HAUPTMAN, H. & KARLE, J. (1953). *Acta Cryst.* **6**, 473–476.
HORTON, D. & WANDER, J. D. (1969). *Carbohyd. Res.* **10**, 279–288.
HUNTER, F. D. & ROSENSTEIN, R. D. (1968). *Acta Cryst.* B**24**, 1652–1660.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JEFFREY, G. A. & KIM, H. S. (1970). *Carbohyd. Res.* **14**, 207–216.
JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL- 3794.
KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635–651.
MUNS, A. R. I. & TOLLIN, P. (1970). *Acta Cryst.* B**26**, 1101–1113.
REED, J. W. & HARRIS, P. M. (1961). *J. Chem. Phys.* **44**, 4498–4512.
RICHE, C. (1973). *Acta Cryst.* A**29**, 133–137.
RICHE, C. (1974). *Acta Cryst.* B**30**, 610–616.
SAENGER. W. & SUCK, D. (1971). *Acta Cryst.* B**27**, 1178–1186, 2105–2112.
SHEFTER, E. (1968). *J. Pharm. Sci.* **57**, 1157–1162.
SLETTEN, J. & JENSEN, L. H. (1969). *Acta Cryst.* B**25**, 1608–1614.
SLETTEN, E., SLETTEN, J. & JENSEN, L. H. (1969). *Acta Cryst.* B**25**, 1330–1338.
SRINIVASAN, R. & CHANDRASEKHARAN, R. (1968). *Acta Cryst.* B**24**, 1698–1700.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
THEWALD, V., BUGG, C. E. & MARSH, R. E. (1970). *Acta Cryst.* B**26**, 1089–1101.
WOLFROM, M. L., VON BEBENBURG, W., PAGNUCO, R. & MCWAIN, P. (1965). *J. Org. Chem.* **30**, 2732–2735.
WOLFROM, M. L., BHAT, H. B., MCWAIN, P. & HORTON, D. (1972*a*). *Carbohyd. Res.* **23**, 289–296.
WOLFROM, M. L., BHAT, H. B., MCWAIN, P. & HORTON, D. (1972*b*). *Carbohyd. Res.* **23**, 296–300.
WOLFROM, M. L., FOSTER, A. B., MCWAIN, P., VON BEBENBURG, W. & THOMPSON, A. (1961). *J. Org. Chem.* **26**, 3095–3097.

Acta Cryst. (1975). B**31**, 2256

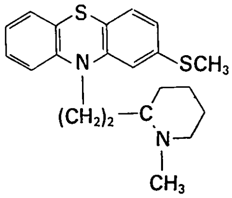
The Crystal and Molecular Structure of Thioridazine, a Derivative of Phenothiazine

BY J. J. H. MCDOWELL

Department of Physics, University of Cape Town, Republic of South Africa

(*Received* 30 *September* 1974; *accepted* 16 *October* 1974)

The crystal structure of thioridazine has been determined from diffractometer data and refined by least-squares methods to a final residual of 4·8%.



Individual anisotropic thermal parameters were refined for all non-hydrogen atoms and the hydrogen atoms were assigned individual isotropic temperature factors derived from the β's of the attached carbon atoms. The space group is $Pna2_1$ with $a=18\cdot337$ (2), $b=12\cdot434$ (2), $c=17\cdot376$ (4) Å. There are two molecules in the asymmetric unit. In the tricyclic group of molecule I the C–S–C angle is 99·0 (4)° and the C–S bonds are 1·786 (8) and 1·762 (9) Å; in molecule II the C–S–C angle is 97·8 (4)° and the C–S bonds are 1·776 (8) and 1·761 (7) Å. The dihedral angles between the two planes of the benzene rings are 145·8° and 134·4° respectively, with the two molecules oriented at an angle of approximately 10° to each other. The piperidine rings have the chair configuration.

Introduction

The crystallographic study of a series of derivatives of phenothiazine has been undertaken in the laboratory of the University of Cape Town with the eventual hope of correlating molecular structure with psychopharmacological properties.

The phenothiazines are divided into three groups according to the chemical nature of the side chain attached to the nitrogen atom: (*a*) dimethylaminopropyl, (*b*) piperazine and (*c*) piperidine radical. Chlorpromazine, psychotropically potent, belonging to the first group, and thiethylperazine, with relatively little tranquillizing or sedative action, belonging to the second, were chosen for complete structural analyses and have been solved (McDowell, 1969, 1970). The structure of thioridazine, a potent representative of the third group, has been determined and is reported here.

Thioridazine or 10-[2-(1-methylpiperid-2-yl)ethyl]-2-methylthiophenothiazine is the well known and widely used drug Melleril. It has a tranquillizing action similar to chlorpromazine but has no therapeutically significant antiemetic or hypothermic action and does not potentiate the action of anaesthetics. It is used mainly for the treatment of schizophrenia and for the control of mania and agitation. It may be used in the management of anxiety states and in children with behaviour problems. The incidence of extrapyramidal side effects is lower than with other phenothiazines (*British Pharmaceutical Codex*, 1973; *Extra Pharmacopoeia*, 1972).

