ter than 3·25 Å to the anions; these are indicated in Fig. 1. There are six N–H···Cl hydrogen bonds shorter than 3·52 Å formed between the cations.

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2-Methoxyphenothiazine

By D. W. Phelps and A. W. Cordes

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701, *U.S.A.*

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Abstract. $C_{13}H_{11}ONS$, orthorhombic, $P2_12_12_1$, $a=11\cdot585$ (7), $b=5\cdot720$ (2), $c=16\cdot459$ (8) Å, $Z=4$, $D_c=1\cdot40$, $D_m=1\cdot40$ (2) g cm^{-3} (by suspension). The C–S and C–N bond distances average 1·779 (5) and 1·39 (1) Å, the CSC angle is 99·4 (4)°, the CNC angle is 121·0 (8)°, and the dihedral angle of the heterocyclic system is 146·4 (2)°.

Introduction. Crystals of the title compound were obtained by slow evaporation of a mixed solvent of methylene chloride, hexane, and 2-propanol in approximate ratios of 5:2:1. Data were collected with a parallelepiped crystal of dimensions 0·81 × 0·31 × 0·43 mm (all ±0·01 mm) in the [010], [001], and [101] directions, mounted with **b** approximately parallel to the φ axis of the G.E. XRD-5 manually operated quarter-circle diffractometer. Zr-filtered Mo $K\alpha$ ($\lambda=0\cdot71069$ Å) radiation was used for unit-cell parameter measurements and intensity-data collection. Systematic absences of $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd indicated space group $P2_12_12_1$. The linear absorption coefficient is 2·70 cm^{-1}; no absorption corrections were made. All 1166 reflections with $0° < 2\theta < 50°$ were scanned (θ–2θ scans) 2° in 2θ at 2° min^{-1}, with 20s stationary backgrounds at each end of the scan. Only the 430 reflections with $I > 2\sigma(I)$ were used for the structure determination; seven of the most intense low-angle reflections were omitted from the refinement because of extinction. The intensities of four reflections measured periodically during the five-day data collection varied less than 1σ and thereby indicated crystal and electronic stability.

The standard deviations for I were calculated by $\sigma(I)=(S+2\cdot25B+0\cdot0016I^2)^{1/2}$ (where S = scan count, B = sum of the background counts, and $I=S-1\cdot5\ B$), except for a number of reflections for which the two background readings differed by more than twice the calculated σ owing to the tailing of the reflection peak. For the latter reflections the standard deviations were set equal to the deviation of the background readings from the mean background value. Neutral atom scattering factors were used (*International Tables for X-ray Crystallography*, 1975) for all atoms.

The trial structure was initiated by analysis of a Patterson map, which revealed the location of the sulfur atom. Hydrogen atoms bonded to the N and methyl C atoms were located on a difference map; phenyl hydrogen atoms were placed at calculated positions (C–H = 0·95 Å). Neither the positional nor the assigned thermal factors of the hydrogen atoms were refined. Successive full-matrix least-squares refinements allowing first the S, then the O and C of the methoxy group, and finally the N, anisotropic thermal motion gave significant changes in R values (Hamilton, 1965). The final refinement consisted of 85 parameters and 423 reflections, and gave an R of 0·048 and R_w of

0·046. The standard deviation of an observation of unit weight was 0·80; only four $\Delta F/\sigma(F)$ values exceeded 2. In the final cycle of refinement no parameter shifted by more than $0{\cdot}23\sigma$. The final difference Fourier map showed a maximum peak of 0·25 e Å^{-3} (=5% of a carbon peak on a regular Fourier map). A final inspection of $\Delta F/\sigma$ showed no apparent θ or F dependence. Table 1 gives the final positional and thermal parameters and Fig. 1 is an *ORTEP* drawing which gives the final bond distances (e.s.d.'s=0·01 Å) and bond angles (e.s.d.'s=0·4° for the angle at S, 0·8° for the other angles).*

