Discussion. Final atomic parameters are in Table 1,* ring torsion angles in Table 2, and interatomic distances and angles in Table 3.

Both isomers contain 14-membered rings (Fig. 2). The *cis* isomer exhibits equal amounts of 3344 {for C(6), C(7)} and 3434 {for C(6′), C(7′)} conformations;† the conformation of the *trans* isomer is 3335. The bends occur at different atoms in the two isomers: at C(3), C(7) {or C(6′)}, C(10), and C(13) in the *cis* isomer, but at C(3), C(6), C(9), and C(12) in the *trans* isomer. The observed torsion angles (Table 2) are closely similar to those predicted for the three lowest-energy conformations of a 14-membered ring (Dale, 1973). The conformations are probably partly controlled by the tendency of the bulky 3-bromoacetoxy and 13-methyl substituents to occupy less-sterically-hindered equatorial sites. In the *cis* isomer this results in the C=O(2) and C=O(4) bonds being approximately parallel, while the configurational difference at C(13) in the *trans* isomer causes a conformational change which results in C=O(2) and C=O(4) being approximately antiparallel.

Bond lengths and angles (Table 3) are generally within normal ranges. The slight (though not statistically significant) elongations of the C—C bonds involving C(6) and C(7) in the *cis* isomer probably result from errors due to the disorder, as do the apparently anomalous angles in this region. The short value observed for the length of the C=O(4) bond in the *trans* compound is probably affected by error due to disorder or to large thermal libration.

We thank Dr L. S. Weiler and J. Ounsworth for crystals and helpful discussion, the Natural Sciences and Engineering Research Council of Canada for financial support, and the University of British Columbia Computing Centre for assistance.

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[*] Anisotropic thermal parameters, H parameters, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42134 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[†] The nomenclature is that of Dale (1973), the numbers indicating the numbers of bonds in the straight-chain portions of the rings.

References

Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180–182.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Dale, J. (1973). *Acta Chem. Scand.* **27**, 1115–1129.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Motherwell, W. D. S. (1978). *PLUTO*78. Program for plotting molecular and crystal structures. Cambridge Data Centre, Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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Structure of 10-Methylphenothiazine 5-Oxide, $C_{13}H_{11}NOS$

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Abstract. $M_r = 229{\cdot}30$, monoclinic, $P2_1/n$, $a = 11{\cdot}289\,(2)$, $b = 10{\cdot}831\,(3)$, $c = 8{\cdot}818\,(2)$ Å, $\beta = 91{\cdot}80\,(2)^\circ$, $V = 1077{\cdot}7\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}413$, $D_m = 1{\cdot}42$ g cm^{-3} (by flotation), $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 2{\cdot}27$ cm^{-1}, $F(000) = 480$, $T = 294$ K, final $R = 0{\cdot}044$ for 1980 observed reflections. The 10-methyl group is in a 'boat-equatorial' and the sulfinyl oxygen is in a 'boat-axial' conformation with respect to the central ring of the phenothiazine ring system. The folding angle between the least-squares planes of the two benzo rings is 151·2 (8)°.

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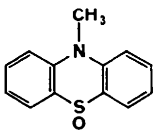
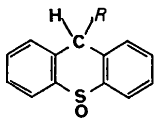
Introduction. This paper reports the determination of the crystal structure of 10-methylphenothiazine 5-oxide (I) and is a continuation of the studies of a series of phenothiazine derivatives. The 10-alkylphenothiazine 5-oxide could exist in two conformations; the 5-oxide group is either in a 'boat-equatorial' or in a 'boat-axial' conformation (Fig. 1). It has been shown that in phenothiazine 5-oxide, the sulfinyl oxygen prefers the 'boat-axial' conformation (Ternay & Chu, 1984). However, in 9-alkylthioxanthene 10-oxide, (II), the 10-oxide group prefers the 'boat-equatorial' conformation and the sulfinyl oxygen governs the stereochemistry of these compounds when the size of the 9-substituent is small (Jackobs & Sundaralingam, 1969; Ternay, Chasar & Sax, 1967). Further, when the size of the 9-substituent is larger than an ethyl group, the 9-alkyl group prefers the 'boat-axial' conformation and the 9-alkyl group governs the stereochemistry of these compounds (Chu, 1975). The purpose of the present study is to determine the conformation of 10-methylphenothiazine 5-oxide and the effect of the 10-methyl and 5-oxide substituents on the configuration and conformation of the phenothiazine ring system.

