** were made with each major component molecule, namely p-NA, p-NP and m-NA, respectively. The R values obtained for **A**, **B** and **C** were 0.060, 0.066 acd 0.041, respectively. The crystal structures are shown in Figures 1a-1c.

The selected crystal data of **A**, **B** and **C** are listed in Table 2 in comparison with those reported for the component compounds, indicating that the crystal structures of **A**, **B** and **C** are isomorphic to those of p-NA, p-NP (β form)[17] and m-NA, respectively. Reflecting these results, the PXD patterns of molecular crystals **A**, **B** and **C** were virtually superimposable to those of the major components, p-

Table 1. Microanalytical Data for Molecular Crystals **A**, **B** and **C**.

Crystal		C (%)	H (%)	N (%)
A	Observed	52.44	4.17	17.28
		52.33	4.16	16.88
		52.18	4.11	17.05
		52.39	4.13	17.18
Calcd. for	$C_{18}H_{17}N_5O_7$	52.05	4.13	16.86
B	Observed	51.81	3.89	12.39
		51.76	3.93	12.42
		52.28	3.96	12.55
Calcd. for	$C_{24}H_{21}N_5O_1$	51.85	3.78	12.60
C	Observed	51.85	4.18	16.85
		51.90	4.19	16.87
		51.94	4.23	16.88
Calcd. for	$C_{18}H_{17}N_5O_7$	51.81	4.13	16.86

Table 2. Comparison of the Crystal Data of **A**, **B**, **C**, p-NA, p-NP, m-NA and m-NP.

Crystal (Form)	Cryst. form[a]	a (A)	b (A)	c (A)	β (°)	Space group	Z	Ref.
A	M	8.508	6.056	12.252	91.73	$P2_1/n$	4	b
B	M	14.990	11.130	3.774	101.58	$P2_1/a$	4	b
C	O	19.347	6.594	4.970	-	$Pca2_1$	4	b
p-NA	M	12.336	6.07	8.592	91.45	$P2_1/n$	4	15)
p-NP (α)	M	11.415	8.780	6.098	103.08	P2H1/a	4	16)
p-NP (β)	M	14.743	11.117	3.785	92.65	$P2_1/n$	4	17)
m-NA	O	6.501	19.330	5.082	-	$Pbc2_1$	4	18)
m-NP (M)	M	11.240	6.891	8.154	98.05	$P2_2/n$	4	19)
m-NP (O)	O	8.123	11.305	6.777	-	$P2_12_12_1$	4	20)

[a] M = monoclinic; O = orthorhombic. [b] This work.

NA, p-NP (β form) and m-NA, respectively.

Figures 2a-2c show the features of the molecular arrangements of the molecular crystals **A**, **B** and **C**, emphasizing the importance of hydrogen bondings. (1) In the crystal lattice of **A** (Figure 2a), $\mathrm{N}{<}^{\mathrm{O}\cdots}_{\mathrm{O}\cdots}\mathrm{H{-}N}$ hydrogen bonds (2.26 and 3.13 Å) with a three center interaction[16] connect molecules in a linear way and the amino group is coplanar to the benzene ring. Another N-O···H-N hydrogen bond (2.53 Å) constitutes a two-dimensional net work. (2) In the case of **B** (Figure 2b) molecules are linearly connected to each other by hydrogen bonds $NO_2\cdots H{-}O$ with a similar three center interaction (2.01 and 2.90 Å). (3) In the crystal lattice of **C** (Figure 2c), somewhat weaker hydrogen bonds, -N···H-N (2.45 Å) and three centerd $N{-}O_2\cdots H{-}N$ (2.49 and 2.81 Å) connect molecules in a two-dimensional way and two amino hydrogens are not coplanar to the benzene ring, since the amino nitrogen atom is near sp^3 hybridization. These lengths of the N-O···H-N hydrogen bonds are comparable to those compiled by Etter and her collaborators[21] for various nitroaniline derivatives.

The available experimental data for the molecular crystals **A**, **B** and **C** cannot discriminate whether they are molecular compounds or solid solutions with a limited solubility. Since the crystal structures of these molecular crystals are isomorphic to those of the major components, the crystal growth is most probably initiated by the primary nucleation of each major component. In the case of **A**, for example, once the primary nucleus of p-nitroaniline is formed, p-nitrophenol molecules are incorporated into the crystal lattice of p-nitroaniline in the definite ratio of 2 : 1.

