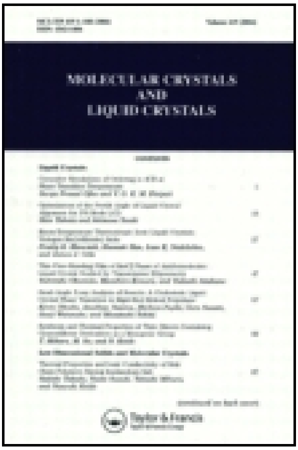

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A Two-Component Molecular Crystal Composed of Phenylurea and Thiourea

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A Two-Component Molecular Crystal Composed of Phenylurea and Thiourea

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Crystallization of an equimolar mixture of thiourea and phenylurea from methanol gave a 1 : 1 two-component molecular compound. X-ray crystallographic analysis of a single crystal revealed that the crystal belongs to an achiral space group, $P2_1/c$.

Keywords: Two-component molecular crystal; X-ray crystallographic analysis; phenylurea; thiourea; intermolecular hydrogen bonds

INTRODUCTION

We have been interested to the preparation and chemical properties of two-component molecular crystals composed of two different organic compounds for the past decade.[1-2] One of the problems we encountered recently is the spontaneous chirality generation phenomenon occurring during the crystallization of such molecular compounds consisting of achiral or optically inactive components.[3-6] During this study, we reached a hypothetical conclusion that a two-

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component molecular cryatsl tends to be chiral, when one of the component molecular crystal tends to be chiral, when one of the components itself undergoes chiral crystallization. This result promoted us to attempt to prepare a two-component molecular crystal using phenylurea (**1**) as one component, since phenylurea crystal is known to belong to a chiral space group, $P2_1$.[7]

MATERIALS AND METHODS

General procedure

All melting points were uncorrected. The spectral data were recorded with the following instruments: the IR spectra, NICOLET IFOSX FT-IR spectrophotometer; elemental analysis, YANACO CHN CORDER MT-3 analyzer.

Preparation of two-component molecular crystal (1•2) from phenylurea (1) and thiourea (2).

A mixture of thiourea (0.273 g; 2 mmol) and phenylurea (o.153 g; 2 mmol) was dissolved in hot acetonitrile (7 mL) and the solution was submitted to spontaneous, slow evaporation in an open flask to deposit the molecular crystal (**1•2**) as colorless prisms, m.p. 158-161°C. IR (KBr): ν 3490, 3400–3080, 1672, 1620, 1594, 1550, 1450, 1410, 1358, 764, 704, 660 cm^{-1}. Anal. Calcd. for $C_8H_{12}N_4OS$: C, 45.24; H, 5.70; N, 26.43 %. Found: C, 45.18; H, 5.71; N, 25.86%.

Attempts to obtaining molecular crystals from thiourea and various counterpart compounds.

An equimolar mixture of thiourea and a counterpart compound (each 2–3 mmol) was dissolved in methanol and the solution was submitted spontaneous evaporation as above. Imidazole, 4-methylimidazole, 1,2,4-triazole, benzimidazole and benzotriazole were used as the counterpart. In all the cases big prisms crystallized in the first stage, which were identified as pure thiourea by their IR ànd melting point determinations.

X-Ray crystalllographic analysis of molecular crystal 1•2.

Data collections were performed on a Rigaku AFC7R automatic four-circle X-ray diffractometer with a graphite monochromated Cu Kα (λ =

1.54178 Å) radiation. Absorption correction was applied. No degradation of the crystal was ascertained in all cases by repeated monitoring of the three representative reflections every 150 reflections. These structure were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Atomic parameters were refined by the full matrix least-squares method at the final stage. All the calculations were carried out on teXan crystallographic software package, Molecular Structure Corporation. The crystal data of the two-component molecular crystal (**1**•**2**) of thiourea and phenylurea are listed in Table 1 and the crystal structure is illustrated in Figures 1–4.

RESULTS AND DISCUSSION

We selected thiourea as the counterpart of phenylurea for the preparation of a two-component molecular crystal. Thiourea crystallizes in a two different space groups, *P*b2$_1$m and *P*bnm, at different temperatures,[8] and is known to form chiral molecular crystals with various compounds such as parabanic acid [9] and lead(II) formate[10].

An equimolar mixture of phenylurea (**1**) and thiourea (**2**) was dissolved in acetonitrile and the solution was submitted to slow evaporation in an open flask, depositing colorless prisms. The IR spectrum and elemental analysis indicated the formation of a 1 : 1 molecular compound (**1**•**2**). The melting point (158-161°C) was between those of phenylurea (145-147°C) and thiourea (174-177°C).

A single crystal of **1**•**2** was submitted to X-ray crystallographic analysis. The crystal data (Table 1) showed that the crystal belongs to an achiral space group, *P*2$_1$/c (# 14) contrary to our expectation. The crystal structure is illustrated in Figures 1–4. The unit cell in the crystal lattice consists of each four molecules of phenylurea and thiourea forming four sets of 1 : 1 molecular compound (Figure 1). The component molecules are connected each other by various types of hydrogen bonds to form a complex structure. A

Table 1. Crystal data of the two-component molecular crystal **1•2**.