Table 1. *Final positional and thermal parameters for* 2-*methoxyphenothiazine*

	x	y	z	B (Å^2)
S	0·1193 (2)	0·1893 (5)	0·1093 (1)	—
N	0·0376 (6)	−0·241 (1)	0·1941 (4)	—
O	0·3903 (5)	−0·351 (2)	0·3462 (4)	—
C(1)	0·2129 (7)	−0·309 (2)	0·2695 (5)	3·8 (2)
C(2)	0·3233 (8)	−0·241 (2)	0·2898 (5)	4·3 (2)
C(3)	0·3753 (9)	−0·055 (2)	0·2510 (5)	4·5 (2)
C(4)	0·3145 (9)	0·068 (2)	0·1941 (6)	4·7 (2)
C(5)	0·2020 (8)	0·011 (2)	0·1756 (5)	4·0 (2)
C(6)	0·1506 (7)	−0·181 (2)	0·2124 (5)	3·5 (2)
C(7)	−0·0059 (6)	−0·214 (2)	0·1155 (5)	3·5 (2)
C(8)	−0·0846 (8)	−0·365 (2)	0·0844 (5)	4·2 (2)
C(9)	−0·1333 (8)	−0·347 (2)	0·0080 (6)	5·0 (2)
C(10)	−0·0998 (9)	−0·157 (2)	−0·0379 (5)	5·1 (2)
C(11)	−0·0194 (8)	0·002 (2)	−0·0098 (5)	4·5 (2)
C(12)	0·0245 (7)	−0·027 (2)	0·0689 (5)	3·8 (2)
C(13)	0·3349 (8)	−0·521 (2)	0·3959 (7)	—
H(N)	0·005	−0·370	0·225	5
H(C4)	0·349	0·205	0·168	5
H(C3)	0·452	−0·011	0·265	5
H(C1)	0·176	−0·440	0·296	5
H(C8)	−0·109	−0·504	0·118	5
H(C9)	−0·186	−0·454	−0·012	5
H(C10)	−0·130	−0·134	−0·092	5
H(C11)	0·003	0·137	−0·042	5
H(1)	0·390	−0·610	0·425	5
H(2)	0·313	−0·649	0·365	5
H(3)	0·282	−0·471	0·424	5

Anisotropic thermal parameters (×10^3)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	11·6 (3)	8·3 (8)	5·0 (1)	0·5 (5)	0·5 (2)	2·1 (4)
N	7·1 (7)	40 (4)	34 (4)	0·7 (13)	0·6 (4)	1·4 (9)
O	7·5 (6)	56 (3)	44 (3)	2 (2)	1·1 (4)	1 (1)
C(13)	12 (1)	44 (4)	59 (6)	1 (2)	1·3 (7)	0 (2)

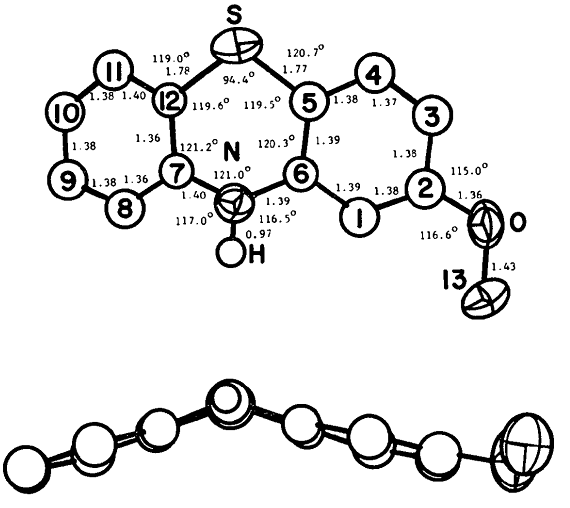

Fig. 1. Top: *ORTEP* drawing of 2-methoxyphenothiazine. Methyl C–H distances (not shown) were 0·82, 0·93, and 0·95 Å. Bottom: View along the N···S line, showing the alignment of H(N) and the methoxy group with respect to the molecular planes. In both of these drawings the temperature factor of the hydrogen atom was reduced to B=2·5 for figure clarity.

Discussion. This structure is of interest for comparison with the structures of unsubstituted phenothiazine (Bell, Blount, Briscoe & Freeman, 1968) and numerous *N*-substituted phenothiazine drug molecules (Phelps & Cordes, 1974 and references therein).

In these molecules the structural parameter which varies the most from one molecule to another is the dihedral angle between the two 'halves' of the heterocyclic system, commonly referred to as the butterfly angle. In general (and excluding the structures of phenothiazine molecules in charge-transfer complexes) the *N*-substituted phenothiazine molecules have been found to have butterfly angles in the 136–144° range.

The only structure report of a phenothiazine not substituted at N (N–H bond), previous to this report, is that of phenothiazine itself. Phenothiazine has a butterfly angle more planar than the average *N*-substituted molecule (153·3 *vs.* 136–144°), and this has led to bonding discussions (*i.e.*, Malrieu & Pullman, 1964) which conclude the N–H bond is probably more nearly equatorial than is the N–C bond of the *N*-substituted phenothiazines. Unfortunately, the H atom was not located in the structure determination of phenothiazine. Thus the 149·4 (3)° butterfly angle and the hydrogen position of methoxyphenothiazine are significant features of this report, as they give the first structural support to this bonding rationale: The *N*-substituted phenothiazine molecules have S···N–C angles in the range of 158–166°, and the S···N–H angle found in methoxyphenothiazine is 174°. (The only *N*-substituted phenothiazine which has structural parameters outside of the normal range also deviates in a similar way: methoxypromazine (Marsau & Gauthier, 1973) has a butterfly angle of 157·4° and an S···N–C angle of 169°.)

