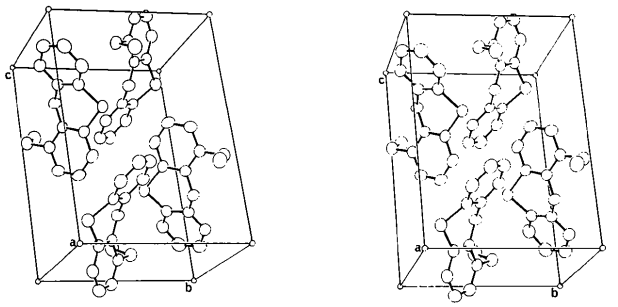

Fig. 3. *ORTEP* stereo drawing of the molecular packing of the title compound in a unit cell.

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, $P2_1/c$, $Z=4$, $M_r=213{\cdot}30$, $a=9{\cdot}063$ (1), $b=8{\cdot}968$ (2), $c=13{\cdot}503$ (1) Å, $\beta=102{\cdot}29$ (1)°, $V=1072{\cdot}4$ (3) Å^3, $D_x=1{\cdot}321$ Mg m^{-3}, μ(Cu $K\alpha$) = 2·28 mm^{-1}. Final $R=0{\cdot}053$ for 1658 observed reflections. 1-Ethylphenothiazine, $C_{14}H_{13}NS$, monoclinic, $P2_1/c$, $Z=4$, $M_r=227{\cdot}33$, $a=9{\cdot}509$ (1), $b=8{\cdot}962$ (1), $c=14{\cdot}036$ (2) Å, $\beta=105{\cdot}34$ (1)°, $V=1153{\cdot}6$ (3) Å^3, $D_x=1{\cdot}309$ Mg m^{-3}, μ(Cu $K\alpha$) = 2·15 mm^{-1}. Final $R=0{\cdot}035$ 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

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Table 1. *Experimental data*

	1-Methylphenothiazine	1-Ethylphenothiazine
X-radiation used for data collection	λ(Cu $K\alpha$) = 1·5418 Å	λ(Cu $K\alpha$) = 1·5418 Å
Total number of reflections $2\theta_{max} = 130°$	1778	1936
Number of observed reflections $I > 3\sigma(I)$	1665	1737
Number of reflections affected by extinction and omitted from the refinement	7	6
2θ values used for the determination of unit-cell parameters	21–70°	64–86°
Crystal size	0·30 × 0·58 × 0·24 mm	0·21 × 0·45 × 0·15 mm
Orientation of crystal along φ axis of diffractometer	*b* axis	*b* axis
Disagreement index, R	0·053	0·035
Weighted disagreement index R_w	0·059	0·036

diffractometer. The experimental data are given in Table 1. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors; no absorption corrections were applied.

The determination and refinement of the structures were carried out in the same way as those described in the preceding paper. The final R index ($\sum||F_o| - |F_c||/\sum|F_o|$) was 0·053, and the weighted disagreement index, R_w, was 0·059 for 1-methylphenothiazine. The R and R_w for 1-ethylphenothiazine are 0·035 and 0·036 respectively. The final atomic parameters are given in Table 2.*