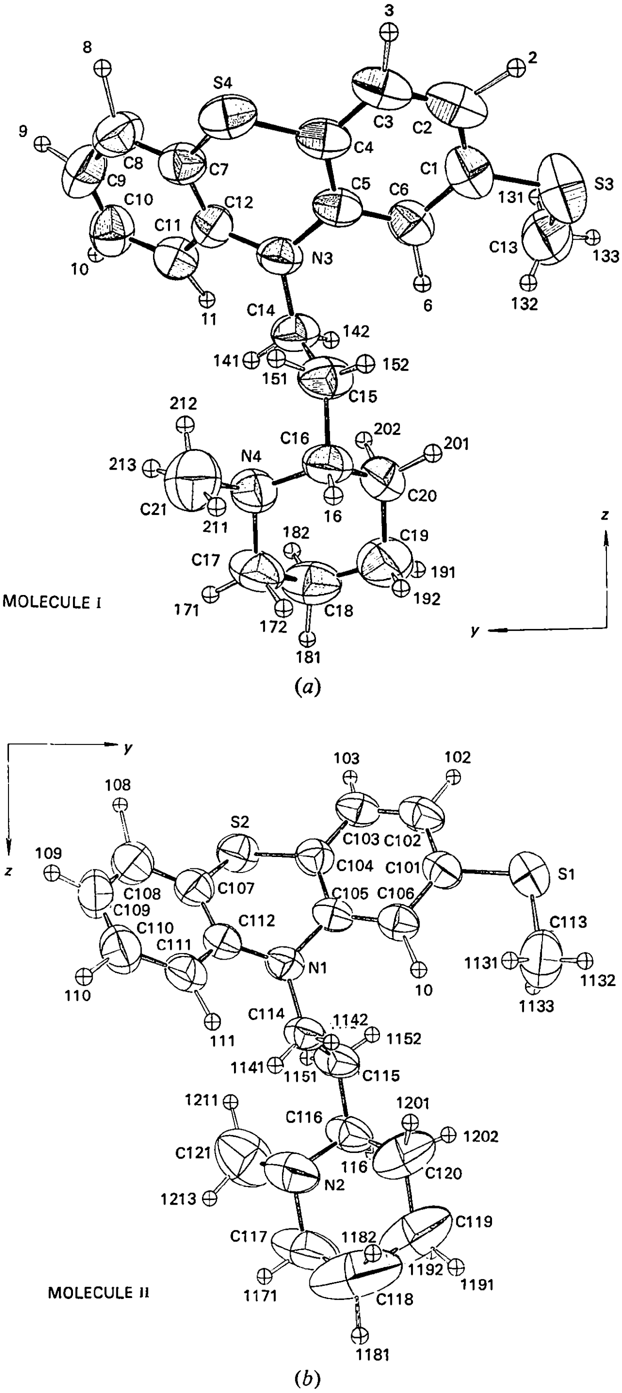


Fig. 1. Thermal vibration ellipsoids and atomic numbering. ⊕ denotes hydrogen atoms. H(1172) on C(117) and H(1212) on C(121) of molecule II are not shown.

Experimental

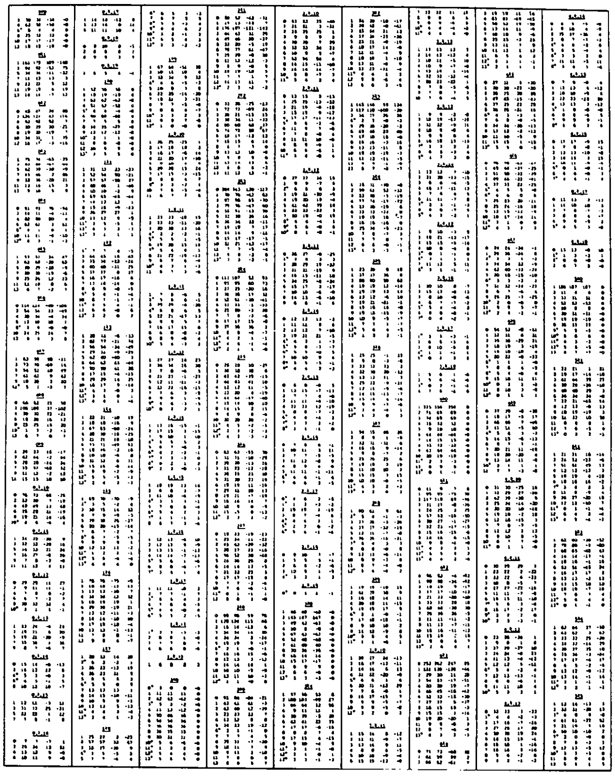
The powdered substance was obtained from Sandoz, Basle. Crystals were prepared by applying prolonged heat to a reflux condenser containing the powder and low b.p. petroleum spirit (32–34°), and subsequent retarded evaporation over a period of approximately three weeks. The crystals were colourless transparent rods of rhombic cross-section which turned yellow if not protected from the air. Cubic-cut crystals were ground into spheres of 0·04–0·08 cm diameter and mounted along one of their axes on fine glass rods; the orientations of the axes were located as the directions of extinction under a polarizing microscope.

X-ray oscillation and Weissenberg photographs, with the use of Ni-filtered Cu $K\alpha$ radiation, taken about all three axes showed an orthorhombic system with $a=18{\cdot}35$, $b=12{\cdot}44$, $c=17{\cdot}40$ Å, in good agreement with the diffractometer values obtained subsequently; $a=18{\cdot}337$ (2), $b=12{\cdot}435$ (2), $c=17{\cdot}376$ (4) Å. The latter values were considered more accurate and were used in all calculations. The conditions for non-extinction were found to be $0kl$, $k+l=2n$; $h0l$, $h=2n$; $h00$, $h=2n$; $0k0$, $k=2n$; $00l$, $l=2n$. These indicated either of two possible space groups, centrosymmetric $Pnma$ with eight equivalent positions, or non-centrosymmetric $Pna2_1$ with four equivalent positions. The measured density was 1·191 g cm^{-3} and the value calculated for eight molecules per unit cell being 1·24 g cm^{-3} implied that for the non-centrosymmetric space group the asymmetric unit must consist of two molecules.