The butterfly angle of methoxyphenothiazine is 146·4 (2)° when the S and N atoms are included in the calculation (Waser, Marsh & Cordes, 1973) of each plane. As is usual, the χ^2 values of these planes are quite high (79 and 35). If the best planes of the phenylene groups only are used, as is normally done, the butterfly angle is 149·4 (3)°; deviations from these planes are shown in Table 2. In all of the dozen phenothiazine structures reported, the butterfly angle

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31103 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atom displacements from the best planes of the phenylene rings in 2-methoxyphenothiazine*

Plane 1		Plane 2	
S*	0·172 (3)	S*	0·123 (3)
N*	0·024 (7)	N*	0·027 (7)
C(1)	−0·014 (9)	C(7)	−0·008 (8)
C(2)	0·019 (9)	C(8)	0·003 (9)
C(3)	−0·006 (9)	C(9)	−0·002 (10)
C(4)	−0·025 (10)	C(10)	0·010 (11)
C(5)	0·017 (9)	C(11)	−0·014 (9)
C(6)	−0·003 (9)	C(12)	0·014 (9)
O*	0·045 (7)	H(N)*	0·013
C(13)*	0·26 (1)		
H(N)*	0·077		
$\chi^2=5\cdot4$		$\chi^2=3\cdot3$	

* Atoms not included in best-plane calculations.

calculation which excludes the N and S atoms gives more planar values, indicating the small displacement of the S and N atoms from the phenylene planes is always toward the outside of the fold.

All of the bond distances and bond angles of the $C_{12}SN$ phenothiazine framework are within the range of values found for a number of other phenothiazine structures, and the methoxy group parameters parallel those of a methoxyphenothiazine drug molecule (Phelps & Cordes, 1974). As shown in Table 2 and Fig. 1, the C and O atoms of the methoxy group are nearly coplanar with the phenylene ring to which the group is attached.

The crystal packing does not result in any intermolecular contacts shorter than the sum of the van der Waals radii for the atoms involved, with the minor exception of the H(N)–N′ (at $-x,y-\frac{1}{2},\frac{1}{2}-z$) distance of 2·55 Å which is 0·15 Å shorter than the nonbonding distance; the N···N′ distance of 3·51 Å is considerably longer than the separation usually attributed to the N–H···N hydrogen bond (Pimentel & McClellan, 1960), however.

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N,N′-Bis-(3-chloropropionyl)piperazine

By Tien-Ming Ko and J. William Moncrief

Department of Chemistry, Emory University, Atlanta, Georgia 30322, *U.S.A.*

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Abstract. $C_{10}H_{16}N_2O_2Cl_2$; monoclinic, $P2_1/c$, $a=11\cdot371(23)$, $b=7\cdot741(11)$, $c=8\cdot245(18)$ Å, $\beta=60\cdot8(2)°$; $D_c=1\cdot40$, $D_x=1\cdot42$ g cm^{-3}, $Z=2$. The structure, refined to $R_1=0\cdot065$, shows considerable steric strain, which may be connected with the oncolytic activity of the compound.

Introduction. Colorless crystals of the title compound, recrystallized from water, were obtained from P. G. Huffman, Abbott Laboratory, Chicago, Illinois. Systematic absences $0k0$, $k=2n+1$, and $h0l$, $l=2n+1$ uniquely identified the space group as $P2_1/c$. Two axes of diffraction data (a,b) were collected with Ni-filtered Cu $K\alpha$ radiation on an automated Supper–Pace diffractometer possessing Weissenberg geometry. After Lp corrections the data were correlated (Simpson, 1963) to give 1092 independent reflections, 750 of which were considered observed, having $I>2\sigma(I)$ (Parker, Flynn & Boer, 1968). An additional 152 high-angle reflections accessible with Cu $K\alpha$ radiation were not measured owing to physical limitations of the diffractometer.

The Cl position was located in the Patterson map and then confirmed by direct methods employing the 154 reflections with $E>1\cdot45$ and *MULTAN* (Germain, Main & Woolfson, 1971). Reflections in the starting set were 112, 012, $11\bar{1}$, 224, 800, 124 and 434 with the first three used for origin specification. The positions of the other seven non-hydrogen atoms in the asymmetric unit were also located in the E map computed with