Discussion. The identification of the atoms and the configuration of the molecules are shown in Fig. 1(*a*) and (*b*) for 1-methyl- and 1-ethylphenothiazines respectively. The two structures are nearly isomorphous as indicated by the unit-cell and atomic parameters. The molecules are folded with the central ring in a boat conformation. The torsion angles and the Cremer & Pople (1975) puckering parameters are shown in Table 3. The folding angles between the least-squares planes of the two benzo rings are 154·8 and 147·4° for 1-methyl- and 1-ethylphenothiazines respectively. The folding angle is 146·1° for 1-isopropylphenothiazine as shown in the preceding paper. Similarly to 10-alkylphenothiazines (Chu & van der Helm, 1975), the magnitude of the folding angle decreases with the increasing size of the alkyl substituent.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36852 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates* (× 10^4, × 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: $B_{eq} = \frac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}/B(Å^2)
1-Methylphenothiazine				
S(5)	6911 (1)	1769 (1)	1342 (1)	4·59 (3)
N(10)	5041 (2)	4177 (3)	2027 (2)	3·93 (9)
C(1)	3119 (3)	4224 (3)	466 (2)	3·93 (11)
C(2)	2590 (3)	3680 (3)	−508 (2)	4·43 (12)
C(3)	3395 (3)	2629 (3)	−932 (2)	4·80 (13)
C(4)	4764 (3)	2119 (3)	−378 (2)	4·45 (13)
C(6)	9120 (3)	3300 (3)	2646 (2)	4·53 (12)
C(7)	9652 (3)	4337 (3)	3394 (2)	5·05 (14)
C(8)	8654 (3)	5334 (3)	3673 (2)	4·81 (13)
C(9)	7133 (3)	5301 (3)	3207 (2)	4·24 (12)
C(11)	4493 (3)	3698 (3)	1028 (2)	3·44 (10)
C(12)	5288 (3)	2624 (3)	608 (2)	3·72 (11)
C(13)	7594 (3)	3225 (3)	2199 (2)	3·72 (11)
C(14)	6588 (3)	4240 (3)	2469 (2)	3·47 (10)
C(15)	2215 (3)	5374 (4)	904 (2)	5·34 (15)
H(N)	452 (3)	497 (4)	230 (2)	6·9 (8)
H(2)	158 (3)	401 (3)	−90 (2)	5·4 (7)
H(3)	306 (3)	222 (4)	−170 (2)	7·5 (9)
H(4)	539 (3)	144 (3)	−66 (2)	4·9 (7)
H(6)	980 (3)	247 (4)	244 (2)	6·3 (7)
H(7)	1083 (3)	441 (3)	379 (2)	5·8 (7)
H(8)	898 (3)	611 (4)	428 (2)	7·4 (9)
H(9)	642 (3)	594 (3)	339 (2)	4·2 (6)
H(15)1	286 (4)	629 (4)	124 (3)	9·1 (10)
H(15)2	125 (4)	565 (4)	38 (3)	8·6 (10)
H(15)3	186 (3)	494 (4)	155 (2)	6·7 (8)
1-Ethylphenothiazine (S-atom coordinates × 10^5)				
S(5)	69090 (5)	15598 (5)	14670 (4)	4·40 (1)
N(10)	5131 (1)	3974 (2)	2029 (1)	3·82 (6)
C(1)	3390 (2)	4179 (2)	401 (1)	3·67 (7)
C(2)	2951 (2)	3695 (2)	−574 (1)	4·38 (8)
C(3)	3732 (2)	2634 (2)	−933 (1)	4·78 (9)
C(4)	4966 (2)	2029 (2)	−322 (1)	4·49 (8)
C(6)	9078 (2)	3157 (2)	2733 (1)	4·64 (9)
C(7)	9593 (2)	4221 (2)	3448 (2)	5·35 (10)
C(8)	8627 (2)	5214 (2)	3693 (1)	5·14 (9)
C(9)	7159 (2)	5157 (2)	3214 (1)	4·42 (8)
C(11)	4639 (2)	3555 (2)	1027 (1)	3·37 (6)
C(12)	5411 (2)	2464 (2)	663 (1)	3·63 (7)
C(13)	7597 (2)	3053 (2)	2281 (1)	3·77 (7)
C(14)	6618 (2)	4070 (2)	2501 (1)	3·55 (7)
C(15)	2464 (2)	5307 (2)	759 (1)	4·30 (8)
C(16)	1375 (2)	4537 (2)	1225 (2)	5·39 (10)
H(N)	460 (2)	467 (2)	220 (1)	4·7 (4)
H(2)	208 (2)	418 (2)	−100 (1)	4·3 (4)
H(3)	348 (2)	236 (2)	−165 (1)	6·5 (5)
H(4)	558 (2)	129 (2)	−55 (1)	5·2 (4)
H(6)	979 (2)	243 (2)	258 (1)	5·2 (4)
H(7)	1062 (2)	427 (2)	383 (1)	7·1 (6)
H(8)	897 (2)	601 (2)	424 (1)	6·8 (5)
H(9)	647 (2)	587 (2)	335 (1)	5·4 (5)
H(15)1	183 (2)	600 (2)	16 (1)	5·0 (4)
H(15)2	311 (2)	600 (2)	125 (1)	4·9 (4)
H(16)1	67 (2)	380 (2)	70 (1)	7·4 (6)
H(16)2	190 (2)	384 (2)	183 (1)	7·4 (6)
H(16)3	71 (2)	533 (3)	140 (2)	8·4 (6)

The C(15) of the methyl substituent in 1-methylphenothiazine is essentially coplanar with the benzo ring and the deviation of C(15) from the least-squares plane of the benzo ring is 0·008 Å. However, the deviation of C(15) from the least-squares

