

1,4-Bis(10-phenothiazinyl)butane

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Abstract. $C_{28}H_{24}N_2S_2$, $M_r = 452.63$, monoclinic, $P2_1/c$, $a = 10.807$ (2), $b = 20.176$ (3), $c = 12.222$ (2) Å, $\beta = 123.31$ (2)°, $V = 2227.1$ Å³, $Z = 4$, $D_m = 1.36$, $D_x = 1.35$ Mg m⁻³, $F(000) = 952$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 0.26$ mm⁻¹, $R = 0.070$ for 917 data with $I > 3\sigma$. Two crystallographically different centrosymmetric molecules *A* and *B* occur, with the asymmetric unit consisting of $\frac{1}{2}A + \frac{1}{2}B$. Columns of alternating *A* and *B* molecules paired in the form of a cross (fourfold pseudo screw operation) lie parallel to *a*. The aliphatic chains lie inside the columns, isolated from the chains of adjacent columns by the phenothiazine groups.

Introduction. Phenothiazine derivatives and their structures are of pharmaceutical interest because of their tranquillizing properties (McDowell, 1969, 1975, 1976). The title compound was prepared from 10-sodiophenothiazine (2 mol) and 1,4-dibromobutane (1 mol) (Frydrych, 1981). Unlike other crystalline phenothiazine derivatives, crystals of the title compound are stable when exposed to light and insoluble in solvents such as ethyl acetate and acetone. The structure determination was initiated to see if the stability might be due to an unusual structure. The material was recrystallized from boiling glacial acetic acid in the form of very small clear needles (max. dimensions 0.5 × 0.1 × 0.02 mm). X-ray examination of a needle photographically, thence on a CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation, enabled the cell dimensions and space group to be determined. Intensity data were collected for $\theta < 24^\circ$ using graphite-monochromatized Mo $K\alpha$ radiation, only 917 unique reflections had $I > 3\sigma$, owing to the smallness of the crystal. Lorentz and polarization, but not absorption, corrections were applied. Statistical tests on quasi-normalized structure factors $E(hkl)$ confirmed a centrosymmetric space group. The phase problem was solved with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The *E* map revealed all the non-H atoms of two crystallographically independent centrosymmetric molecules *A* and *B*. The asymmetric unit is thus $\frac{1}{2}A + \frac{1}{2}B$. For

full-matrix least-squares refinement *SHELX* (Sheldrick, 1976) was utilized. H atoms were constrained to chemically reasonable positions and the non-H atoms of both half-molecules were refined isotropically except for C(2), C(3), S(5), C(7), C(8), C(15) and C(16) in

Table 1. Fractional atomic coordinates and isotropic thermal parameters (Å²) for the non-H atoms, with e.s.d.'s in parentheses

Values without e.s.d.'s are equivalent isotropic temperature factors (Hamilton, 1959).

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} , U_{iso}
Molecule A				
C(1)	0.4742 (14)	0.4951 (7)	0.3441 (11)	0.053 (4)
C(2)	0.6179 (14)	0.4697 (7)	0.4131 (12)	0.059
C(3)	0.6464 (15)	0.4040 (7)	0.4508 (12)	0.068
C(4)	0.5285 (14)	0.3623 (6)	0.4128 (11)	0.059 (4)
S(5)	0.2370 (4)	0.3324 (1)	0.3010 (4)	0.060
C(6)	0.0312 (14)	0.3641 (6)	0.3557 (11)	0.050 (4)
C(7)	-0.0617 (13)	0.4066 (7)	0.3623 (11)	0.059
C(8)	-0.0685 (13)	0.4738 (7)	0.3326 (11)	0.051
C(9)	0.0251 (13)	0.4964 (6)	0.2934 (11)	0.048 (4)
N(10)	0.2075 (10)	0.4762 (4)	0.2409 (8)	0.043 (3)
C(11)	0.3546 (12)	0.4538 (5)	0.3110 (11)	0.039 (3)
C(12)	0.3851 (13)	0.3873 (5)	0.3490 (11)	0.042 (3)
C(13)	0.1201 (12)	0.3879 (5)	0.3156 (10)	0.036 (3)
C(14)	0.1192 (12)	0.4535 (5)	0.2828 (10)	0.039 (3)
C(15)	0.1683 (13)	0.5358 (5)	0.1602 (11)	0.052
C(16)	0.0135 (13)	0.5318 (5)	0.0396 (11)	0.050
Molecule B				
C(1)	0.7215 (16)	0.3200 (6)	-0.0038 (13)	0.067 (4)
C(2)	0.7925 (18)	0.2872 (8)	-0.0516 (19)	0.095
C(3)	0.7208 (18)	0.2705 (8)	-0.1782 (20)	0.095
C(4)	0.5747 (16)	0.2853 (6)	-0.2666 (14)	0.076 (5)
S(5)	0.3214 (4)	0.3491 (2)	-0.3322 (3)	0.066
C(6)	0.1030 (15)	0.3252 (6)	-0.2882 (13)	0.058 (4)
C(7)	0.0517 (17)	0.3217 (7)	-0.2087 (19)	0.081
C(8)	0.1431 (19)	0.3303 (7)	-0.0738 (19)	0.079
C(9)	0.2883 (16)	0.3467 (6)	-0.0235 (15)	0.073 (4)
N(10)	0.4930 (11)	0.3718 (4)	-0.0494 (10)	0.056 (3)
C(11)	0.5706 (13)	0.3380 (6)	-0.0916 (11)	0.051 (3)
C(12)	0.5020 (13)	0.3208 (6)	-0.2214 (2)	0.048 (3)
C(13)	0.2519 (12)	0.3423 (5)	-0.2315 (11)	0.045 (3)
C(14)	0.3456 (13)	0.3548 (5)	-0.0974 (11)	0.048 (3)
C(15)	0.5682 (15)	0.4124 (6)	0.0701 (12)	0.078
C(16)	0.5039 (15)	0.4800 (6)	0.0532 (10)	0.064

