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Phenazine and 10*H*-phenothiazine cocrystal stabilized by N-H...N and C-H...S hydrogen bonds

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RESEARCH ARTICLE



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ABSTRACT

A 1:1 co-crystal of phenazine and phenothiazine was prepared. The crystal structure was determined by using a single crystal X-ray crystallography technique. Analysis of the crystal revealed that the molecular complex crystallizes in monoclinic $P2_1/n$ space group, $C_{12}H_8N_2 \cdot C_{12}H_9NS$, $a = 9.068(2) \text{ \AA}$, $b = 8.872(2) \text{ \AA}$, $c = 23.935(4) \text{ \AA}$, $\beta = 92.16(4)^\circ$, $V = 1924.1(6) \text{ \AA}^3$, $Z = 4$, $T = 293(2) \text{ K}$, $\mu(\text{MoK}\alpha) = 0.182 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.310 \text{ g/cm}^3$, 8057 reflections measured ($3.4^\circ \leq 2\theta \leq 46.54^\circ$), 2751 unique ($R_{\text{int}} = 0.0559$, $R_{\text{sigma}} = 0.0618$) which were used in all calculations. The final R_1 was 0.0548 ($> 2\sigma(I)$) and wR_2 was 0.1029 (all data). The molecules recognize each other through N-H...N and C-H...N hydrogen bonds, thus producing a tetramer unit. These units further interact with one another via C-H...S hydrogen bonds.

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1. Introduction

The supramolecular structures of simple organic molecules, peptides, proteins, etc., that occur due to hydrogen bonding, have attracted a lot of attention due to their fascinating, aesthetic architectures, and potential applications [1-5]. In recent times, hydrogen bonded foldamers inhibiting human immunodeficiency virus HIV and mimicking charge surface of double stranded DNA have also been reported [6,7]. Synthesis of more than two-component systems (three and four-component systems) [8,9] has been reported using hydrogen bonding as a tool. As part of our ongoing research program aimed at creating novel supramolecular assemblies [10], we were interested in synthesizing a ternary assembly based on molecular recognition principles [11]. For this purpose, and taking into account the fact that 3,5-dinitrobenzamide (i) forms molecular complexes with aza-donor compounds such as 4,4'-bipyridine (ii), we chose to cocrystallize (i) with phenazine (iii) and phenothiazine (iv), hoping that a ternary assembly would result (Scheme 1). However, characterization of the single crystals obtained from a methanol solution by X-ray diffraction method revealed that only (iii) and (iv) co-crystallized. We have determined the crystal structure and analyzed the packing arrangement of the molecules in this complex, as neither three-

dimensional coordinates nor analyses of non-covalent interactions are available from the preliminary information reported in the literature [12,13], although unit cell parameters are available.

2. Experimental

2.1. Synthesis

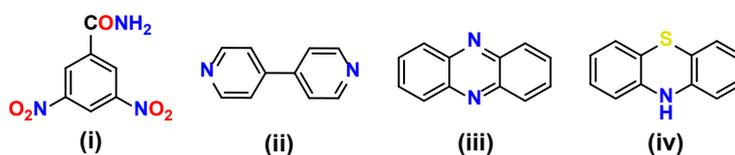
Commercially available (Aldrich) 3,5-dinitrobenzamide (0.5 mmol), phenazine (0.5 mmol), and phenothiazine (0.5 mmol) were mixed in a methanol solution. Crystals suitable for X-ray diffraction analysis were obtained at ambient temperature over a period of four days.

2.2. Crystal structure determination and refinement

All operations were performed on a Bruker-Nonius Kappa APEX1 diffractometer [14], using graphite-monochromated MoK α radiation. All diffractometer manipulations, including data collection, integration, and absorption corrections, were carried out using Bruker APEX1 software [15]. The preliminary cell constants were obtained from three sets of 16 frames. Data collection was carried out at 298 K, using a frame time of 5 s and a detector distance of 50 mm.

Table 1. Crystal data and details of the structure refinement for the molecular complex.

Empirical formula	C ₂₄ H ₁₇ N ₃ S
Formula weight	379.4784
Temperature (K)	298(2)
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , (Å)	9.068(2)
<i>b</i> , (Å)	8.872(2)
<i>c</i> , (Å)	23.935(4)
β (°)	92.16(4)
Volume (Å ³)	1924.1(6)
<i>Z</i>	4
ρ_{calc} (g/cm ³)	1.310
μ (mm ⁻¹)	0.182
<i>F</i> (000)	792.0
Crystal size (mm ³)	0.21 × 0.18 × 0.11
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection (°)	3.4 to 46.54
Index ranges	-10 ≤ <i>h</i> ≤ 10, -9 ≤ <i>k</i> ≤ 9, -26 ≤ <i>l</i> ≤ 15
Reflections collected	8057
Independent reflections	2751 [<i>R</i> _{int} = 0.0559, <i>R</i> _{sigma} = 0.0618]
Data/restraints/parameters	2751/0/321
Goodness-of-fit on <i>F</i> ²	0.951
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0548, <i>wR</i> ₂ = 0.0883
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1008, <i>wR</i> ₂ = 0.1029
Largest diff. peak/hole (e.Å ⁻³)	0.15/-0.14