The best crystal (of diameter 0·05 cm) was mounted on a Hilger & Watts four-circle automatic diffractometer and exposed to Zr-filtered Mo $K\alpha$ radiation. The measured data extended to $h,k,l(\max)=20,13,19$ respectively. A total number of 3165 reflexions was recorded, including 282 systematically extinct and 758 which were not significantly different from background level and thus rated as less-thans (unobserveds). The integrated intensities were collected over 45 s involving 30 steps of 0·02° in ω. Two reference reflexions were chosen and recorded at the beginning of the data collection and after every set of 100 readings. The intensities of these selected reflexions were checked to confirm that the variances did not exceed 4% throughout the data collection. Individual background intensities left and right were measured but the more accurate method of estimating background and peak-spread

Table 1. *Observed and calculated structure factors*

Within each group the columns, reading from left to right, contain the values of k, $K|F_o|$, F_c, A_c and B_c. An asterisk indicates F_{unobs}.



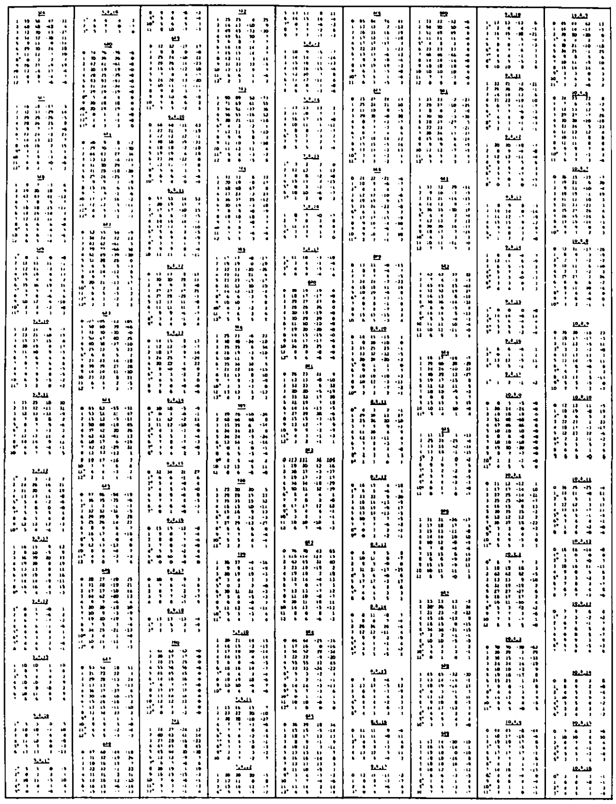
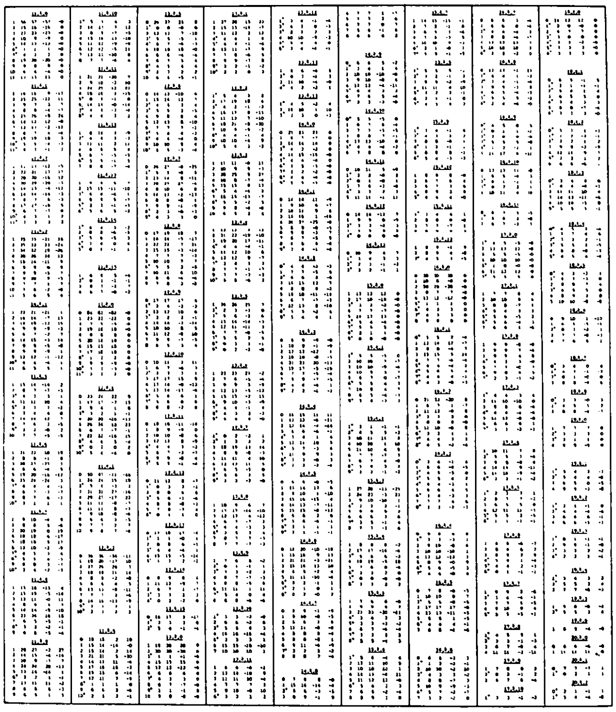


Table 1 (*cont.*)



corrections described for thiethylperazine (McDowell, 1970) was applied.

The value of μR for Mo $K\alpha$ radiation was calculated to be 0·07 (where R is the radius of the spherical crystal and μ the absorption coefficient); as the corresponding correction factor A^* is 1·16 throughout the range of θ, absorption corrections were not applied. The usual corrections were made for Lorentz and polarization factors. Using the sub-program *NORMSF* (Maslen, 1967) of the X-RAY (1972) program system, preliminary scale and temperature factors were estimated by Wilson's (1942) method. The statistical survey of the intensities of the reflexions gave an $N(z)$ distribution (Howells, Phillips & Rogers, 1950) which was unfortunately indeterminate as to whether the space group was centrosymmetric or non-centrosymmetric.

Solution and refinement of the structure

A three-dimensional Patterson function, sharpened in accordance with the formula

$$|F|^2=\frac{(\sin^2\theta/\lambda^2+0{\cdot}16)F_o^2\exp(B\sin^2\theta/\lambda^2)}{(\sum f_i)^2}$$

was calculated (McDowell, 1970). The analytical scattering factor values computed from numerical Hartree–Fock wave functions by Cromer & Mann (1968) were used for S, N and C; for H, the values given by Stewart, Davidson & Simpson (1965) were used.

Initially, attempts were made to locate the two sulphur atoms of one molecule making the assumption that the space group was *Pnma*. Fourier syntheses phased on one atom were computed and the lowest R index was 0·67, where $R=\sum||F_o|-|F_c||/\sum|F_o|$. Of the six best results, five implied atom locations on a mirror plane in the space group *Pnma*. This would have the effect of reducing the eight equivalent positions to four; thus it was difficult to see how the eight molecules in the unit cell could be placed in the space group *Pnma*. From the above results as well as from other indications, such as the distribution of the Patterson peaks, the non-centrosymmetric space group $Pna2_1$ with two molecules in the asymmetric unit was therefore assumed.

Only three of the four sulphur atoms were correctly located from the Patterson peaks, and a Fourier computation phased on the three atoms gave an R of 0·49. A number of successive syntheses was required to locate S(3) and the remaining 46 N and C atoms. It is of interest to note that the high value of the estimated preliminary temperature factor ($B=6·15$) proved a correct forecast of the difficulties which were to be encountered in solving the structure by Fourier methods.

