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Two-Component Molecular Crystals Composed of Nitrobenzoic Acids and Aromatic Or Heterocyclic Bases

Teruki Sugiyama [a], Jiben Meng [a], Zhong Wen [a], Jinliang Li [a] & Teruo Matsuura [b]

[a] Department of Chemistry, Nankai University, Tianjin, 300071, P. R. China

[b] Emeritus Professor, Kyoto University, 21-26 Kawashima-Gondencho, Saikyoku, Kyoto, 615-8195, Japan

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TWO-COMPONENT MOLECULAR CRYSTALS COMPOSED OF NITROBENZOIC ACIDS AND AROMATIC OR HETEROCYCLIC BASES

Teruki Sugiyama, Jiben Meng, Zhong Wen, and Jinliang Li*
Department of Chemistry, Nankai University,
Tianjin 300071, P. R. China

Teruo Matsuura
Emeritus Professor, Kyoto University,
21-26 Kawashima-Gondencho, Saikyoku,
Kyoto 615-8195, Japan

Slow evaporation of a solution of nitrobenzoic acids and aromatic or heterocyclic bases gave various two-component molecular crystals, which were characterized by IR spectroscopy and elemental analyses and in some case by X-ray crystallographic analysis of their single crystals.

Keywords: two-component molecular crystals; hydrogen bondings; X-ray crystallographic analysis; nitrobenzoic acids; aromatic and heterocyclic bases

INTRODUCTION

For the past decade, we have been interested to the preparation and chemical properties of two-component molecular crystals composed of two different organic compounds [1–2]. One of the important problems is the spontaneous chirality generation phenomenon occurring during the crystallization of such molecular compounds consisting of achiral or optically inactive components [3–6]. Other aims of this work are to contribute to the discovery of new functional solid materials such as nonlinear optics and to know how the components interact intermolecularly in their crystal lattice. In order to throw light on these problems, we have made a systematic investigation on the formation of two-component molecular crystals formed from nitrobenzoic acid derivatives and aromatic or heterocyclic bases, as well as the exploration for new types of two-component molecular crystals.

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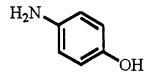
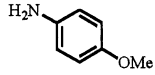
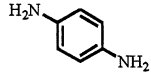
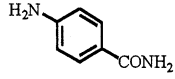
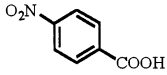
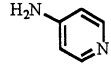
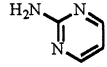
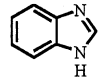
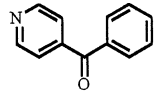
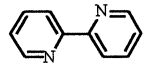
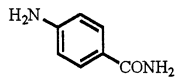
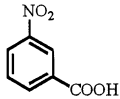
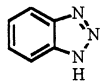
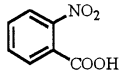
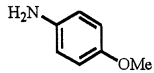
*Corresponding author

TABLE 1 Two-Component Molecular Crystals of Nitrobenzoic Acids and Aromatic or Heteroaromatic Bases

Component A	Component B	No.	A:B	m.p. (°C) (Solvent)	Colour and crystal shape
		**1**	1:1	199–200 (EtOH)	Pale yellow powder
		**2**	1:1	182–186 (EtOH)	Colourless plates
		**3**	2:1	180–184 (MeCN)	Pale yellow needles
		**4**	1:1	216–217 (MeOH)	Orange yellow long plates
		**5**	1:1	228–232 (MeCN)	Colourless needles
		**6**	1:1	185–187 (MeOH/MeCN)	Colourless needles
		**7**	1:1	195–196 (MeCN/EtOH)	Colourless prisms [7]
		**8**	1:1	162–164 (MeOH)	Colourless prisms [7]
		**9**	1:1	143–144 (MeOH)	Colourless powder
		**10**	2:1	185–187 (MeCN)	Yellow rods

(*Continued*)

TABLE 1 *Continued*

Component A	Component B	No.	A:B	m.p. (°C) (Solvent)	Colour and crystal shape
		**11**	1:1	190–191 (MeCN/MeOH)	Yellow long Plates
		**12**	1:1	163–165 (MeCN/MeOH)	Colourless plates [7]
		**13**	1:1	146–147 (MeCN/MeOH)	Colourless plates [7]
		**14**	1:1	133–133.5 (MeCN/MeOH)	Colourless plates [7]
		**15**	1:1	115–118 (MeCN)	Colourless plates

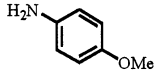
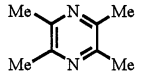
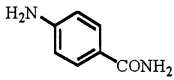
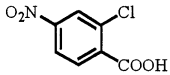
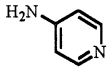
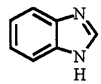
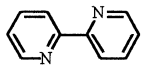
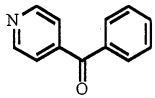
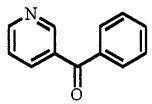
RESULTS AND DISCUSSION

Nitrobenzoic Acids (*p*-, *m*- and *o*-) as the Acid Component

Two-component molecular crystals were prepared by the spontaneous crystallization from a solution of a nitrobenzoic acid and an aromatic or a heterocyclic base. Although such molecular compounds between an acid and a base were considered to easily crystallize by the formation of intermolecular hydrogen bondings or by the salt formation, the isolation of molecular crystals were not always successful. For example, in attempts to obtain molecular crystals using nitrobenzoic acid (*p*-, *m*- and *o*-) and sulfanilamide (4-aminobenzene-sulfonamide), both components crystallized separately but gave no molecular crystal.