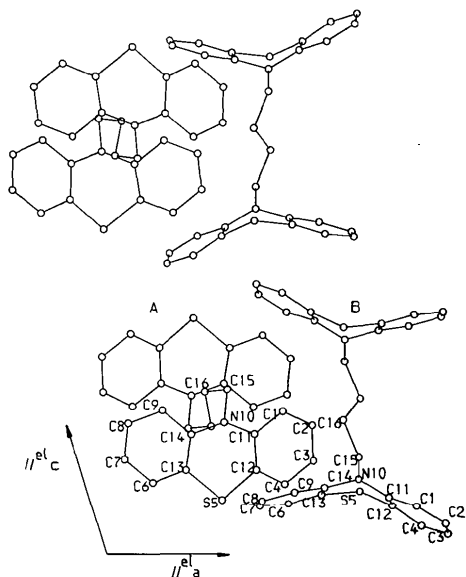


Fig. 1. Projection of the molecules on (010), showing the atom numbering.

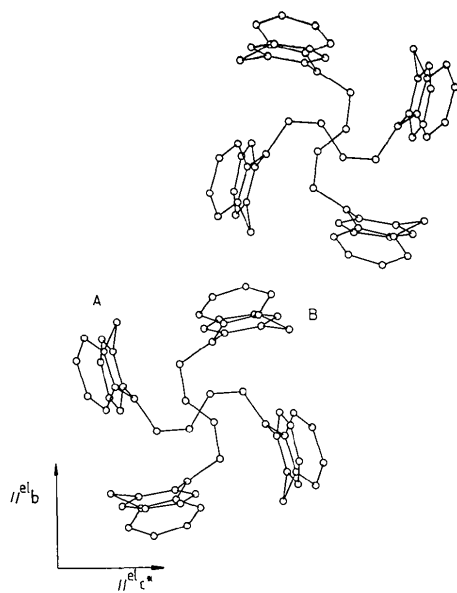


Fig. 2. Projection of the molecules on (100).

both molecules, which were refined anisotropically (see Fig. 1 for atom numbering). These atoms were expected to have the larger thermal vibrations. The final residual was 0.070 ($R_w = 0.052$, $w = 2.0392/\sigma^2$). Fluctuations on the final difference Fourier map did not exceed ± 0.3 e \AA^{-3} . Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and all computations were performed on the joint CDC 7600/ICL 1906A computer system of the University of

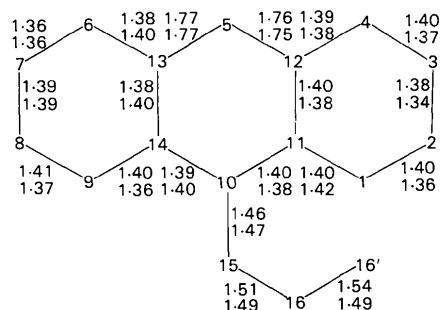


Fig. 3. Bond lengths (\AA) for molecules *A* (upper entries) and *B*. Average e.s.d. is 0.015 \AA .

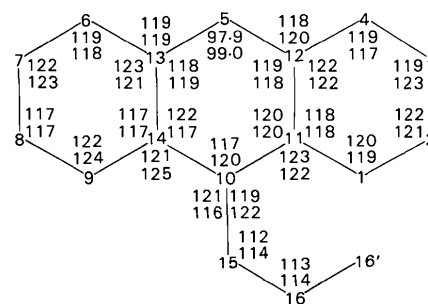


Fig. 4. Bond angles ($^\circ$) for molecules *A* (upper entries) and *B*. Average e.s.d. is 1 $^\circ$.