Four cycles of full-matrix least-squares refinement of the coordinates and individual isotropic B's of the 50 non-hydrogen atoms, followed by three cycles with anisotropic temperature factors brought R down to a value of 0·08. The sub-program used was *CRYLSQ* of X-RAY (1972) and the function minimized was $R_1=\sum w(hkl)\{|F_o(hkl)-F_c(hkl)|\}^2$ with equal weights given to all terms in the initial stages.

From the first difference Fourier synthesis 39 of the 52 hydrogen atoms could be identified clearly; the positions of the remaining 13 – those attached to carbon atoms with high thermal motion – were not so well defined. However all 52 hydrogen atoms were placed, assigned the isotropic temperature factors derived from the β's of the attached C atoms, and the H-atom coordinates were refined for two cycles. Successive dif-

Table 2. *Final atomic fractional coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^4$) *with estimated standard deviations*

Anisotropic temperature factor $=\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$ with $\beta_{11}=2\pi^2a^{*2}U_{11}$, $\beta_{12}=2\pi^2a^*b^*U_{12}$ *etc.* The least-squares standard errors are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(3)	1245(2)	3897(2)	1783(2)	64	100	107	- 3	11	24
S(4)	0576(1)	8685(2)	2669(1)	43	136	40	4	5	- 9
N(3)	1226(3)	8008(5)	1163(3)	42	91	32	- 3	1	5
N(4)	0717(3)	8480(5)	-1180(3)	47	93	37	3	7	3
C(1)	1078(4)	5267(6)	1999(5)	34	98	66	- 3	- 7	19
C(2)	0787(4)	5486(8)	2709(5)	43	154	45	- 1	- 0	26
C(3)	0667(4)	6533(8)	2904(4)	44	147	38	- 2	3	20
C(4)	0804(4)	7359(7)	2404(4)	31	123	36	- 1	- 1	6
C(5)	1090(3)	7160(6)	1673(4)	29	107	34	- 0	- 2	6
C(6)	1244(4)	6091(6)	1466(4)	40	91	47	3	- 3	10
C(7)	1271(4)	9387(6)	2155(4)	38	102	41	5	- 1	- 0
C(8)	1532(5)	10340(7)	2464(5)	60	118	48	- 3	- 6	-18
C(9)	2010(6)	10938(7)	2040(7)	62	98	74	- 2	- 6	-29
C(10)	2269(4)	10580(7)	1341(6)	45	97	71	- 9	- 6	- 3
C(11)	2031(4)	9582(6)	1051(4)	39	99	47	- 1	2	3
C(12)	1515(3)	8987(5)	1457(4)	34	80	43	4	- 4	- 6
C(13)	2021(8)	3914(8)	1177(6)	121	114	67	4	32	-10
C(14)	1285(4)	7808(6)	0335(4)	41	106	31	- 8	3	- 1
C(15)	0554(4)	7426(7)	0010(4)	41	131	36	-21	3	7
C(16)	0522(4)	7426(7)	-0866(4)	46	109	31	-13	- 3	8
C(17)	0669(5)	8474(7)	-2027(4)	60	129	33	8	3	14
C(18)	1190(5)	7674(9)	-2369(5)	63	164	37	8	5	- 1
C(19)	1023(6)	6594(8)	-2096(5)	88	136	46	21	6	-12
C(20)	1036(6)	6603(6)	-1190(5)	78	88	41	3	- 2	8
C(21)	0206(5)	9308(8)	-0908(6)	65	132	73	35	3	-17
S(1)	1011(1)	5263(2)	5000(0)	76	89	55	9	- 1	11
S(2)	2168(1)	0551(2)	4572(1)	46	114	45	18	4	1
N(1)	1396(3)	1310(4)	5939(3)	42	83	32	- 1	4	5
N(2)	1721(4)	1389(7)	8356(4)	65	172	47	-15	5	15
C(101)	1318(4)	3922(5)	4905(4)	40	86	40	- 1	- 3	10
C(102)	1631(4)	3657(7)	4211(4)	49	114	40	-13	2	20
C(103)	1879(4)	2615(7)	4100(4)	40	119	35	2	7	9
C(104)	1809(4)	1857(6)	4676(4)	36	92	40	7	- 1	2
C(105)	1487(3)	2130(6)	5384(4)	31	92	32	- 3	1	9
C(106)	1234(3)	3171(6)	5501(4)	32	91	36	- 7	- 0	6
C(107)	1454(4)	-0158(6)	5041(4)	50	91	42	15	-12	2
C(108)	1219(5)	-1158(6)	4762(5)	69	96	55	20	-21	- 0
C(109)	0695(6)	-1680(7)	5158(6)	90	64	66	-10	-35	7
C(110)	0338(5)	-1230(7)	5795(6)	68	94	60	-20	-20	16
C(111)	0570(4)	-0240(6)	6054(4)	54	89	36	- 4	-11	13
C(112)	1138(4)	0309(5)	5691(4)	41	81	35	4	- 5	6
C(113)	0653(5)	5317(7)	5958(7)	69	94	83	7	13	- 3
C(114)	1264(4)	1621(5)	6750(4)	40	95	29	-14	1	7
C(115)	1937(4)	2181(6)	7078(4)	43	119	35	-23	- 0	12
C(116)	1904(4)	2361(7)	7940(4)	51	124	37	-35	- 3	14
C(117)	1702(9)	1586(13)	9225(6)	104	260	38	-79	-14	27
C(118)	1115(10)	2359(23)	9419(8)	90	436	67	-105	24	-73
C(119)	1281(7)	3342(15)	9023(9)	79	284	88	-46	21	-86
C(120)	1326(5)	3190(10)	8129(5)	57	205	58	-17	1	-43
C(121)	2224(6)	0597(11)	8229(8)	71	204	99	23	2	41

Table 2 (*cont.*)

Final hydrogen atomic fractional coordinates ($\times 10^3$) and isotropic temperature factors with estimated standard deviations.

