1-Isopropylphenothiazine

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Abstract. $C_{15}H_{15}NS$, orthorhombic, $P2_12_12_1$, $Z = 4$, $M_r = 241.36$, $a = 7.716$ (1), $b = 8.366$ (2), $c = 19.963$ (4) Å, $V = 1288.7$ (4) Å^3, $D_x = 1.244$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, μ(Cu $K\alpha$) = 1.96 mm^{-1}. Final $R = 0.059$ for 1139 observed reflections. The molecule is folded with the central ring in a boat conformation. The folding angle between the least-squares planes of the two benzo rings is 146.1°.

Introduction. The crystal structures of a number of phenothiazines have been determined in order to evaluate the effects of different substituents upon the geometry of phenothiazines and on the chemical reactivity of 10-substituted phenothiazines (Chu & van der Helm, 1974, 1975, 1976; Chu & Yang, 1977). A systematic study of the structures of 1- and 10-substituted, and of 1,10-disubstituted phenothiazines has been undertaken in this laboratory during the past few years. The purposes of this study include: (*a*) the determination of rotational barriers in these systems; (*b*) the determination of structural effects upon NMR parameters in these systems; and (*c*) the correlation of structures in the solid state with those in solution. The crystal structure and synthesis of 1-isopropyl-phenothiazine are presented in this paper. The crystal structures of 1-methyl- and 1-ethylphenothiazines are discussed in the succeeding paper (Chu, Napoleone, Ternay & Chang, 1982).

The 1-alkylphenothiazines were prepared by the reaction of the appropriate 2-alkyldiphenylamine with sulfur in the presence of iodine. Typically, 0.2 mol of amine, 0.4 mol of sulfur, and 5×10^{-3} mol of iodine in 50 ml of *o*-dichlorobenzene were refluxed for 2 h under a nitrogen atmosphere. After cooling to room temperature, the resulting green solid was separated and sublimed. Crude of 1-isopropylphenothiazine was sublimed (423 K, 20.00 Pa) to produce the desired crystal (m.p. 390–392 K) with a 31% yield.

The unit-cell parameters were obtained from a least-squares analysis of 15 reflections with 2θ values ranging from 26 to 76°. The space group $P2_12_12_1$ was deduced from systematic absences (*h*00 absent with *h* odd, 0*k*0 absent with *k* odd, 00*l* absent with *l* odd). The intensity data were collected on a Syntex $P2_1$ automatic diffractometer with a crystal of approximately 0.45 × 0.27 × 0.21 mm. The crystal was mounted with **a** approximately along the φ axis of the diffractometer. A $\theta/2\theta$ scanning mode with graphite-monochromatized Cu $K\alpha$ radiation was used to measure 1270 independent reflections with 2θ values below 130°, of which 1143 reflections were considered as observed by the criterion $I > 3.0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. Four reflections were affected by extinction and were omitted from the refinement. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors; no absorption corrections were applied.

The structure was determined by the application of direct methods with the weighted multisolution tangent-refinement program, *MULTAN* (Germain, Main & Woolfson, 1971). The *E* map showed the positions of all non-H atoms. The refinement was carried out by the block-diagonal least-squares method (Shiono, 1971) with anisotropic temperature factors. Most of the H positions were located in a difference Fourier synthesis except some H atoms associated with methyl groups. The positions of these H atoms were calculated by using the C–H bond length of 1.0 Å and ideal tetrahedral bond angles. The isotropic temperature factors were used for the H atoms in the refinement. The weight of the reflection was assigned as $1/[\sigma(F)]^2$, where $\sigma(F)$ was calculated from counting statistics. The quantity $\sum w(||F_o| - |F_c||)^2$ was minimized. The atomic scattering factors used for S, N, and C atoms were those from *International Tables for X-ray Crystallography* (1962). For H, the values given by Stewart, Davidson & Simpson (1965) were used. Since the crystal belongs to a non-centrosymmetric space group, the anomalous-dispersion correction (Cromer & Liber-

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Table 1. *Fractional atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *and isotropic thermal parameters*

E.s.d.'s are given in parentheses and refer to the last positions of respective values.