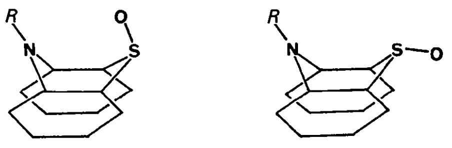


(I)



(II)

Experimental. Compound (I) prepared by oxidizing 10-methylphenothiazine with sodium nitrite in methylene chloride–acetic acid solution, white transparent crystals in the form of flat needles obtained by recrystallization from a solution of 15% CH_2Cl_2–85% absolute ethanol, unit-cell parameters by least-squares analysis of 15 reflections with 2θ values ranging from 17·4 to 29·2° measured on the diffractometer, $P2_1/n$ deduced from systematic absences ($h0l$ absent with $h+l$ odd, $0k0$ absent with k odd), Syntex $P2_1$ automatic diffractometer, crystal 0·61 × 0·58 × 0·15 mm, $\theta/2\theta$ scanning mode, graphite-monochromated Mo $K\alpha$ radiation, 2875 total measured reflections with $2\theta < 55°$ including standard reflections, internal agreement: 0·017, 2493 independent reflections, hkl: $h\,\pm 14$, $k\,0\rightarrow 14$, $l\,0\rightarrow 11$, 1981 observed, $I > 3\sigma(I)$; Lorentz-polarization corrections, no absorption or extinction corrections; direct methods, *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refinement by full-matrix least squares using *SHELX*76 (Sheldrick, 1976) with observed reflections, anisotropic, hydrogen positions located in difference Fourier syntheses, isotropic temperature factors for hydrogen atoms, $w = 1/[\sigma(F) + 0{\cdot}0045F^2]^2$ in final stage of refinement, $\sigma(F)$ from counting statistics, $[\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$ minimized, strongest reflection (310) omitted in refinement due to measurement error ($F_o = 169$, $F_c = 120$), $(\Delta/\sigma)_{\max} = 0{\cdot}34$, $R = 0{\cdot}044$, $wR = 0{\cdot}051$ for 1980 observed reflections, maximum height in final difference Fourier synthesis 0·040 e Å^{-3}, atomic scattering factors for sulfur, oxygen, nitrogen, carbon, and hydrogen and dispersion correction for sulfur from *International Tables for X-ray Crystallography* (1974).



'boat-axial' 'boat-equatorial'

Fig. 1. The conformation of sulfinyl oxygen in 10-alkylphenothiazine 5-oxide.

