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Molecular Crystals and Liquid Crystals

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Intermolecular Interactions And Generation of Chirality in the Formation of Two-Component Molecular Crystals between Chloronitrobenzoic Acids and 4-Benzoylpyridine Or P-Anisidine

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INTERMOLECULAR INTERACTIONS AND GENERATION OF CHIRALITY IN THE FORMATION OF TWO-COMPONENT MOLECULAR CRYSTALS BETWEEN CHLORONITROBENZOIC ACIDS AND 4-BENZOYLPYRIDINE OR *p*-ANISIDINE

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Two-component molecular crystals using chloronitrobenzoic acids and 4-benzoylpyridine or p-anisidine as components were verified by a combination of techniques: solution NMR, solid-state IR spectra and differential scanning calorimetry (DSC) of the molecular crystals and X-ray crystallographic analysis of their single crystals.

Keywords: two-component molecular crystals; hydrogen bondings; X-ray crystallographic analysis; π-π stacking interactions; chiral crystallization; chloronitrobenzoic acids; 4-benzoylpyridine; *p*-anisidine

INTRODUCTION

Two different organic molecules in two-component molecular crystals we have prepared [1–2] are principally connected by intermolecular interactions such as π-π stacking interactions [3] and C—H $\cdots$ O hydrogen bondings [4] besides traditional hydrogen bondings. These weaker interactions play a significant role to design organic solid materials with predicting the interaction in the molecular crystals [5]. And the use of chloronitrobenzoic acids and various bases as components induces their two-component molecular crystals to crystallize readily as large single crystals suitable for

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X-ray analysis [1]. In other words, chloronitrobenzoic acid can transform poor quality crystal of bases to high quality two-component molecular crystals, and may provide useful organic solid materials. Furthermore, chiral crystallization in two-component molecular crystals is a useful way to design absolute asymmetric syntheses [2b,6] and new solid materials with SHG activity. It is still difficult, however, to predict the generation of chirality by the participating molecules. Therefore understanding of the intermolecular interactions and the packing modes for chiral molecular crystals by single X-ray analysis would be very important to predict the generation of chirality.

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RESULTS AND DISSCUSSION

Chloronitrobenzoic Acids and 4-Benzoylpyridine as Components

We have succeeded in the preparation and characterization of five two-component molecular crystals **1–5** using chloronitrobenzoic acids and 4-benzoylpyridine as components (Table 1). For all of the five molecular crystals, it was confirmed by the X-ray crystallographic analysis of their single crystals that the ratio of acid to base as components was 1:1 and the their molecular pair was connected through COOH $\cdots$ N hydrogen bonding with no proton transfer. It can be seen that these molecular crystals form different molecular arrangements with a variety of intermolecular interactions by the brief alternation of substituents of chloronitrobenzoic acids (Fig. 1).

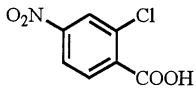
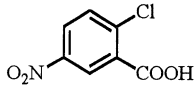
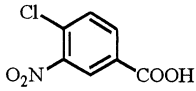
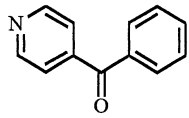
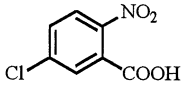
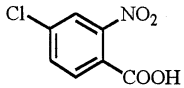
In molecular crystals **1**, this forms an uncommon dimer structure with N $\cdots$ O electrostatic interactions, **2** has a feature of Cl $\cdots$ O electrostatic interactions, **3** has a double long-chain structure with the weaker C$-$H $\cdots$ O=C hydrogen bondings, **4** has a large cyclic structure with the weaker C$-$H $\cdots$ O=C hydrogen bondings and the traditional N $\cdots$ H$-$O hydrogen bondings, and **5** has a long chain structure with the weaker C$-$H $\cdots$ O=C hydrogen bondings.

Thus in their molecular structure the weaker intermolecular interactions such as the hydrogen bondings (C$-$H $\cdots$ O=C and C$-$H $\cdots$ O=N), $\pi-\pi$ stacking interactions and electrostatic interactions (Cl $\cdots$ O and N $\cdots$ O) play a significant role in determining the packing modes of molecular crystals.