B_{eq} is calculated from the relation: $B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

|	x	y	z	B_{eq}/B (Å^2)
S(5)	8738 (2)	5130 (2)	5680 (1)	6·28 (6)
N(10)	5680 (5)	3629 (4)	5053 (2)	5·09 (19)
C(1)	5728 (6)	5213 (5)	4019 (2)	4·58 (20)
C(2)	6562 (7)	6416 (5)	3654 (2)	5·67 (25)
C(3)	7939 (7)	7259 (6)	3910 (3)	6·64 (29)
C(4)	8566 (6)	6888 (6)	4534 (3)	5·86 (25)
C(6)	6686 (8)	4739 (7)	6795 (2)	6·91 (30)
C(7)	5275 (9)	4152 (7)	7133 (2)	7·62 (33)
C(8)	3974 (8)	3374 (7)	6780 (2)	6·92 (31)
C(9)	4073 (7)	3215 (6)	6086 (2)	5·68 (26)
C(11)	6397 (6)	4850 (5)	4655 (2)	4·20 (18)
C(12)	7801 (6)	5701 (6)	4902 (2)	4·70 (21)
C(13)	6822 (7)	4561 (5)	6107 (2)	5·21 (23)
C(14)	5521 (6)	3815 (5)	5750 (2)	4·61 (20)
C(15)	4127 (7)	4381 (5)	3752 (2)	5·26 (24)
C(16)	2503 (7)	5181 (8)	4013 (3)	7·61 (33)
C(17)	4068 (8)	4231 (9)	2990 (3)	8·39 (37)
H(N)	483 (4)	316 (4)	489 (1)	3·0 (8)
H(2)	607 (5)	663 (6)	319 (2)	8·2 (13)
H(3)	850 (5)	799 (4)	365 (2)	4·4 (9)
H(4)	943 (4)	743 (4)	471 (1)	3·6 (8)
H(6)	753 (6)	530 (6)	706 (2)	7·6 (13)
H(7)	506 (7)	425 (6)	762 (2)	8·2 (13)
H(8)	292 (6)	302 (7)	701 (2)	9·4 (15)
H(9)	298 (7)	298 (7)	578 (3)	12·2 (18)
H(15)	413 (5)	330 (5)	390 (2)	6·8 (12)
H(16)1	249 (6)	522 (7)	460 (2)	9·5 (15)
H(16)2	144 (6)	467 (6)	384 (2)	9·6 (15)
H(16)3	249 (6)	619 (6)	387 (2)	9·7 (17)
H(17)1	300 (6)	359 (6)	289 (2)	8·9 (14)
H(17)2	526 (8)	364 (7)	281 (2)	12·6 (19)
H(17)3	409 (7)	525 (8)	278 (2)	13·1 (21)
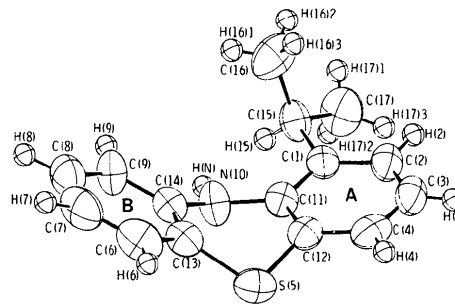
Fig. 1. *ORTEP* drawing (Johnson, 1965) of one molecule of the title compound. The torsion angles around the central ring are: N(10)–C(11)–C(12)–S(5) 4·5 (6), C(11)–C(12)–S(5)–C(13) –36·4 (4), C(12)–S(5)–C(13)–C(14) 36·4 (4), S(5)–C(13)–C(14)–N(10) –4·8 (6), C(13)–C(14)–N(10)–C(11) –39·1 (6), C(14)–N(10)–C(11)–C(12) 38·9 (6)°.
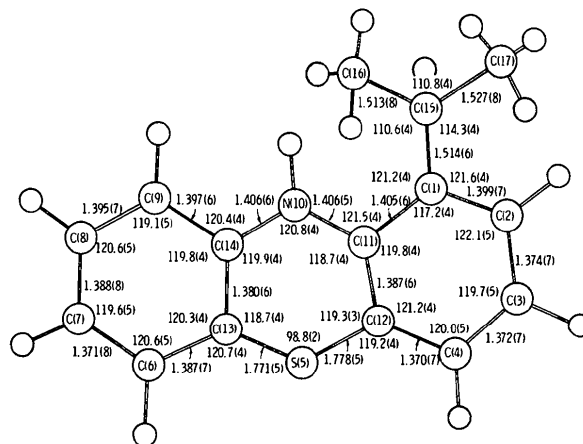

Fig. 2. Bond lengths (Å) and bond angles (°) of the title compound with e.s.d.'s in parentheses.

man, 1970) of S was applied in the least-squares refinement. The refinement converged at $R = 0·059$ for the parameters shown in Table 1* and at $R = 0·064$ for the mirror-related structure. The weighted disagreement index R_w, was 0·064.