Discussion. The final parameters are given in Table 1.* The identification of the atoms and the configuration of the molecule are shown in the *ORTEP* (Johnson, 1965) drawing in Fig. 2. The phenothiazine ring system is folded with the central ring in a boat conformation as shown by the torsion angles around the central ring in Fig. 2. The Cremer & Pople (1975) puckering parameters of the central ring are $q_2 = 0{\cdot}455$, $q_3 = 0{\cdot}125$ Å, $Q = 0{\cdot}472$ Å, $\varphi_2 = 357{\cdot}6°$, and $\theta = 105{\cdot}3°$. For ideal boat conformation, these values are $q_2 = Q$, $q_3 = 0$ Å, $\varphi_2 = 360°$, and $\theta = 90°$. The 10-methyl substituent is in an equatorial conformation which was also observed in 10-methylphenothiazine (Chu & van der Helm, 1974). Furthermore, as has been observed in phenothiazine 5-oxide (Ternay & Chu, 1984), the sulfinyl oxygen in the title compound is also in a 'boat-axial' conformation. The benzo rings are planar and the equations of the least-squares planes are $9{\cdot}225\,(6)x - 5{\cdot}380\,(9)y - 2{\cdot}803\,(8)z = 0{\cdot}59\,(1)$ and $10{\cdot}952\,(3)x - 2{\cdot}42\,(1)y + 0{\cdot}563\,(9)z = 3{\cdot}959\,(4)$ (where x, y, z are in fractional coordinates) for rings A and B respectively. The deviations of the atoms from the planes range from 0·002 (3) to 0·017 (3) Å. The folding angle between the least-squares planes of the two benzo rings is 151·2 (8)° as compared to that of 143·7° in 10-methylphenothiazine (Chu & van der Helm, 1974) and 162·9° in phenothiazine 5-oxide (Ternay & Chu, 1984). Since the folding angle in phenothiazine (Bell, Blount, Briscoe & Freeman, 1968) is 153·3°, it is apparent that the folding angle of the phenothiazine ring is smaller in the 10-methyl substituted systems.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42148 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bond lengths and bond angles, with their standard deviations, are shown in Fig. 3. The bond lengths and bond angles of the title compound (I) are in good agreement with those of other phenothiazines (Chu & van der Helm, 1974, 1975, 1976). The mean C—S bond length of 1·759 (2) Å is in the same range as observed in other phenothiazines; however, the C—S—C bond angle of 96·0 (1)° in (I) is smaller than the range of 97·3–99·0° found in other phenothiazines. Furthermore, the C—S—C bond angle in phenothiazine 5-oxide (Ternay & Chu, 1984) is 98·6 (3)°. These facts demonstrate that the bonding characteristic of sulfur in phenothiazines does not depend primarily on the coordination number of sulfur but depends to a large extent on the folding angles of the phenothiazine ring systems. This is contrary to that observed in thioxanthene sulfides and sulfoxides. The mean values of C—S bond lengths and C—S—C bond angles are 1·766 (1) Å and 100·37 (4)°, respectively, in thioxanthene sulfides when the coordination number of sulfur is two, and those values are 1·781 (1) Å and 96·58 (7)°, respectively, in thioxanthene sulfoxides when the coordination number of sulfur is three (Chu, 1975).

The packing of the molecules in the unit cell is shown in the stereoscopic drawing in Fig. 4. There are no intermolecular contacts less than van der Waals distances.

Table 1. *Fractional atomic coordinates* ($\times 10^4$, $\times 10^5$ *for sulfur*) *for non-hydrogen and* ($\times 10^3$) *for hydrogen atoms with 'equivalent' isotropic thermal parameters for non-hydrogen* ($\times 10^4$) *and isotropic for hydrogen atoms* ($\times 10^3$); *e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}/U(Å^2)
C(1)	5056 (2)	3581 (2)	7674 (2)	462 (4)*
C(2)	5554 (2)	3707 (2)	9117 (3)	551 (5)
C(3)	5405 (2)	2823 (2)	10220 (3)	582 (5)
C(4)	4707 (2)	1820 (2)	9879 (2)	490 (4)
C(4a)	4166 (1)	1684 (2)	8438 (2)	355 (3)
S(5)	31134 (4)	4924 (4)	82345 (5)	393 (1)
O(5)	1913 (1)	1059 (1)	8392 (2)	491 (3)
C(5a)	3330 (1)	226 (2)	6298 (2)	380 (3)
C(6)	3111 (2)	−966 (2)	5772 (3)	503 (5)
C(7)	3132 (2)	−1214 (2)	4237 (3)	620 (6)
C(8)	3382 (2)	−274 (3)	3239 (3)	607 (5)
C(9)	3617 (2)	902 (2)	3747 (2)	489 (4)
C(9a)	3614 (1)	1185 (2)	5301 (2)	361 (3)
N(10)	3895 (1)	2371 (1)	5827 (1)	375 (3)
C(10a)	4357 (1)	2545 (2)	7297 (2)	346 (3)
C(11)	3995 (2)	3371 (2)	4729 (2)	520 (5)
H(1)	530 (2)	417 (2)	685 (3)	64 (6)
H(2)	604 (2)	439 (2)	931 (3)	47 (6)
H(3)	582 (2)	284 (2)	1125 (3)	66 (7)
H(4)	453 (2)	122 (3)	1064 (3)	72 (7)
H(6)	294 (3)	−162 (3)	644 (3)	78 (8)
H(7)	299 (3)	−215 (3)	392 (3)	81 (8)
H(8)	333 (2)	−47 (2)	202 (3)	72 (7)
H(9)	381 (3)	153 (3)	303 (3)	87 (9)
H(11)1	389 (2)	420 (2)	521 (3)	46 (5)
H(11)2	339 (3)	328 (3)	397 (3)	74 (8)
H(11)3	480 (2)	334 (2)	424 (2)	54 (6)