MOLECULE I

	x	y	z	B
H(2)	056(4)	469(6)	307(4)	6.88
H(3)	039(4)	646(6)	346(5)	6.53
H(6)	137(4)	592(6)	080(4)	5.69
H(8)	137(4)	1052(6)	317(4)	7.10
H(9)	228(4)	1162(6)	234(4)	8.08
H(10)	276(5)	1092(7)	101(5)	7.09
H(11)	215(4)	913(6)	056(4)	5.75
H(141)	145(4)	846(6)	001(4)	5.27
H(142)	172(4)	727(6)	016(4)	5.27
H(151)	030(4)	811(6)	028(5)	5.90
H(152)	027(4)	689(6)	020(4)	5.90
H(16)	-010	740	-100	5.48
H(171)	084(4)	916(6)	-234(5)	6.49
H(172)	006(4)	811(6)	-220(4)	6.49
H(181)	121(5)	776(7)	-301(6)	7.45
H(182)	180(5)	794(7)	-222(6)	7.45
H(191)	144(5)	607(7)	-233(6)	8.04
H(192)	038(5)	645(8)	-215(6)	8.04
H(201)	092(4)	589(6)	-090(4)	7.45
H(202)	172(4)	680(6)	-096(4)	7.45
H(211)	-033(4)	897(6)	-101(4)	7.96
H(212)	040	940	-040	7.96
H(213)	055(4)	991(6)	-088(5)	7.96
H(131)	246(4)	395(6)	157(4)	10.33
H(132)	184(4)	425(6)	070(4)	10.33
H(133)	240	310	110	10.33

MOLECULE II

	x	y	z	B
H(102)	171(4)	423(6)	375(4)	6.40
H(103)	218(4)	253(6)	365(4)	5.70
H(106)	085(4)	342(6)	605(4)	4.77
H(108)	139(4)	-138(6)	406(4)	7.67
H(109)	046(5)	-233(7)	494(5)	8.37
H(110)	-020	-170	610	7.31
H(111)	035(4)	018(6)	659(4)	5.59
H(1141)	105(4)	113(6)	709(4)	4.88
H(1142)	082(4)	202(6)	684(4)	4.88
H(1151)	243(4)	170(6)	705(5)	5.65
H(1152)	202(4)	279(6)	678(4)	5.65
H(116)	240	280	820	6.72
H(1171)	168(4)	090(6)	953(5)	11.71
H(1172)	197(4)	201(6)	943(4)	11.71
H(1181)	104(4)	240(6)	1023(4)	11.69
H(1182)	062(6)	259(9)	911(7)	11.69
H(1191)	080	390	930	11.69
H(1192)	176(4)	366(6)	928(4)	11.69
H(1201)	072(5)	322(8)	773(6)	8.71
H(1202)	137(4)	392(6)	792(4)	8.71
H(1211)	234(4)	037(6)	758(4)	11.24
H(1212)	280	090	830	11.24
H(1213)	220	000	870	11.24
H(1131)	021(4)	472(6)	599(4)	8.27
H(1132)	030	590	600	8.27
H(1133)	110	530	625	8.27

ference Fourier syntheses and refinement cycles, in which the H-atom coordinates and all parameters of the S, N, C atoms were varied, improved the positions of the hydrogen atoms and brought R down to 0·057. However, ten 'maverick' H atoms which showed a tendency to 'drift' were put back to their original Fourier locations.

At this stage a weighting scheme was applied to all reflexions, using the sub-programs *WTLSSQ* and *WTANAL* of X-RAY (1972). The chosen scheme,

Table 3. *Bond lengths and angles with estimated standard deviations*

(The e.s.d.'s in the bond lengths $\times 10^3$ and the e.s.d.'s in the bond angles $\times 10$ are given in parentheses.)

MOLECULE I

Bond	ℓ	Angle	θ
C(1) - C(2)	1.371(13) Å	C(6) - C(1) - C(2)	121.9(8)°
C(2) - C(3)	1.362(14)	C(1) - C(2) - C(3)	118.4(8)
C(3) - C(4)	1.369(12)	C(2) - C(3) - C(4)	122.0(7)
C(4) - C(5)	1.396(9)	C(3) - C(4) - C(5)	120.8(8)
C(5) - C(6)	1.405(10)	C(4) - C(5) - C(6)	118.4(7)
C(6) - C(1)	1.413(11)	C(5) - C(6) - C(1)	118.4(7)
C(7) - C(8)	1.387(12)	C(12) - C(7) - C(8)	122.4(7)
C(8) - C(9)	1.366(14)	C(7) - C(8) - C(9)	118.5(8)
C(9) - C(10)	1.378(15)	C(8) - C(9) - C(10)	121.4(9)
C(10) - C(11)	1.410(12)	C(9) - C(10) - C(11)	119.6(8)
C(11) - C(12)	1.394(10)	C(10) - C(11) - C(12)	119.8(7)
C(12) - C(7)	1.384(10)	C(11) - C(12) - C(7)	118.2(6)
C(7) - S(4)	1.786(8)	C(4) - S(4) - C(7)	99.0(4)
C(4) - S(4)	1.762(9)	S(4) - C(7) - C(12)	119.6(6)
C(12) - N(3)	1.423(9)	S(4) - C(7) - C(8)	118.0(6)
C(5) - N(3)	1.399(9)	C(7) - C(12) - N(3)	120.1(6)
S(3) - C(1)	1.772(8)	C(11) - C(12) - N(3)	121.7(6)
S(3) - C(13)	1.771(14)	C(12) - N(3) - C(5)	118.9(5)
		N(3) - C(5) - C(4)	120.6(7)
		N(3) - C(5) - C(6)	121.0(6)
		C(5) - C(4) - S(4)	119.6(6)
		C(3) - C(4) - S(4)	119.6(6)
N(3) - C(14)	1.464(9)	C(6) - C(1) - S(3)	121.4(7)
C(14) - C(15)	1.531(10)	C(2) - C(1) - S(3)	116.6(7)
C(15) - C(16)	1.523(10)	C(1) - S(3) - C(13)	104.7(4)
C(16) - N(4)	1.463(10)		
N(4) - C(17)	1.474(10)	C(12) - N(3) - C(14)	118.0(6)
C(17) - C(18)	1.502(13)	C(5) - N(3) - C(14)	120.5(6)
C(18) - C(19)	1.457(15)	N(3) - C(14) - C(15)	110.6(5)
C(19) - C(20)	1.574(12)	C(14) - C(15) - C(16)	113.8(6)
C(20) - C(16)	1.501(12)	C(15) - C(16) - C(20)	110.5(6)
N(4) - C(21)	1.469(11)	C(15) - C(16) - N(4)	111.3(6)
		C(16) - N(4) - C(21)	110.6(6)
		C(17) - N(4) - C(21)	106.7(6)
		C(16) - N(4) - C(17)	110.6(6)
		N(4) - C(17) - C(18)	111.2(7)
		C(17) - C(18) - C(19)	110.3(8)
		C(18) - C(19) - C(20)	108.5(8)
		C(19) - C(20) - C(16)	111.7(7)
		C(20) - C(16) - N(4)	108.6(6)