Chloronitrobenzoic Acids and *p*-Anisidine as Components

Table 2 is a list of four two-component molecular crystals **6–9** between chloronitrobenzoic acids and *p*-anisidine, which were obtained by the spontaneous crystallization from a solution. Compared to the two-

TABLE 1 Two-component Molecular Crystals Between Chloronitrobenzoic Acids and 4-Bensoylpyridine

Chloronitrobenzoic acids	4-Benzoylpyridine	No.	m.p. (°C) (solvent)	Colour and space group
		**1**	118–120 (MeOH)	Colourless $P2_1/c$
		**2**	122–123 (MeOH)	Colourless Pbca
		**3**	121–122 (MeOH)	Pale Green $C2/c$
		**4**	101–102 (MeOH)	Colourless P-1
		**5**	118–119 (MeOH)	Colourless $P2_1/c$

component molecular crystals composed of chloronitrobenzoic acids and 4-benzoylpyridine **1–5**, the molecular pair of acid and base is connected through $COO^- \cdots HN^+$ hydrogen bonding, indicating that the proton transfer has occurred to form a salt bridge in each case. Now we have successfully prepared two chiral two-component molecular crystals of four compounds.

For the feature of packing modes of chiral molecular crystals 7, it has a column structure along the hydrogen bonding of $COO^- \cdots HN^+$, which consists of the linear structures that are alternately connected with 2-chloro-5-nitrobenzoic acid and *p*-anisidine [Fig. 2(a)]. In addition, its column structures which has a 2_1 symmetry with a salt bridge in the b axis, are packed in the same direction to cause the generation of $P2_1$ chiral space group in the formation of 7 [7]. The chiral molecular crystal **8** has the virtually same arrangement as 7 besides the hydrogen bondings of $C{-}H \cdots O{=}N$ participating into the linear structures [Fig. 2(b)]. The achiral molecular crystal **9** has the complicated hydrogen network with no 2_1

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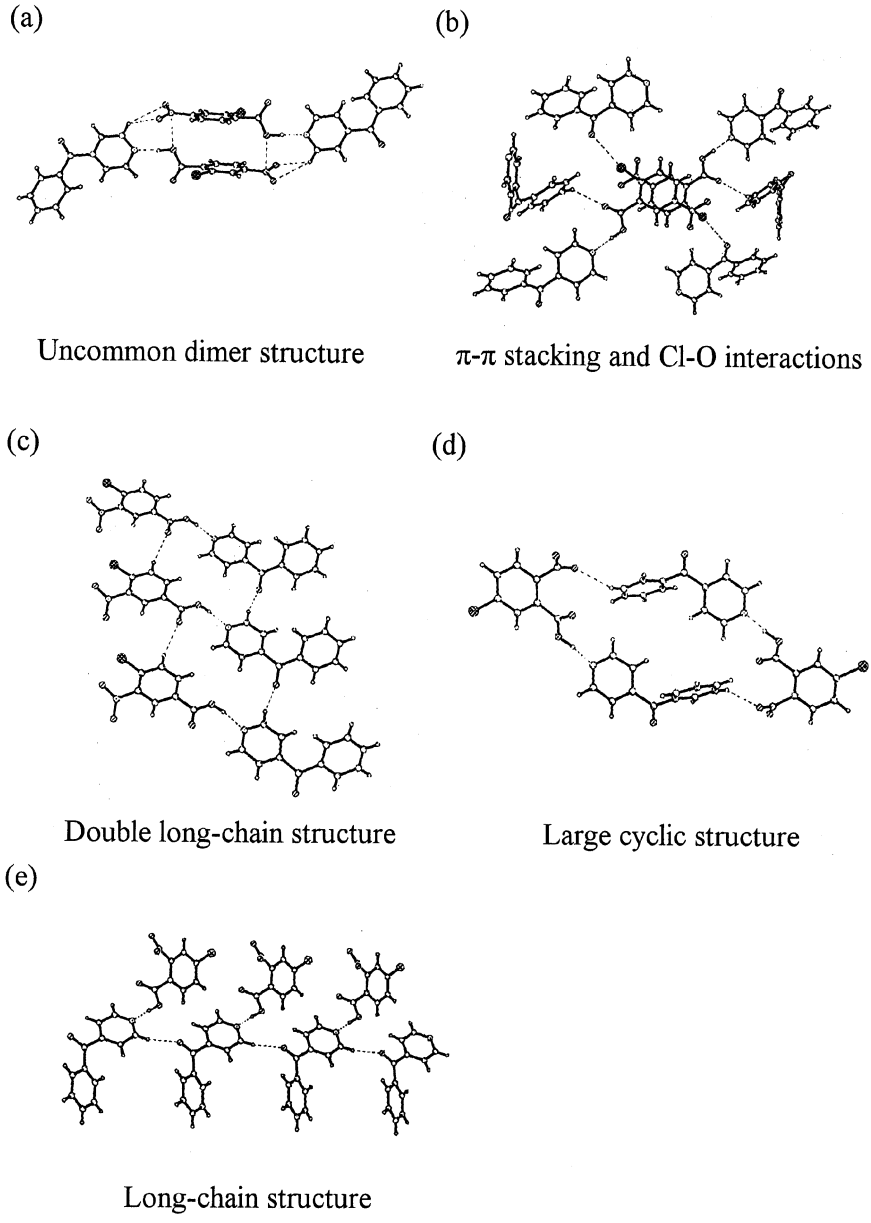

FIGURE 1 The characteristic molecular arrangements in two-component molecular crystals **1** (a), **2** (b), **3** (c), **4** (d) and **5** (e).

