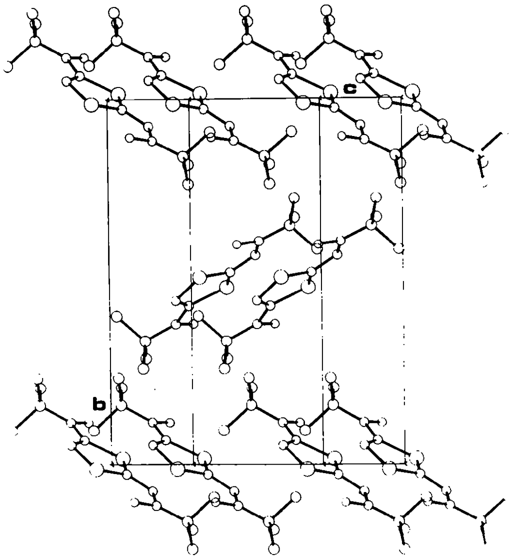

Fig. 5. Packing of the molecules in the unit cell.

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10-(1,3-Dimethyl-3-piperidylmethyl)phenothiazine Hydrochloride

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Abstract. $C_{20}H_{24}N_2S.HCl$, monoclinic, $P2_1/c$, $Z = 4$, $M_r = 360{\cdot}93$, $a = 13{\cdot}791\,(2)$, $b = 10{\cdot}900\,(2)$, $c = 13{\cdot}192\,(2)$ Å, $\beta = 104{\cdot}44\,(2)°$, $V = 1920{\cdot}40$ Å^3, $D_x = 1{\cdot}248$, $D_m = 1{\cdot}26$ g cm^{-3} (by flotation), λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 27·45 cm^{-1}, final residual R = 0·062. The folding angle of the phenothiazine ring is smaller than that in other *N*-derivatives of phenothiazine.

Introduction. Single crystals of the title compound were grown in the form of clear prisms from isopropyl alcohol solutions. The unit-cell parameters were obtained from the measurement of '+' and '−' 2θ values of 20 reflections, and the intensity data were collected on a Nonius CAD-4 automatic diffractometer. The space group, $P2_1/c$, was deduced from systematic absences ($h0l$ absent with l odd, $0k0$ absent with k odd). An $\omega/2\theta$ scanning mode with Ni-filtered Cu $K\alpha$ radiation was used to measure 3625 independent reflections with 2θ values below 140°, of which 3124 reflections were considered as observed by the criterion $I > 2{\cdot}0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors, and no absorption corrections were applied.

The structure was determined by the heavy-atom method. The refinement was carried out by the full-matrix least-squares method (Busing, Martin & Levy, 1962) with isotropic temperature factors and the block-diagonal least-squares method (Shiono, 1971) with anisotropic temperature factors. All the H atoms were located on difference Fourier syntheses. The isotropic temperature factors were used for H atoms in the final

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *for non-hydrogen atoms and fractional coordinates* ($\times 10^3$) *and thermal parameters for hydrogen atoms*

The estimated standard deviations are given in parentheses and refer to the last positions of respective values.