MOLECULE II

Bond	ℓ	Angle	θ
C(101) - C(102)	1.376(10) Å	C(106) - C(101) - C(102)	122.2(6)°
C(102) - C(103)	1.386(12)	C(101) - C(102) - C(103)	118.9(7)
C(103) - C(104)	1.381(11)	C(102) - C(103) - C(104)	120.5(7)
C(104) - C(105)	1.406(10)	C(103) - C(104) - C(105)	120.5(7)
C(105) - C(106)	1.390(10)	C(104) - C(105) - C(106)	119.5(6)
C(106) - C(101)	1.403(10)	C(105) - C(106) - C(101)	118.4(6)
C(107) - C(108)	1.403(11)	C(112) - C(107) - C(108)	121.4(7)
C(108) - C(109)	1.348(13)	C(107) - C(108) - C(109)	118.0(8)
C(109) - C(110)	1.402(14)	C(108) - C(109) - C(110)	122.8(8)
C(110) - C(111)	1.378(12)	C(109) - C(110) - C(111)	118.1(8)
C(111) - C(112)	1.396(10)	C(110) - C(111) - C(112)	121.2(7)
C(112) - C(107)	1.397(10)	C(111) - C(112) - C(107)	118.2(6)
C(107) - S(2)	1.776(8)	C(104) - S(2) - C(107)	97.8(4)
C(104) - S(2)	1.761(7)	S(2) - C(107) - C(112)	118.1(5)
C(112) - N(1)	1.400(9)	S(2) - C(107) - C(108)	120.6(6)
C(105) - N(1)	1.413(9)	C(107) - C(112) - N(1)	118.6(6)
S(1) - C(101)	1.768(7)	C(111) - C(112) - N(1)	123.2(6)
S(1) - C(113)	1.791(11)	C(112) - N(1) - C(105)	118.1(5)
		N(1) - C(105) - C(104)	118.2(6)
		N(1) - C(105) - C(106)	122.2(6)
		C(105) - C(104) - S(2)	118.0(5)
		C(103) - C(104) - S(2)	121.4(6)
N(1) - C(114)	1.481(8)	C(106) - C(101) - S(1)	121.6(5)
C(114) - C(115)	1.526(10)	C(102) - C(101) - S(1)	116.2(5)
C(115) - C(116)	1.515(10)	C(101) - S(1) - C(113)	103.8(4)
C(116) - N(2)	1.447(12)		
N(2) - C(117)	1.531(13)	C(112) - N(1) - C(114)	118.1(5)
C(117) - C(118)	1.482(28)	C(105) - N(1) - C(114)	118.7(5)
C(118) - C(119)	1.435(31)	N(1) - C(114) - C(115)	110.1(5)
C(119) - C(120)	1.567(18)	C(114) - C(115) - C(116)	113.9(6)
C(120) - C(116)	1.514(14)	C(115) - C(116) - C(120)	110.1(7)
N(2) - C(121)	1.367(15)	C(115) - C(116) - N(2)	112.3(7)
		C(116) - N(2) - C(121)	111.4(8)
		C(117) - N(2) - C(121)	106.8(9)
		C(116) - N(2) - C(117)	111.4(8)
		N(2) - C(117) - C(118)	110.1(10)
		C(117) - C(118) - C(119)	106.9(14)
		C(118) - C(119) - C(120)	112.5(14)
		C(119) - C(120) - C(116)	109.5(9)
		C(120) - C(116) - N(2)	107.5(7)

Table 3 (*cont.*)