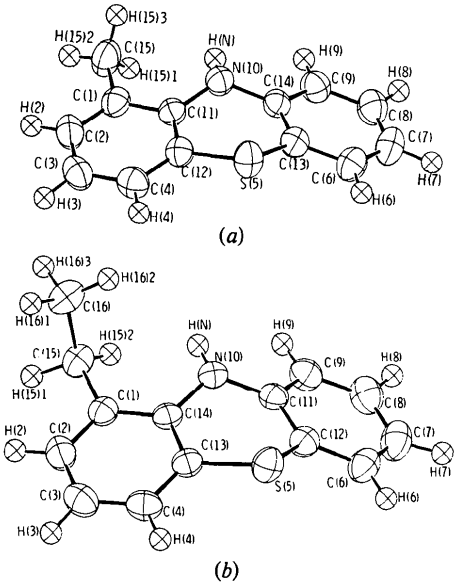

Fig. 1. *ORTEP* drawings (Johnson, 1965) of one molecule of (*a*) 1-methylphenothiazine and (*b*) 1-ethylphenothiazine.

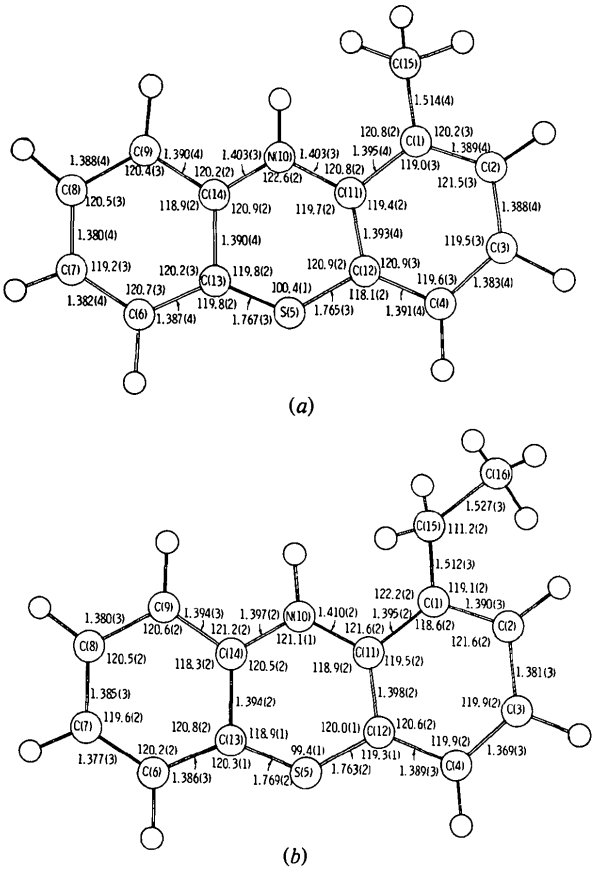

Fig. 2. Bond lengths (Å) and bond angles (°) of (*a*) 1-methylphenothiazine and (*b*) 1-ethylphenothiazine. The e.s.d.'s are in parentheses.

Table 3. *Conformation of the central ring*

Cremer & Pople (1975) puckering parameters

	Ideal boat	1-Methylphenothiazine	1-Ethylphenothiazine
q_2	$Q \sin\theta$	0·450 Å	0·523 Å
q_3	$Q \cos\theta$	0·069	0·078
Q		0·455	0·529
φ	0 or 180°	179·9°	181·1°
θ	90 or 270°	81·3	81·5

Torsion angles

	1-Methylphenothiazine	1-Ethylphenothiazine
S(5)–C(13)–C(14)–N(10)	−3·6 (4)°	−4·8 (2)°
C(13)–C(14)–N(10)–C(11)	−32·2 (4)	−36·8 (2)
C(14)–N(10)–C(11)–C(12)	31·8 (4)	37·3 (2)
N(10)–C(11)–C(12)–S(5)	4·1 (4)	3·6 (2)
C(11)–C(12)–S(5)–C(13)	−30·1 (3)	−34·1 (2)
C(12)–S(5)–C(13)–C(14)	29·6 (2)	34·6 (2)

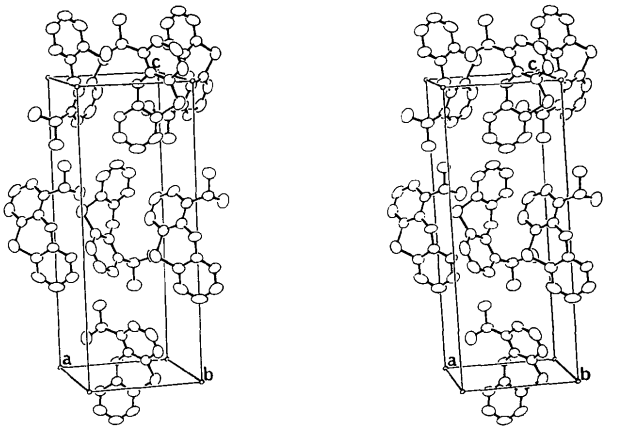

Fig. 3. *ORTEP* stereodrawing of the molecular packing of 1-ethylphenothiazine in a unit cell.