**Scheme 1**

The optimized strategy used for data collection consisted of four phi and six omega scan sets, with 0.5 steps in phi or omega; completeness was 99.2 %. The structure was obtained and solved by direct methods using SHELXTL [16]. All non-hydrogen atoms of the molecule were refined anisotropically. All hydrogen atoms were located from the difference Fourier map, and their parameters were refined in the isotropic approximation of atomic displacements. The crystallographic data are summarized in Table 1.

3. Results and discussion

The single-crystal X-ray structure revealed that the title compound crystallizes in a 1:1 molar ratio, in the space group *P*2₁/*n* with *Z* = 4. Figure 1 shows the asymmetric unit and atomic labeling scheme of the molecular complex. Selected bond lengths and angles are given in Table 2.

The packing analysis reveals that the phenazine and phenothiazine molecules interact with one another through the formation of centrosymmetric N-H...N (H...N = 2.34 (2) Å, N...N = 3.12 (5) Å, and N-H...N = 176°) and C-H...N (H...N = 2.64 (7) Å, C...N = 3.12 (4) Å, and C-H...N = 176°) hydrogen bonds, to form tetrameric unit as shown in Figure 2a. This recognition pattern further interacts with one another through C-H...S (H...S = 2.92 (3) Å, C...S = 3.85 (6) Å, and C-H...S = 167°) hydrogen bonding (see Table 3). The characteristics of these hydrogen bonds are consistent with the values reported in the literature [17,18]. For instance, Desiraju *et al.* reported a 1:1 molecular complex of a co-crystal in which the structure is stabilized by N-H...N and C-H...S hydrogen bonding forming a herring-bone pattern [19]. Three-dimensional arrangement of the molecular complex is shown in Figure 3.

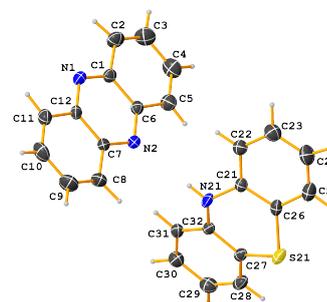
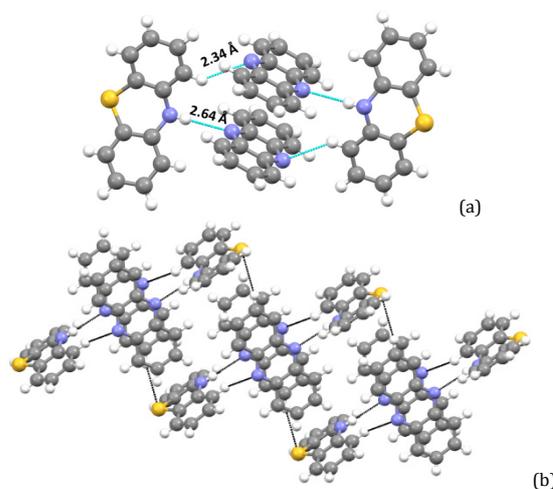
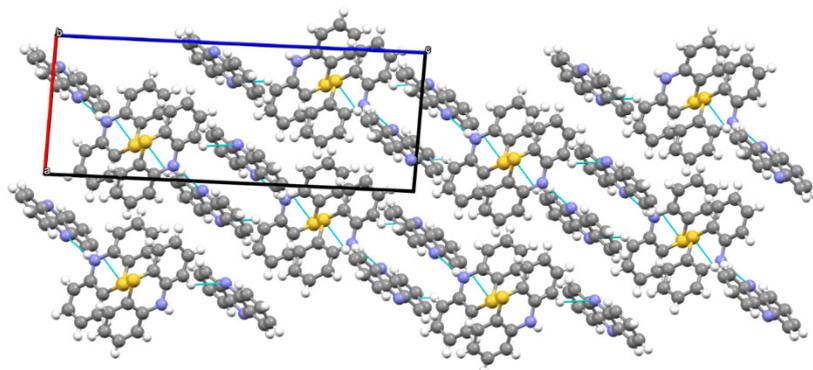
**Figure 1.** A view of the title complex, showing displacement ellipsoids at the 40% probability level and the atom-numbering scheme.**Figure 2.** The packing (a) between the four molecules forming a tetramer and (b) molecules extending further by CH...S hydrogen bonding.