Bond	ℓ	Angle	θ	Angle	θ
C(2) - H(2)	1.25(1) Å	C(1) - C(2) - H(2)	115.3(8)°	C(101) - C(102) - H(102)	123.2(7)°
C(3) - H(3)	1.10(1)	C(3) - C(2) - H(2)	125.5(8)	C(103) - C(102) - H(102)	117.9(7)
C(6) - H(6)	1.19(1)	C(2) - C(3) - H(3)	102.2(8)	C(102) - C(103) - H(103)	114.1(8)
C(8) - H(8)	1.29(1)	C(4) - C(3) - H(3)	135.2(9)	C(104) - C(103) - H(103)	124.1(8)
C(9) - H(9)	1.10(1)	C(5) - C(6) - H(6)	116.8(6)	C(105) - C(106) - H(106)	122.8(6)
C(10) - H(10)	1.15(1)	C(1) - C(6) - H(6)	123.1(7)	C(101) - C(106) - H(106)	118.0(6)
C(11) - H(11)	1.05(1)	C(7) - C(8) - H(8)	115.9(7)	C(107) - C(108) - H(108)	116.4(7)
		C(9) - C(8) - H(8)	125.0(8)	C(109) - C(108) - H(108)	123.4(8)
C(13) - H(131)	1.05(1)	C(8) - C(9) - H(9)	116.7(10)	C(108) - C(109) - H(109)	120.8(10)
- H(132)	0.99(1)	C(10) - C(9) - H(9)	120.4(9)	C(110) - C(109) - H(109)	114.9(10)
- H(133)	1.23(1)	C(9) - C(10) - H(10)	126.1(8)	C(109) - C(110) - H(110)	120.7(8)
		C(11) - C(10) - H(10)	112.9(8)	C(111) - C(110) - H(110)	121.1(8)
C(14) - H(141)	1.04(1)	C(10) - C(11) - H(11)	134.6(8)	C(110) - C(111) - H(111)	124.5(7)
- H(142)	1.09(1)	C(12) - C(11) - H(11)	105.6(6)	C(112) - C(111) - H(111)	114.1(6)
C(15) - H(151)	1.08(1)				
- H(152)	0.92(1)	S(3) - C(13) - H(131)	103.1(8)	S(1) - C(113) - H(1131)	106.8(7)
		S(3) - C(13) - H(132)	103.5(10)	S(1) - C(113) - H(1132)	109.9(8)
C(16) - H(16)	1.16(1)	S(3) - C(13) - H(133)	120.4(7)	S(1) - C(113) - H(1133)	100.1(8)
C(17) - H(171)	1.05(1)	H(131) - C(13) - H(132)	141.7(13)	H(1131) - C(113) - H(1132)	90.5(8)
- H(172)	1.24(1)	H(131) - C(13) - H(133)	70.9(8)	H(1131) - C(113) - H(1133)	126.0(10)
C(18) - H(181)	1.12(1)	H(132) - C(13) - H(133)	116.7(10)	H(1132) - C(113) - H(1133)	122.8(10)
- H(182)	1.20(1)				
C(19) - H(191)	1.08(1)	N(3) - C(14) - H(141)	114.7(6)	N(1) - C(114) - H(1141)	119.9(6)
- H(192)	1.19(1)	N(3) - C(14) - H(142)	115.9(6)	N(1) - C(114) - H(1142)	115.1(6)
C(20) - H(201)	1.05(1)	C(15) - C(14) - H(141)	107.9(6)	C(115) - C(114) - H(1141)	113.3(6)
- H(202)	1.33(1)	C(15) - C(14) - H(142)	110.1(6)	C(115) - C(114) - H(1142)	113.1(6)
		H(141) - C(14) - H(142)	96.8(5)	H(1141) - C(114) - H(1142)	83.0(5)
C(21) - H(211)	1.09(1)	C(14) - C(15) - H(151)	88.8(6)	C(114) - C(115) - H(1151)	114.2(6)
- H(212)	0.96(1)	C(14) - C(15) - H(152)	126.5(7)	C(114) - C(115) - H(1152)	106.8(6)
- H(213)	0.98(1)	C(16) - C(15) - H(151)	114.4(7)	C(116) - C(115) - H(1151)	98.7(6)
		C(16) - C(15) - H(152)	110.3(7)	C(116) - C(115) - H(1152)	116.1(7)
		H(151) - C(15) - H(152)	99.2(6)	H(1151) - C(115) - H(1152)	107.0(7)
C(102) - H(102)	1.09(1)	C(15) - C(16) - H(16)	103.7(6)	C(115) - C(116) - H(116)	115.2(7)
C(103) - H(103)	0.96(1)	C(20) - C(16) - H(16)	121.4(7)	C(120) - C(116) - H(116)	98.3(7)
C(106) - H(106)	1.23(1)	N(4) - C(16) - H(16)	100.9(6)	N(2) - C(116) - H(116)	112.5(6)
C(108) - H(108)	1.29(1)	N(4) - C(17) - H(171)	119.2(7)	N(2) - C(117) - H(1171)	112.6(12)
C(109) - H(109)	0.99(1)	N(4) - C(17) - H(172)	107.6(6)	N(2) - C(117) - H(1172)	122.2(13)
C(110) - H(110)	1.26(1)	C(18) - C(17) - H(171)	98.5(7)	C(118) - C(117) - H(1171)	113.4(14)
C(111) - H(111)	1.14(1)	C(18) - C(17) - H(172)	103.5(7)	C(118) - C(117) - H(1172)	85.3(15)
		H(171) - C(17) - H(172)	115.4(7)	H(1171) - C(117) - H(1172)	110.3(13)
C(113) - H(1131)	1.10(1)	C(17) - C(18) - H(181)	110.6(8)	C(117) - C(118) - H(1181)	108.7(14)
- H(1132)	0.97(1)	C(17) - C(18) - H(182)	109.1(8)	C(117) - C(118) - H(1182)	131.5(17)
- H(1133)	0.96(1)	C(19) - C(18) - H(181)	114.7(9)	C(119) - C(118) - H(1181)	117.8(19)
		C(19) - C(18) - H(182)	112.0(8)	C(119) - C(118) - H(1182)	73.5(15)
C(114) - H(1141)	0.93(1)	H(181) - C(18) - H(182)	99.7(7)	H(1181) - C(118) - H(1182)	113.4(14)
- H(1142)	0.97(1)	C(18) - C(19) - H(191)	106.5(9)	C(118) - C(119) - H(1191)	98.2(13)
C(115) - H(1151)	1.09(1)	C(18) - C(19) - H(192)	108.8(8)	C(118) - C(119) - H(1192)	106.6(14)
- H(1152)	0.93(1)	C(20) - C(19) - H(191)	112.1(8)	C(120) - C(119) - H(1191)	119.8(12)
		C(20) - C(19) - H(192)	95.5(7)	C(120) - C(119) - H(1192)	114.8(12)
C(116) - H(116)	1.15(1)	H(191) - C(19) - H(192)	124.4(9)	H(1191) - C(119) - H(1192)	102.9(14)
C(117) - H(1171)	1.00(1)	C(19) - C(20) - H(201)	118.7(7)	C(119) - C(120) - H(1201)	118.5(8)
- H(1172)	0.80(1)	C(19) - C(20) - H(202)	108.5(7)	C(119) - C(120) - H(1202)	105.1(11)
C(118) - H(1181)	1.42(1)	C(16) - C(20) - H(201)	105.7(7)	C(116) - C(120) - H(1201)	119.8(8)
- H(1182)	1.09(2)	C(16) - C(20) - H(202)	110.4(6)	C(116) - C(120) - H(1202)	119.7(9)
C(119) - H(1191)	1.22(2)	H(201) - C(20) - H(202)	101.3(7)	H(1201) - C(120) - H(1202)	81.0(7)
- H(1192)	1.07(1)				
C(120) - H(1201)	1.32(1)	N(4) - C(21) - H(211)	104.5(7)	N(2) - C(121) - H(1211)	116.7(11)
- H(1202)	0.99(1)	N(4) - C(21) - H(212)	98.3(7)	N(2) - C(121) - H(1212)	111.9(11)
		N(4) - C(21) - H(213)	98.1(7)	N(2) - C(121) - H(1213)	109.7(10)
C(121) - H(1211)	1.18(1)	H(211) - C(21) - H(212)	122.2(9)	H(1211) - C(121) - H(1212)	90.6(9)
- H(1212)	1.13(1)	H(211) - C(21) - H(213)	153.0(10)	H(1211) - C(121) - H(1213)	123.6(12)
- H(1213)	1.11(1)	H(212) - C(21) - H(213)	67.5(6)	H(1212) - C(121) - H(1213)	100.5(10)