plane of the benzo ring is 0·048 Å in 1-ethylphenothiazine, and is 0·098 Å in 1-isopropylphenothiazine (Chu *et al.*, 1982). The non-planarity of the alkyl substituent is due to the non-bonded interaction when the size of the alkyl substituent increases. The conformation of the ethyl substituent in 1-ethylphenothiazine is similar to that of the C(15)–C(16) bond in 1-isopropylphenothiazine. The torsion angles of C(2)–C(1)–C(15)–C(16) are 93·1 (2) (it is −93·0° for the mirror-related molecule since 1-ethylphenothiazine belongs to a centrosymmetric space group) and −94·2 (5)° in 1-ethylphenothiazine and 1-isopropylphenothiazine respectively.

The bond lengths and bond angles with their standard deviations for 1-methyl- and 1-ethylphenothiazines are shown in Fig. 2(*a*) and (*b*) respectively. The C–S and C–N bond lengths within the central ring are in good agreement with those observed in other phenothiazines (Chu & van der Helm, 1975, 1976). The size of the C–S–C and C–N–C bond angles within the central ring varies with

the size of the 1-alkyl substituents and is correlated with the size of the folding angle as in other phenothiazines. All the C–H bond lengths and C–C–H and H–C–H bond angles are within reasonable ranges of magnitudes. The packing of 1-ethylphenothiazine in the crystal is shown in Fig. 3. There are no intermolecular contacts less than van der Waals distances.

This research was supported by grants (N-495 and Y-484) from the Robert A. Welch Foundation, Houston, Texas. The authors wish to thank Dr R. Shiono of the University of Pittsburgh for making the *ORTEP* plots.

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Methyl 4,6-Bis(*O*-*p*-chlorobenzoyl)-2,3-dideoxy-3-*C*-(methoxycarbonylmethyl)-α-D-*ribo*-hexopyranoside

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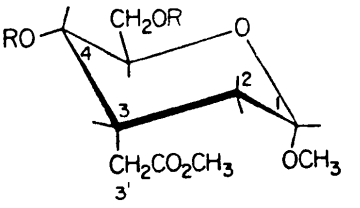
Abstract. Crystals of the title compound, $C_{24}H_{24}Cl_2O_8$, $M_r = 511{\cdot}35$, are monoclinic, $P2_1$, $a = 5{\cdot}752$ (3), $b = 15{\cdot}436$ (3), $c = 13{\cdot}698$ (3) Å, $\beta = 93{\cdot}74$ (3)°, $D_m = 1{\cdot}43$, $D_x = 1{\cdot}40$ Mg m^{-3}, $Z = 2$. The structure was determined from Cu $K\alpha$ diffractometer data (with great difficulty), and refined to $R = 0{\cdot}042$ for 898 reflexions. The six-membered pyranose ring is in the chair conformation, with the bulkier 4,6-*p*-chlorobenzoyl substituents equatorial, and the 1-OMe and 3-CH_2CO_2Me groups axial. Bond lengths and angles and intermolecular distances are normal. The extremities of the *p*-chlorobenzoyl groups exhibit large thermal librations [r.m.s. displacement as large as 0·56 (1) Å for one Cl].

Introduction. The title compound [(1), R = ClC_6H_4CO–] is a branched-chain sugar which was of interest because of possible antibiotic properties, and an X-ray crystal analysis was undertaken to verify structural assignments based on NMR data (Rosenthal & Catsoulacos, 1968). The X-ray study was begun in 1967 (by DLH shortly after arrival in Vancouver from Antarctica, after a journey by Land Rover through South America).



The unit-cell dimensions were obtained by least-squares refinement based on 2θ values for 30 reflexions, and intensities were measured on a Datex automated GE XRD-6 diffractometer with nickel-filtered Cu $K\alpha$ radiation and a θ–2θ scan technique. The scan speed was 1° min^{-1}, with 40 s background measurements before and after the scan. The intensities exhibited a rapid decrease with increasing θ, so that the data set was rather limited. Of 1028 reflexions in the range $0 < \theta \leq 45°$, 898 had $I/\sigma(I) > 2{\cdot}0$, where $\sigma(I) = S + B + (0{\cdot}02S)^2$, S = scan and B = normalized background count. Crystal dimensions were 0·25 × 0·05 × 0·04 mm, and no absorption corrections were considered necessary ($\mu = 28$ cm^{-1}).

Early attempts to determine the structure involved Patterson methods and efforts to pack the *p*-chloro-

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