Table 1 is a list of the two-component molecular crystals successfully obtained from simple nitrobenzoic acids (*p*-, *m*- and *o*-) and various organic bases. Among them molecular crystals **7**, **8**, **12**, **13** and **14** were succeeded to obtain as single crystals. Their molecular structures were established by X-ray crystallography [7]. It should be noticed that molecular crystal **13** crystallized into chiral space group ($P2_1$) and that the two enantiomer

TABLE 2 Two-Component Molecular Crystals between Chloronitrobenzoic Acids and Aromatic or Heteroaromatic Bases

Component A	Component B	No.	A:B	m.p. (°C) (Solvent)	Colour and crystal shape
		**16**	1:1	171–174 (EtOH)	Colourless prisms [9]
		**17**	2:1	153–154 (MeOH)	Yellowish green plates
		**18**	1:1	144–145 (MeOH)	Orange yellow plates
		**19**	1:1	151–152 (MeCN/MeOH)	Colourless prisms
		**20**	1:1	179–180 (MeOH)	Colourless prisms
		**21**	2:1	170–171 (MeCN/MeOH)	Colourless needles
		**22**	1:1	118–120 (MeOH)	Colourless prisms [9]
		**23**	1:1	89–91 (MeOH)	Colourless powder

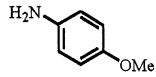
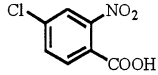
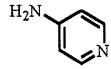
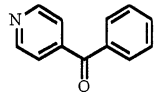
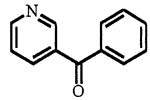
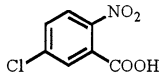
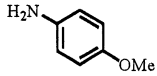
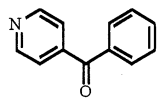
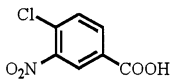
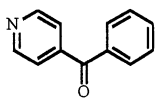
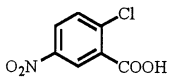
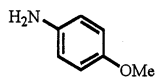
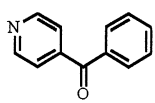
(Continued)

crystals were obtained and characterized by the solid-state circular dichroism spectra which appeared as mirror image [8].

Chloronitrobenzoic Acids as the Acid Component

When we used a number of chloronitrobenzoic acids as the acid component, the formation of molecular crystals with aromatic and heterocyclic bases proceeded more easily as compared with simple nitrobenzoic acids. Table 2 listed the two-component molecular crystals forming between

TABLE 2 *Continued*

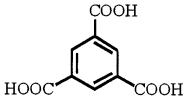
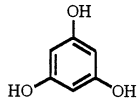
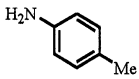
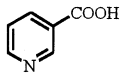
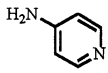
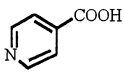
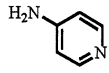
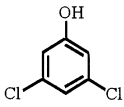
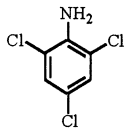
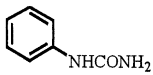
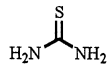
Component A	Component B	No.	A:B	m.p. (°C) (Solvent)	Colour and crystal shape
		**24**	1:1	149–150 (MeOH)	Pale green prisms [9]
		**25**	1:1	144–145 (MeCN)	Colourless prisms
		**26**	1:1	118–119 (MeOH)	Colourless prisms [9]
		**27**	1:1	85–86 (MeOH)	Colourless prisms
		**28**	1:1	141–146 (MeCN)	Yellowish green prisms [9]
		**29**	1:1	101–102 (MeOH)	Colourless prisms [9]
		**30**	1:1	122–123 (MeOH)	Pale green prisms [9]
		**31**	1:1	153–154 (EtOH)	Yellowish green prisms [9]
		**32**	1:1	122–123 (MeOH)	Colourless prisms [9]

chloronitrobenzoic acids and various bases. Among these 17 molecular crystals, 15 molecular crystals **16–20**, **22**, **24–31** and **32** were succeeded to obtain as single crystals. Their molecular structures were established by X-ray crystallographic analysis. Both of two molecular crystals **28** and **31** were found to crystallize into chiral space group $P2_1$. The details of their molecular structures will be discussed in the subsequent paper [9].

Miscellaneous Organic Compounds as the Components

In the earlier attempts to prepare two-component molecular crystals using various types of organic compounds as the components, we succeeded to obtain molecular crystals listed in Table 3. These molecular crystals were characterized by IR spectroscopy and the ratio of components was

TABLE 3 Two-Component Molecular Crystals between Two Different Organic Compounds

Component A	Component B	No.	A:B	m.p. (°C) (Solvent)	Colour and crystal shape
		**33**	2:1	>300 (MeOH)	Colourless prisms
		**34**	1:1	>290 dec. (MeOH)	Colourless fine needles
		**35**	3:2	190–191 (MeOH)	Colourless plates
		**36**	3:2	158–161 (MeOH/EtOAc)	Colourless prisms
		**37**	1:1	47–48 (PhH/c-hexane)	Colourless prisms
		**38**	1:1	158–161 (MeCN)	Colourless prisms [10]

obtained by elemental analyses. Except a molecular crystal between phenylurea and thiourea **38** [10], no single crystal suitable for X-ray analysis was obtained, showing that it is not always successful to obtained suitable single crystals.

CONCLUSION

By the introduction of a chlorine atom to nitrobenzoic acids, molecular crystals between chloronitrobenzoic acids and organic bases crystallized more easily to large single crystals than the corresponding series of nitrobenzoic acids. Chlorine atoms may play a space-filling role in their crystallization process.

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