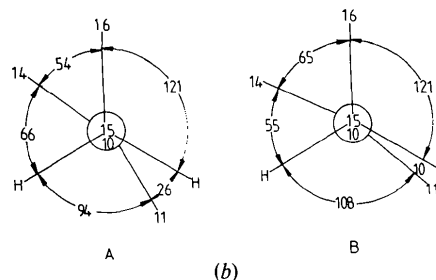
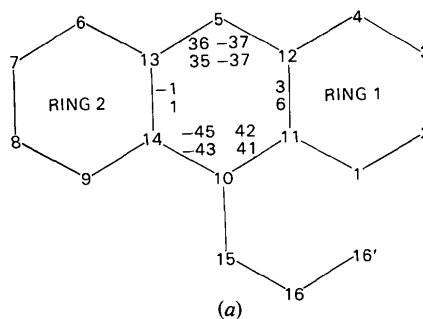


Fig. 5. (a) Torsion angles ($^\circ$). Average e.s.d. is 2 $^\circ$. (b) Dihedral angles ($^\circ$) associated with bonds C(15)-N(10). Average e.s.d. is 2 $^\circ$.

Manchester Regional Computer Centre. Table 1* lists the final atomic parameters. Figs. 1 and 2 are views indicating the columnar packing of the pairs of molecules (see below). Figs. 3 and 4 give bond lengths and angles. Fig. 5 gives torsion angles (Klyne & Prelog, 1960) and dihedral angles for views down the C(15)–N(10) bonds of molecules *A* and *B*.

Discussion. Molecule *A* is centred at Wyckoff position 2(*c*) ($00\frac{1}{2}, 0\frac{1}{2}, 0$) of space group $P2_1/c$. Molecule *B* is centred at 2(*d*) ($\frac{1}{2}, 0\frac{1}{2}, \frac{1}{2}, 0$). Molecules *A* and *B* are thus stacked alternately in columns parallel to **a**. Pairs of molecules are related by pseudo fourfold screw axes lying along the columns, so that viewed down **a** a pair of molecules takes the form of a cross (Fig. 2). The columns comprise an aliphatic core and an outer sheath of phenothiazine groups (Figs. 1 and 2), such that aliphatic chains of adjacent columns are isolated from each other by the intervening phenothiazine groups. It is not unusual for phenothiazine derivatives to crystallize with two phenothiazine units in the asymmetric unit (e.g. McDowell, 1975; Chu & van der Helm, 1976, 1977; Chu & Yang, 1977) but no other example appears to possess a packing arrangement isolating the aliphatic side chains.

The geometries of the two independent phenothiazine units are unexceptional compared with results for other N-substituted phenothiazines with the substituent extending on the convex side of the ring system (Chu & van der Helm, 1975). There are, however, slight differences between the two independent molecules *A* and *B*; e.g. the dihedral angles between the phenyl rings of the phenothiazine units are 139 (1) and 134 (1)° respectively. There is also a slight asymmetry in the CNC angles in molecule *B* (see Fig. 4). This asymmetry can be understood if one looks at the dihedral angles about the N–C bonds (Fig. 5).

* Lists of coordinates for the geometrically placed H atoms, anisotropic vibrational parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36954 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Molecule *A* is similar to *N*-ethylphenothiazine; however, in molecule *B*, C(15) is slightly further away from ring atom C(1), and a C(15)–H bond is more eclipsed with the N–C(11) bond. The increased interaction of this H atom with the ring atoms probably contributes to the decrease in the inter-ring dihedral angle of molecule *B* compared with *A*. None of these points is sufficiently unusual to explain the exceptional crystalline stability which must be due to the particular packing of the molecules.

There are no intermolecular contacts significantly below the sum of the van der Waals radii, although there are S...C(6) distances of about 3.4 Å between adjacent columns: both A[S(5)]...B[C(6)] and B[S(5)]...A[C(6)]. The distance A[C(16)]...B[C(8)] within the columns is also ~3.4 Å.

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References

- CHU, S. S. C. & VAN DER HELM, D. (1975). *Acta Cryst.* B31, 1179–1183.
 CHU, S. S. C. & VAN DER HELM, D. (1976). *Acta Cryst.* B32, 1012–1016.
 CHU, S. S. C. & VAN DER HELM, D. (1977). *Acta Cryst.* B33, 873–876.
 CHU, S. S. C. & YANG, H. T. (1977). *Acta Cryst.* B33, 1892–1896.
 FRYDRYCH, C. H. (1981). PhD thesis, Univ. of Manchester Institute of Science and Technology.
 HAMILTON, W. C. (1959). *Acta Cryst.* 12, 609–610.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 KLYNE, W. & PRELOG, V. (1960). *Experientia*, 16, 521–523.
 MCDOWELL, J. J. H. (1969). *Acta Cryst.* B25, 2175–2181.
 MCDOWELL, J. J. H. (1975). *Acta Cryst.* B31, 2256–2264.
 MCDOWELL, J. J. H. (1976). *Acta Cryst.* B32, 5–10.
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 SHELDRIK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.