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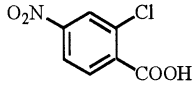
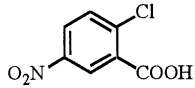
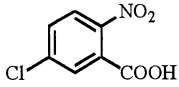
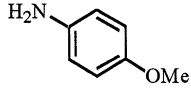
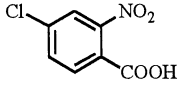
TABLE 2 Two-Component Molecular Crystals Between Chloronitrobenzoic Acids and *p*-Anisidine

Chloronitrobenzoic acids	*p*-Anisidine	No.	m.p. (°C) (solvent)	Colour and Space group
		**6**	171–174 (EtOH)	Colourless *P*bca
		**7**	153–154 (MeOH)	Pale green ***P*2$_1$ (chiral)**
		**8**	141–146 (MeCN)	Yellowish green ***P*2$_1$ (chiral)**
		**9**	149–150 (MeOH)	Colourless $P2_1/c$

symmetry column structures. (Fig. 3) Next, the packing mode of achiral molecular crystal **6** is showed in Figure 4. Although it also has no 2_1 symmetry column structures, it has a trimeric plane structure that is composed of three benzoic acids molecules.

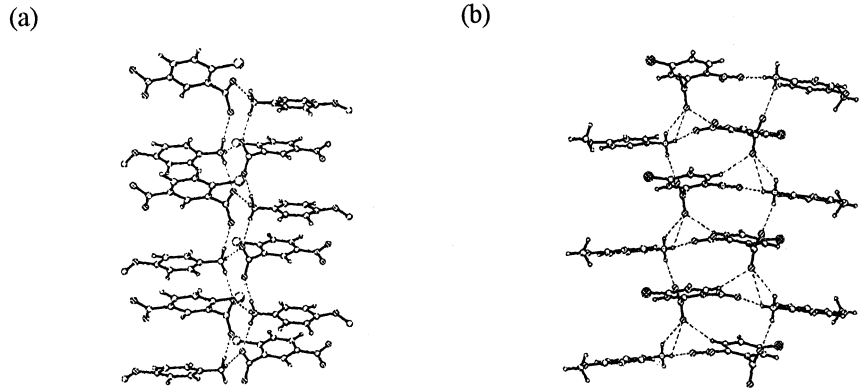


FIGURE 2 The generation of chirality in the formation of **7** and **8**.

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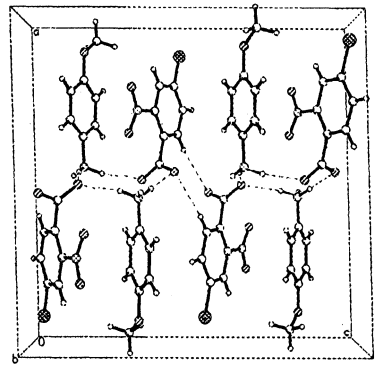

FIGURE 3 The molecular arrangements in the unit cell of **9**.

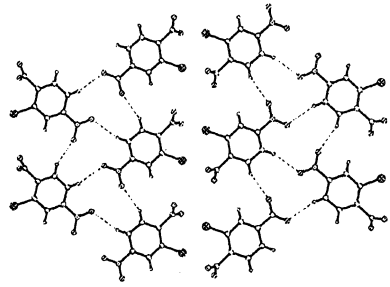

FIGURE 4 The trimeric plane structure with hydrogen network in **6**.

CONCLUSION

The present results are indicating that the brief alternation of substituents of chloronitrobenzoic acids affected the packing modes of two-component molecular crystals with 4-benzoylpyridine and *p*-anisidine. In both cases the weaker intermolecular interactions such as π-π stacking interaction and C—H···O hydrogen bonding also affected the packing modes. In the latter cases particularly, the generation of chirality can be seen in the formation of certain molecular crystal. However the present results are indicating that further systematic study may be necessary for more two-component molecular crystals using chloronitrobenzoic acids as components.

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