Crystal data	
Empirical formula	$C_8H_{12}N_4OS$
Formula weight	212.27
Crystal color, habit	Colorless prismatic
Crystal dimension	0.30 x 0.30 x 0.30 mm
Crystal system	Monoclinic
Space group	$P2_1/c$ (# 14)
Lattice parameters	a = 5.781(3) Å
	b = 12.564(3) Å
	c = 14.623(3) Å
	β = 100.11(3)°
	V = 1045.7(6) Å^3
Z value	4
D*calc*	1.348 g/cm^3
F000	448.00
m (CuKα)	25.60 cm^{-1}
Data collection	
Radiation	CuKα (l = 1.54178 Å)
2θmax	120.1°
No. of reflections measured	Total: 1834
	Unique: 1651 (R*int* = 0.013)
Final refinement	
No. of observation, I > 300σ(I))	1526
No. of variables	149
R	0.033
Rw	0.077

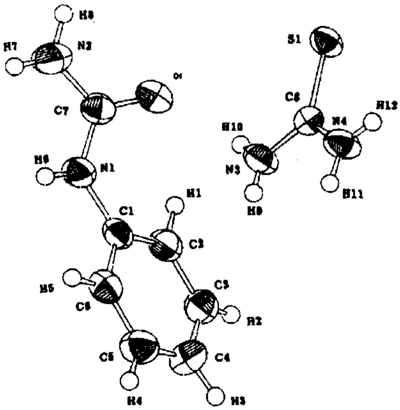


Figure 1. The molecular structure of **1•2**. An ORTEP drawing.

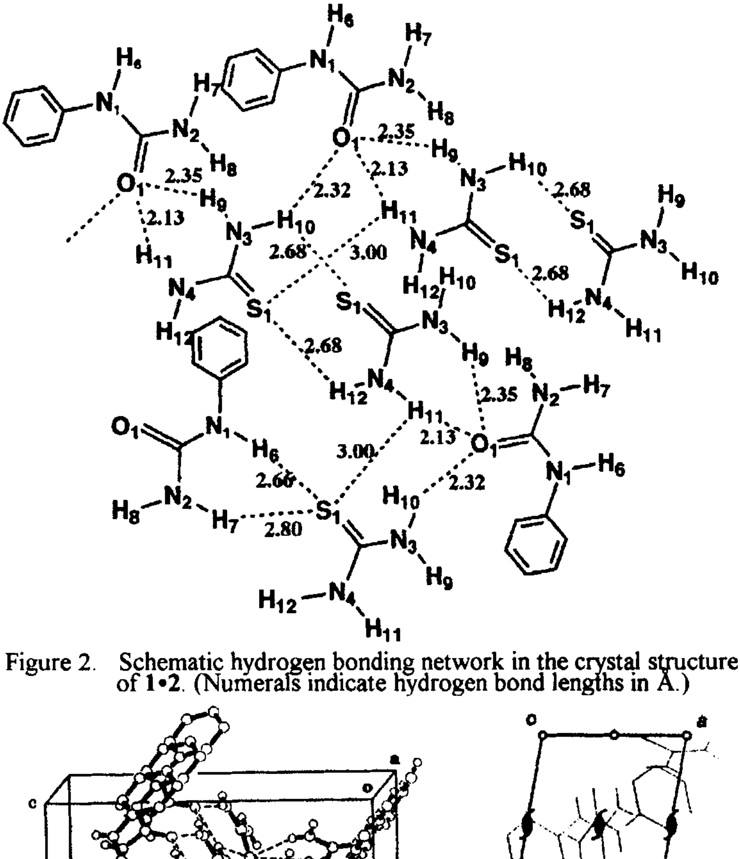
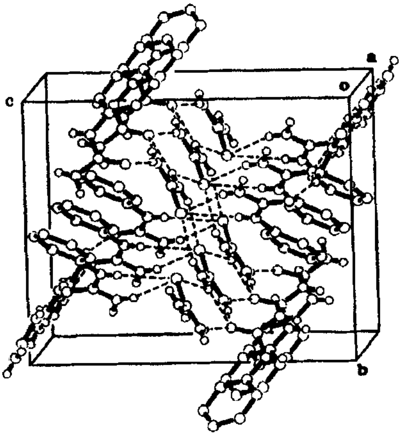


Figure 2. Schematic hydrogen bonding network in the crystal structure of 1•2. (Numerals indicate hydrogen bond lengths in Å.)



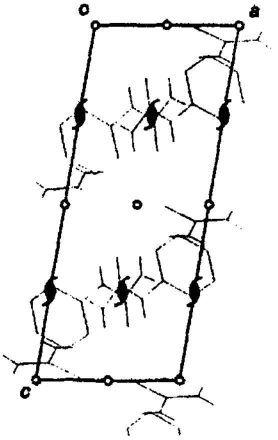


Figure 3. The crystal structure of 1•2.

Figure 4. Symmetry elements in the crystal structure of 1•2. (Project on ac face.)

linear chain structure is formed along the a-axis with the aid of a number of hydrogen bonds (Figure 3): N3–H9• • •O1 (2.35Å); N4–H11• • •O1 (2.13Å); N3–H10• • •O1 (2.32Å); N4–H11• • •S1 (3.00Å). This hydrogen bonding chain structure is more easily seen in a schematic diagram of Figure 2. This diagram also shows further hydrogen bonding network branching from the linear chain. There are two cyclic hydrogen bonding structures. One is the formation of thiourea dimer by hydrogen bonds N3–H10• • •S1 (2.68Å) abd N4–H12• • •S1 (2.68Å), and the other is a further connection between phenylurea and thiourea by hydrogen bonds N1–H6• • •S1 (2.66Å) and N2–H7• • •S1 (2.80Å).

As seen in Figure 4, the hydrogen bonding network is arranged along the two-fold screw axes parallel to the b-axis of the unit cell. However, these chiral structures are cancelled each other due to the presence of centers of symmetry.

In our exploratory study for the design of chiral molecular crystals, attempts have been made for obtaining other two-component molecular crystals using imidazole, 4-methyl-imidazole, 1,2,4-triazole, benzimidazole and benzotriazole as the counterpart of thiourea. In all the experiments done in methanol solutions, however, crystals deposited in the early stage of slow evaporation were found to be thiourea but no formation of two-component molecular crystal was observed.

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