	x	*y*	*z*		*x*	*y*	*z*	*B* (Å^2)
Cl	−790 (0)	3180 (1)	477 (0)	H(1)	225 (2)	510 (2)	−83 (2)	5·0 (6)
S	4656 (0)	2087 (1)	763 (1)	H(2)	326 (2)	582 (2)	−195 (2)	5·0 (6)
N(10)	2698 (1)	3227 (2)	518 (1)	H(3)	465 (2)	488 (3)	−199 (2)	7·4 (8)
C(1)	2893 (2)	4716 (2)	−835 (2)	H(4)	531 (2)	315 (3)	−78 (2)	6·3 (8)
C(2)	3449 (2)	5138 (3)	−1508 (2)	H(6)	414 (2)	−42 (2)	67 (2)	5·2 (6)
C(3)	4359 (2)	4611 (3)	−1519 (2)	H(7)	254 (3)	−149 (3)	24 (3)	8·8 (11)
C(4)	4719 (2)	3676 (3)	−848 (2)	H(8)	109 (2)	−44 (3)	17 (2)	8·2 (9)
C(6)	3501 (3)	−19 (3)	521 (2)	H(9)	118 (2)	165 (3)	39 (2)	6·6 (8)
C(7)	2606 (3)	−638 (2)	412 (2)	H(15)1	185 (2)	464 (2)	42 (2)	3·9 (5)
C(8)	1750 (3)	3 (3)	361 (2)	H(15)2	128 (2)	355 (2)	61 (2)	4·6 (6)
C(9)	1752 (2)	1282 (2)	413 (2)	H′(1)	96 (2)	615 (3)	100 (3)	6·2 (8)
C(11)	3249 (2)	3758 (2)	−151 (2)	H′(2)1	127 (2)	485 (2)	300 (2)	4·4 (5)
C(12)	4182 (2)	3262 (2)	−147 (2)	H′(2)2	59 (2)	441 (2)	190 (2)	4·9 (6)
C(13)	3521 (2)	1267 (2)	591 (2)	H′(4)1	327 (2)	501 (3)	320 (2)	7·5 (8)
C(14)	2646 (2)	1923 (2)	515 (2)	H′(4)2	365 (2)	467 (3)	218 (3)	7·4 (8)
C(15)	1917 (2)	3942 (2)	814 (2)	H′(5)1	277 (2)	633 (3)	116 (2)	6·3 (8)
N′(1)	1082 (2)	6103 (2)	1811 (1)	H′(5)2	354 (3)	681 (3)	230 (3)	7·4 (9)
C′(2)	1221 (2)	4830 (2)	2228 (2)	H′(6)1	205 (2)	691 (3)	300 (2)	6·9 (8)
C′(3)	2141 (2)	4195 (2)	2006 (2)	H′(6)2	172 (3)	778 (4)	184 (3)	11·1 (11)
C′(4)	3062 (2)	5014 (3)	2382 (2)	H′(7)1	30 (3)	666 (3)	265 (3)	8·0 (10)
C′(5)	2893 (2)	6324 (3)	1996 (2)	H′(7)2	-39 (3)	620 (3)	166 (3)	7·4 (9)
C′(6)	1975 (2)	6881 (2)	2255 (2)	H′(7)3	3 (2)	743 (3)	159 (2)	8·0 (8)
C′(7)	140 (2)	6641 (3)	1995 (2)	H′(8)1	163 (3)	255 (4)	239 (3)	10·5 (10)
C′(8)	2275 (3)	2994 (3)	2628 (2)	H′(8)2	236 (3)	324 (3)	335 (3)	6·5 (8)
				H′(8)3	296 (3)	263 (4)	265 (3)	12·1 (11)

refinements. The weight of the reflection was assigned as $1/[\sigma(F)]^2$, where $\sigma(F)$ was calculated from counting statistics. The quantity $\Sigma w(||F_o| - |F_c||)^2$ was minimized. The final R index $(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0·062. The magnitude of $[\Sigma w(F_o - F_c)^2/(m - n)]^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 0·99. The atomic scattering factors used for the Cl^- ion, and S, N and C atoms were those from *International Tables for X-ray Crystallography* (1962), and for H the values of Stewart, Davidson & Simpson (1965) were used. The final positional and thermal parameters are given in Table 1.*

Discussion. 10-(1,3-Dimethyl-3-piperidylmethyl)phenothiazine (I) is a 3-methyl (on piperidyl ring) derivative of meprazine (trade name Pacatal) which possesses tranquilizing activity. Due to the difficulties associated with the growth of single crystals of meprazine, the methyl derivative of meprazine has been studied in this work. The determination of the crystal structure of (I) will contribute to the understanding of the effect of different substituents on the conformation and configuration of the phenothiazine ring system and to the understanding of the structure requirements for the different pharmacological activities of the phenothiazine derivatives.

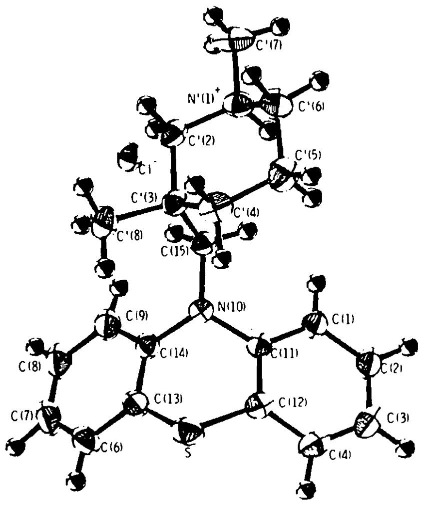

Fig. 1. *ORTEP* drawing of one molecule of 10-(1,3-dimethyl-3-piperidylmethyl)phenothiazine hydrochloride.