* The standard deviations of U_{eq}'s were calculated in accordance with the expressions derived by Schomaker & Marsh (1983).

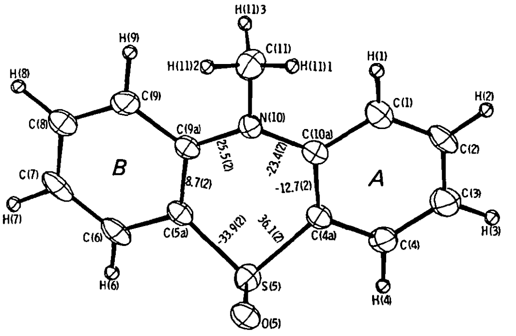

Fig. 2. *ORTEP* drawing of molecule (I) with the torsion angles (°) shown around the central ring.

The support of the Robert A. Welch Foundation to SSCC and ERB is gratefully acknowledged.

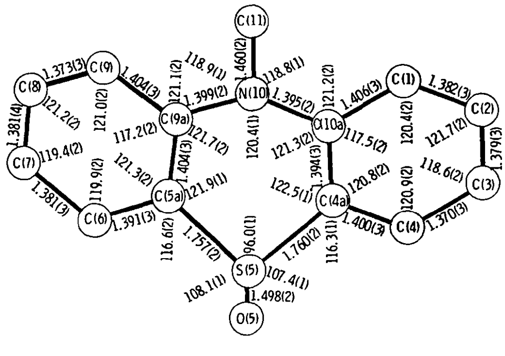

Fig. 3. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses of molecule (I).

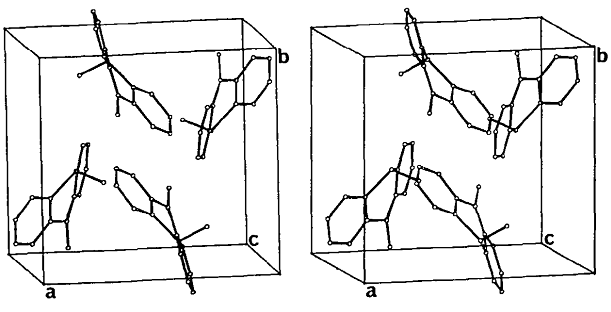

Fig. 4. Stereoscopic drawing of molecular packing of (I), excluding hydrogen atoms, in the unit cell.

References

Bell, J. D., Blount, J. F., Briscoe, O. V. & Freeman, H. C. (1968). *J. Chem. Soc. D*, pp. 1656–1657.
Chu, S. S. C. (1975). *Acta Cryst.* B**31**, 1082–1087.
Chu, S. S. C. & van der Helm, D. (1974). *Acta Cryst.* B**30**, 2489–2490.
Chu, S. S. C. & van der Helm, D. (1975). *Acta Cryst.* B**31**, 1179–1183.
Chu, S. S. C. & van der Helm, D. (1976). *Acta Cryst.* B**32**, 1012–1016.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Jackobs, J. & Sundaralingam, M. (1969). *Acta Cryst.* B**25**, 2487–2496.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
Schomaker, V. & Marsh, R. E. (1983). *Acta Cryst.* A**39**, 819–820.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Ternay, A. L. Jr, Chasar, D. W. & Sax, M. (1967). *J. Org. Chem.* **32**, 2465–2470.
Ternay, A. L. Jr & Chu, S. S. C. (1984). In the press.