Discussion. The identification of the atoms and the configuration of the title compound are shown in Fig. 1. The molecule is folded with the central ring in a boat conformation as shown by the ring torsion angles in Fig. 1, and by the Cremer & Pople (1975) puckering parameters, which are $q_2 = 0·556$, $q_3 = 0·085$, $Q = 0·562$ Å, $\varphi_2 = 180·3$ and $\theta = 81·3°$. For ideal boat conformation, these parameters are: $q_2 = Q$, $q_3 = 0$, $\varphi_2 = 180$, $\theta = 90°$. The two benzo rings are planar and the deviations of the atoms from the least-squares planes range from 0·000 to 0·011 Å for ring A and from 0·003 to 0·009 Å for ring B (Fig. 1). The folding

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36851 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
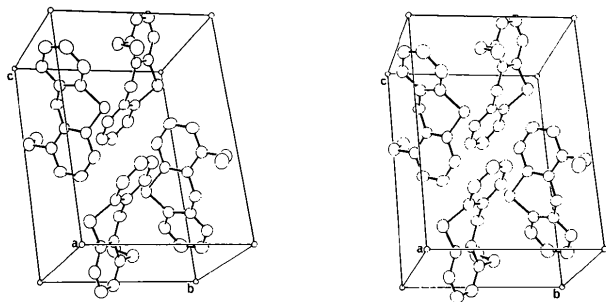
angle between the two benzo rings is 146·1° which is similar to the angle, 146·8°, found in one of two crystallographically independent molecules of 10-isopropylphenothiazine (Chu & van der Helm, 1976). However, the folding angle of the other molecule of 10-isopropylphenothiazine is 136·1°. The difference in the folding angle is apparently due to the difference in intermolecular contacts. The C(15) of the isopropyl substituent deviates from the least-squares plane of ring A by 0·098 Å. The conformation of the isopropyl substituent can be shown by the torsion angles about the C(1)–C(15) bond. The torsion angles of C(2)–C(1)–C(15)–C(16) and C(2)–C(1)–C(15)–C(17) are –94·2 (5) and 31·7 (6)° respectively.

The bond lengths and bond angles with their standard deviations are shown in Fig. 2. The C–S and C–N bond lengths and the C–S–C and C–N–C bond angles have similar magnitudes to those in 10-substituted phenothiazines. All the C–H bond lengths and C–C–H and H–C–H bond angles are within

Fig. 3. *ORTEP* stereo drawing of the molecular packing of the title compound in a unit cell.

reasonable ranges of magnitudes. The packing of the molecules in the crystal is shown in Fig. 3 and there are no intermolecular contacts less than van der Waals distances.

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1-Methylphenothiazine and 1-Ethylphenothiazine, a Nearly Isomorphous Pair

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Abstract. 1-Methylphenothiazine, $C_{13}H_{11}NS$, monoclinic, $P2_1/c$, $Z = 4$, $M_r = 213.30$, $a = 9.063$ (1), $b = 8.968$ (2), $c = 13.503$ (1) Å, $\beta = 102.29$ (1)°, $V = 1072.4$ (3) Å^3, $D_x = 1.321$ Mg m^{-3}, $\mu(\text{Cu } K\alpha) = 2.28$ mm^{-1}. Final $R = 0.053$ for 1658 observed reflections. 1-Ethylphenothiazine, $C_{14}H_{13}NS$, monoclinic, $P2_1/c$, $Z = 4$, $M_r = 227.33$, $a = 9.509$ (1), $b = 8.962$ (1), $c = 14.036$ (2) Å, $\beta = 105.34$ (1)°, $V = 1153.6$ (3) Å^3, $D_x = 1.309$ Mg m^{-3}, $\mu(\text{Cu } K\alpha) = 2.15$ mm^{-1}. Final $R = 0.035$ for 1731 observed reflections. The crystal structures of 1-methylphenothiazine and 1-ethylphenothiazine are nearly isomorphous. The folding angles are 154.8 and 147.4° for 1-methyl- and 1-ethylphenothiazines respectively.

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Introduction. These structures were determined as a continuous study of 1- and 10-substituted, and 1,10-disubstituted phenothiazines as described in the preceding paper (Chu, Napoleone, Ternay & Chang, 1982). The preparation of 1-methyl- and 1-ethylphenothiazines was carried out in the same manner as that of 1-isopropylphenothiazine (Chu *et al.*, 1982). Crude of 1-methylphenothiazine was sublimed (383 K, 2.67 Pa) to produce the desired material (m.p. 411–412 K) in 42% yield. Crude of 1-ethylphenothiazine was sublimed (443 K, 26.67 Pa) with a 53% yield of the desired product (m.p. 394–396 K).

The unit-cell parameters of each compound were obtained from a least-squares analysis of 15 reflections with 2θ values measured on a Syntex $P2_1$ automatic