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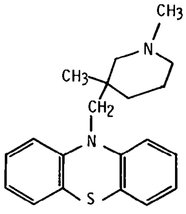
* Lists of structure factors and anisotropic temperature factors for the non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33131 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.



(I)

An *ORTEP* drawing (Johnson, 1965) of the configuration of (I) is shown in Fig. 1. The identification of the atoms and the bond lengths and bond angles (of non-hydrogen atoms) are shown in Fig. 2. The mean value of the two C—S bond lengths is 1·767 (3) Å, and the C—S—C bond angle is 96·5 (1)°. The mean value of the two C—N bond lengths within the central ring is 1·424 (3) Å, and the C—N—C bond angle within the central ring is 116·0 (2)°. The folding angle between the least-squares planes of the two benzene rings is 128·6°. Both the C—S and C—N bond lengths are in good agreement with those in other phenothiazine derivatives (Chu & van der Helm, 1975, 1976, 1977). However, the folding angle is smaller than that in other *N*-derivatives of phenothiazine since the C—S—C and C—N—C bond angles within the central ring are also smaller in (I). This result further demonstrates that the folding angle of the phenothiazine ring is correlated to the magnitude of C—S—C and C—N—C bond angles.

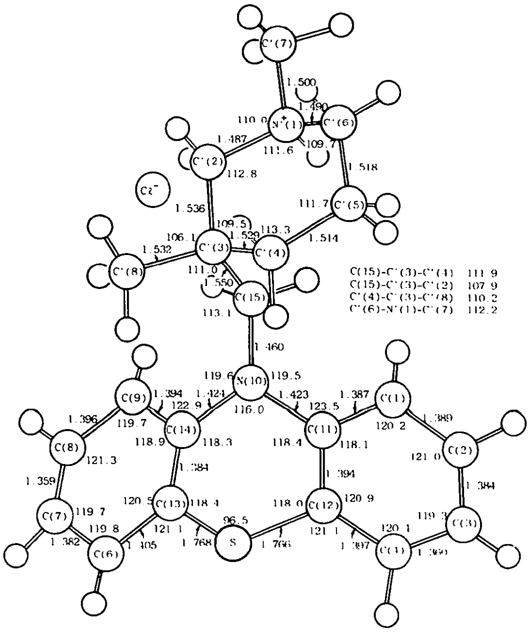


Fig. 2. Bond lengths (Å) and bond angles (°) of 10-(1,3-dimethyl-3-piperidylmethyl)phenothiazine hydrochloride. The r.m.s. standard deviation of the bond lengths is 0·005 Å and that of the bond angles is 0·2°.

Table 2. *Torsion angles* (°)

The angle is positive if measured clockwise.

Piperidyl ring	
C'(6)—N'(1)—C'(2)—C'(3)	−58·2
N'(1)—C'(2)—C'(3)—C'(4)	52·2
C'(2)—C'(3)—C'(4)—C'(5)	−49·8
C'(3)—C'(4)—C'(5)—C'(6)	53·2
C'(4)—C'(5)—C'(6)—N'(1)	−56·2
C'(5)—C'(6)—N'(1)—C'(2)	58·9
Methylene link	
C(11)—N(10)—C(15)—C'(3)	−116·7
C(14)—N(10)—C(15)—C'(3)	88·8
N(10)—C(15)—C'(3)—C'(2)	−174·1
N(10)—C(15)—C'(3)—C'(4)	65·3
N(10)—C(15)—C'(3)—C'(8)	−58·2
Central phenothiazine ring	
C(14)—N(10)—C(11)—C(12)	−45·97
N(10)—C(11)—C(12)—S	−4·84
C(11)—C(12)—S—C(13)	42·74
C(12)—S—C(13)—C(14)	−42·30
S—C(13)—C(14)—N(10)	3·61
C(13)—C(14)—N(10)—C(11)	46·68