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Structure of 1-(*trans*-2-Bromoethenyl)pyrene,* $C_{18}H_{11}Br$

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Abstract. $M_r = 307{\cdot}20$, monoclinic, $P2_1/c$, $a = 20{\cdot}506\,(3)$, $b = 3{\cdot}877\,(1)$, $c = 16{\cdot}236\,(6)$ Å, $\beta = 106{\cdot}79\,(2)^\circ$, $V = 1235{\cdot}6\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}651$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 32{\cdot}7$ cm^{-1}, $F(000) = 616$, $T = 115$ K, final $R = 0{\cdot}0423$ for 2265 observed reflections. The molecules are arranged herringbone fashion in parallel stacks separated by 3·487 (4) Å in the unit cell. The torsion angle between the bromoethenyl group and the pyrene ring is 24·9 (4)°. One ring of the pyrene portion is slightly twisted to allow the other three rings to be planar.

Introduction. 1-(*trans*-2-Bromoethenyl)pyrene is one of a series of compounds being studied as substrates for enzymes and as competitive and suicide inhibitors of cytochrome P-450-dependent benzo[*a*]pyrene hydroxylase activity in liver microsomes (Gan, Acebo & Alworth, 1984). Kinetic studies show that 1-(*trans*-2-bromoethenyl)pyrene binds to both benzoflavone-induced and phenobarbital-induced microsomes and can also function as a substrate. It serves as a competitive inhibitor of benzo[*a*]pyrene metabolism for some isozymes. It is a suicide substrate for both types of microsomes, but only inhibitits some of the isozymes present in phenobarbital-induced microsomes (Alworth, 1984). Olefinic bonds are known to undergo expoxidation due to the catalytic action of cytochrome P-450. Suicide inhibitors of the enzyme cause prosthetic heme alkylation through an intermediate in the oxidation sequence prior to or during formation of the epoxide (Ortiz de Montellano & Correia, 1983).

Experimental. Crystal obtained from Dr W. L. Alworth, Tulane University. Approximate dimensions: 0·45 × 0·65 × 0·40 mm; mounted on a glass fiber. Enraf–Nonius CAD-4 diffractometer, graphite-crystal monochromator, Mo $K\alpha$ radiation, low temperature (115 K). Lattice parameters from 25 reflections with $21 < \theta < 29^\circ$. Systematic absences, $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$. Absorption as a function of ψ observed, and empirical absorption correction applied, relative transmission coefficients ranging from 0·676 to 0·998 with an average value of 0·808; reflections measured with ranges $1 < \theta < 30^\circ$, $-28 \leq h \leq 28$, $-5 \leq k \leq 0$, $0 \leq l \leq 22$, $\omega{:}2\theta$ scans. Intensities of three standard reflections decreased by 2·6% and were used to correct data. 3619 total reflections measured, 2988 unique, 2265 considered observed $[F > 3\sigma(F)]$. Corrected for Lorentz and polarization effects. Structure determined by direct methods using *MULTAN*80 [Main *et al.*, 1980; modified by Frenz (1982)]. Peaks corresponding to 19 non-H atoms located in E map and 11 H atoms from subsequent Fourier syntheses. Structure refined by full-matrix least squares; $\sum w(|F_o| - |F_c|)^2$ minimized. H positions and thermal parameters refined isotropically; other atoms refined anisotropically. Final $R = 0{\cdot}042$, $wR = 0{\cdot}069$ for 215 variables, $w = 1/\sigma(F)^2$, where $\sigma(F^2)^2 = \sigma^2_{\text{cs}} +$

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* (*E*)-1-(2-Bromovinyl)pyrene.