Table 2. Bond lengths and angles for the molecular complex.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)		
C1	C2	1.424(5)	C21	C22	1.378(4)		
C1	C6	1.419(4)	C21	C26	1.391(4)		
C1	N1	1.333(4)	C21	N21	1.386(4)		
C2	C3	1.335(6)	C22	C23	1.371(5)		
C3	C4	1.397(6)	C23	C24	1.365(6)		
C4	C5	1.346(6)	C24	C25	1.373(6)		
C5	C6	1.423(5)	C25	C26	1.376(5)		
C6	N2	1.334(3)	C26	S21	1.757(3)		
C7	C8	1.408(5)	C26	C28	1.385(5)		
C7	C12	1.419(4)	C27	C32	1.384(4)		
C7	N2	1.340(3)	C27	S21	1.760(3)		
C8	C9	1.332(6)	C28	C29	1.370(5)		
C9	C10	1.395(7)	C29	C30	1.378(5)		
C10	C11	1.353(6)	C30	C31	1.368(5)		
C11	C12	1.416(4)	C31	C32	1.378(4)		
C12	N1	1.331(4)	C32	N21	1.393(4)		
Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
C6	C1	C2	118.5(4)	N21	C21	C26	120.3(3)
N1	C1	C2	119.6(4)	C23	C22	C21	121.4(4)
N1	C1	C6	121.9(3)	C24	C23	C22	119.2(5)
C3	C2	C1	120.8(5)	C23	C24	C25	120.3(5)
C2	C3	C4	120.8(5)	C24	C25	C26	120.9(5)
C5	C4	C3	120.9(5)	C21	C26	S21	121.7(3)
C4	C5	C6	120.7(5)	C25	C26	C21	119.0(4)
C1	C6	C5	118.2(4)	C25	C26	S21	119.3(3)
N2	C6	C1	121.6(3)	C28	C27	S21	119.6(3)
N2	C6	C5	120.2(3)	C32	C27	C28	118.7(3)
C8	C7	C12	119.4(4)	C32	C27	S21	121.5(3)
N2	C7	C8	119.2(3)	C29	C28	C27	121.1(4)
N2	C7	C12	121.4(3)	C28	C29	C30	120.2(4)
C9	C8	C7	120.0(5)	C31	C30	C29	118.9(4)
C8	C9	C10	121.4(5)	C30	C31	C32	121.6(4)
C11	C10	C9	121.0(5)	C27	C32	N21	120.6(3)
C10	C11	C12	119.6(5)	C31	C32	C27	119.5(3)
C11	C12	C7	118.5(4)	C31	C32	N21	119.9(3)
N1	C12	C7	122.0(3)	C12	N1	C1	116.5(3)
N1	C12	C11	119.5(3)	C6	N2	C7	116.6(3)
C22	C21	C26	119.1(4)	C21	N21	C32	124.3(3)
C22	C21	N21	120.6(3)	C26	S21	C27	100.80(16)

Table 3. Hydrogen bond parameters (distances, Å and angles, °).

Hydrogen bonds	D-H	H...A	D...A	∠D-H...A
N-H...N ⁱ	0.78	2.345	3.119(6)	175
C-H...N ⁱⁱ	0.94	2.637	3.394(9)	138
C4-H4...S21 ⁱⁱⁱ	0.95	2.921	3.852(11)	167

Symmetry code: (i) $x, -1+y, z$; (ii) x, y, z ; (iii) $1-x, 1-y, -z$.**Figure 3.** View of the molecular complex along the b axis in three dimensions.

4. Conclusions

Preparation of a 1:1 co-crystal formed between phenazine and 10H-phenothiazine is reported. Single crystal X-ray crystallographic studies of the co-crystal revealed that the structure is stabilized by N-H...N and C-H...N hydrogen bonds, which further interact through C-H...S hydrogen bonds between phenazine and 10H-phenothiazine to form supramolecular assembly.

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Supporting information

CCDC-2096713 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallo-

graphic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest. Ethical approval: All ethical guidelines have been adhered. Sample availability: Samples of the compounds are available from the author.

CRedit authorship contribution statement

Conceptualization: Jayarama Prakasha Reddy; Methodology: Jayarama Prakasha Reddy, Tahir Mehmood, Bhumiben Chandubhai Patel; Software: Jayarama Prakasha Reddy; Validation: Jayarama Prakasha Reddy, Tahir Mehmood, Bhumiben Chandubhai Patel; Formal Analysis: Jayarama Prakasha Reddy, Tahir Mehmood, Bhumiben Chandubhai Patel; Investigation: Jayarama Prakasha Reddy, Tahir Mehmood, Bhumiben Chandubhai Patel; Resources: NIL; Data Curation: Jayarama Prakasha Reddy; Writing - Original Draft: Jayarama Prakasha Reddy; Writing - Review and Editing: Jayarama Prakasha Reddy; Visualization: Jayarama Prakasha Reddy, Tahir Mehmood, Bhumiben Chandubhai Patel; Funding acquisition: Jayarama Prakasha Reddy; Supervision: Jayarama Prakasha Reddy; Project Administration: Jayarama Prakasha Reddy.

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