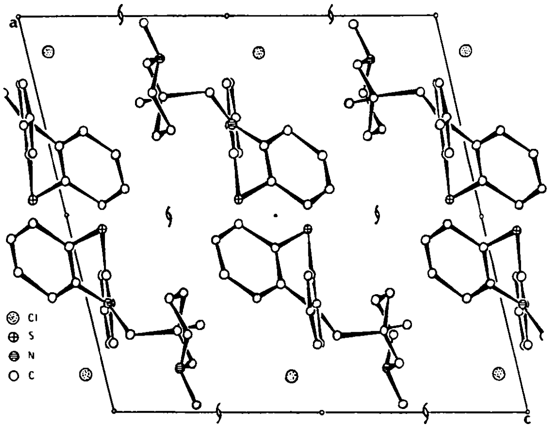


Fig. 3. The molecular packing of 10-(1,3-dimethyl-3-piperidylmethyl)phenothiazine hydrochloride, excluding hydrogen atoms, in the unit cell projected down the *b* axis.

The piperidyl ring is in a chair conformation; both the *N*-methyl and 3-methyl groups are in equatorial conformations. The methylene link to the phenothiazine ring is in an axial conformation with respect to the piperidyl ring. This is in contrast to the structure of methixene (Chu, 1972) in which the methylene link to the thioxanthene ring is in an equatorial conformation with respect to the piperidyl ring. The difference can be attributed to the different conformation of the piperidyl methyl group with respect to the tricyclic ring system.

In phenothiazine, the three bonds around the N atom are approximately planar in configuration. However, the piperidylmethyl group is in a 'boat-axial' conformation with respect to the thioxanthene ring. The torsion angles of the piperidyl ring and the methylene link between the two ring systems are given in Table 2.

The C—H bond lengths range from 0·84 to 1·14 Å with a mean value of 0·98 Å and a r.m.s. standard deviation of 0·03 Å. The C—C—H bond angles involving benzene rings range from 108 to 131° with a mean value of 120°, and the C—C—H and H—C—H bond angles involving tetrahedral C atoms range from 100 to 125° with a mean value of 109°. The r.m.s. standard deviation of these bond angles is 2°.

The packing of the molecules in the crystal is illustrated in Fig. 3. There are no intermolecular contacts less than van der Waals distances. The closest intermolecular distances are 3·56 and 3·47 Å between C(1) and C′(8) and between C(11) and C′(8) respectively. There is no close contact between the Cl^- and the rest of the molecule. The closest contacts are 3·62 and 3·74 Å between Cl^- and C′(2) and between Cl^- and C(15) respectively.

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4,4′-Dichlorobiphenyl: Crystal Packing in *para*-Substituted Biphenyls

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Abstract. $C_{12}H_8Cl_2$, monoclinic, $P2_1/n$, $a = 15{\cdot}780$ (4), $b = 13{\cdot}740$ (4), $c = 9{\cdot}682$ (3) Å, $\beta = 96{\cdot}23$ (3)°, $Z = 8$, $M_r = 233{\cdot}10$, $D_c = 1{\cdot}420$, $D_m = 1{\cdot}39$ (1) g cm^{-3}. The molecules are arranged in the unit cell with their long directions approximately parallel to **b**; in projection on the *ac* plane these axes form a pseudo-hexagonal array. This crystal is isostructural with several other biphenyl derivatives, and like them has a twist angle between the phenyl rings close to the expected mean gas-phase value of 42°.

Introduction. Biphenyl, $C_{12}H_{10}$, has long intrigued chemists since X-ray data suggest that an important conformational change, a decrease in the inter-ring twist angle from 42 to 0°, occurs upon crystallization (Hargreaves & Rizvi, 1962). More recently, a disordered model has been put forth to explain the apparent molecular planarity (Charbonneau & Delugeard, 1977). We decided to study the 4,4′-dihalobiphenyls with the aim of investigating the effect of the size of the *para* substituent on the crystal packing, and consequently on the molecular geometry. Being located on the periphery of the molecule, the halogen atoms should perturb only intermolecular contacts and should have little direct influence on the conformational preference of these biphenyl species.

Preliminary photographs of colorless $C_{12}H_8Cl_2$ crystals grown from benzene showed absences corre-