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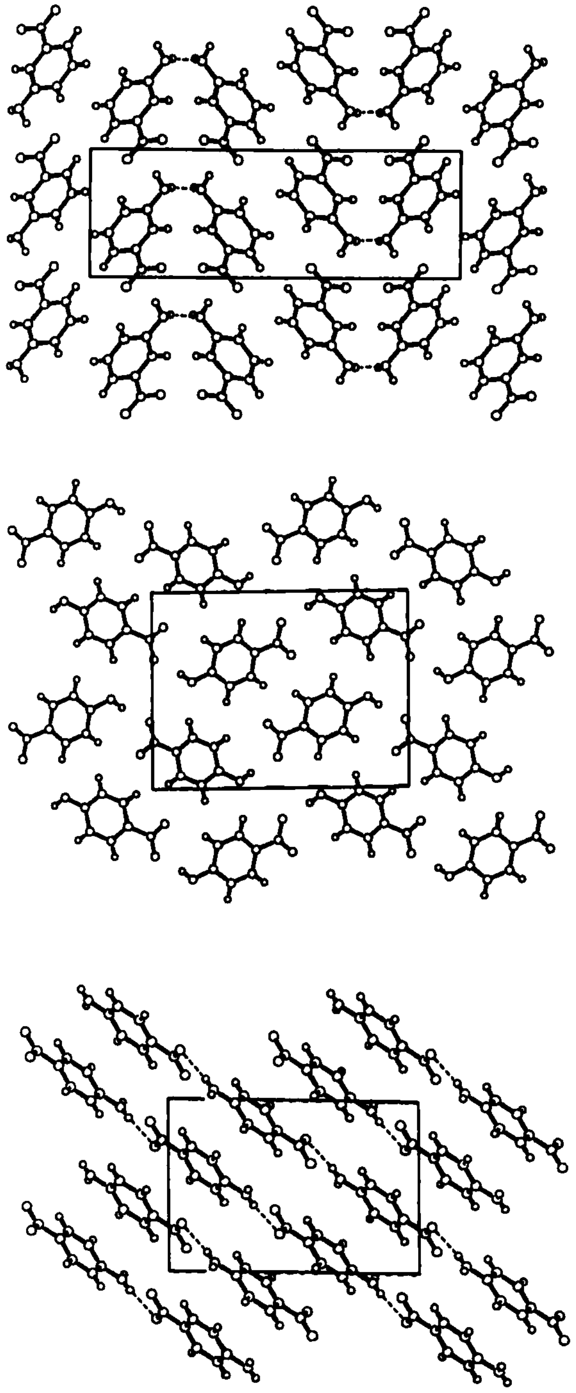


(a) A

(b) B

(c) C

Figure 1. Crystal structures of (a) A, (b) B and (c) C.

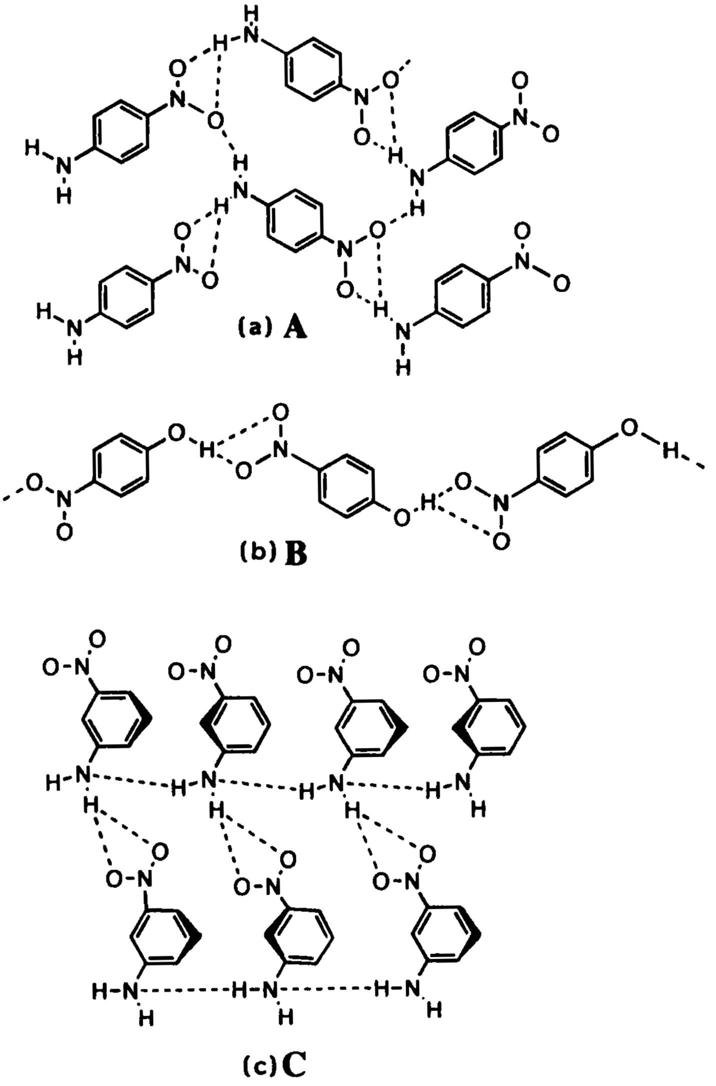
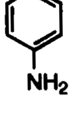
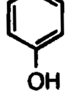


Figure 2. Hydrogen bonding features in the crystal structures of (a) **A**, (b) **B** and (c) **C**.



p-NA



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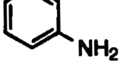
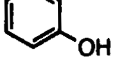


m-NA



m-NP

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