which proved very satisfactory, gives unit weights to most reflexions but down-weights those with large F_{obs} and/or small $\sin\theta$ values, as follows:

$$w(hkl)=\frac{\sin\theta}{A}\cdot\frac{C}{F_o}=X\,.\,Y\,.$$

For $\sin\theta > A, X=1$; for $\sin\theta < A, X=\sin\theta/A$; for $F_o < C$, $Y=1$; for $F_o > C$, $Y=C/F_o$. Values of 0·2 and 50 were assigned to A and C respectively.

Two cycles of refinement of the coordinates and β's of all non-hydrogen atoms gave a final R value of 0·048 for 2883 reflexions. In the last cycle the average parameter shifts expressed as fractions of the estimated standard deviations were about 0·8. Table 1 lists observed and calculated structure factors; final atomic fractional coordinates and thermal-motion parameters are given in Table 2.

Description and discussion of the structure

Table 3 gives interatomic distances and angles with associated standard deviations which were calculated from the results of the last refinement cycle. The atomic numbering of the two molecules of the asymmetric unit is shown in Fig. 1.

The C–C bond lengths within the four benzene rings are all between 1·35 and 1·41 Å; the average values for the benzene rings are 1·386, 1·387, 1·390, 1·387 Å, in fair agreement with the values reported for benzene: 1·392 Å, Cox, Cruickshank & Smith (1958); 1·394 Å, Sutton (1965).

The sulphur–carbon bonds around S(3) and S(1) are all shorter [S(3)–C(1) 1·772; S(3)–C(13) 1·771; S(1)–C(101) 1·768; S(1)–C(113) 1·791 Å] than Abrahams's (1956) single-bond value of 1·82 Å, which was also the case in thiethylperazine. The sulphur–carbon bonds within the rings [*i.e.* atoms S(2), S(4)] average 1·774 Å in molecule I and 1·769 Å in molecule II, implying double-bond character of about 9%. The shortened S–C bonds in a heterocyclic ring have been found in many similar compounds, *e.g.* thianthrene, 1·76 Å (Lynton & Cox, 1956); phenoxthionine, 1·75 Å (Hosoya, 1966); phenothiazine, 1·77 Å (Bell, Blount, Briscoe & Freeman, 1968), as well as in both chlorpromazine and thiethylperazine.

An interesting although disconcerting feature of the refinement was the tendency of several of the H atoms to move outward, so that the corresponding C–H bonds are longer than accepted C–H single-bond distances, although the average value for molecule I is 1·11 Å, for molecule II, 1·09 Å. In addition several angles involving hydrogen in the side chain are quite far from the tetrahedral value. However, in the refinement process consisting of 606 simultaneous variables (assuming S, N, C coordinates and β's and H coordinates), the results proved relatively insensitive to the exact hydrogen locations, provided only that all H atoms were included. For example, during one test cycle which was performed with all hydrogens in 'ideal' positions (*i.e.* given standard C–H bond lengths and angles), the R value increased only slightly (approximately 1 %).

All angles of the tricyclic group are close to 120°, with the exception of the C–S–C angles which are 99·0° and 97·8° in molecules I and II respectively. These values, together with contracted C–S(2) and C–S(4) lengths, may be interpreted in terms of π-bonding molecular orbitals formed by the carbon atoms with the 3*d* orbitals of the sulphur atom. Similar C–S–C angles and C–S bonds were found in the branched side-chain derivatives isothazine (Marsau & Calas, 1971), thiazinamium (Marsau & Cam, 1973) and promethazine (Marsau & Busetta, 1973).

The best planes for the benzene rings were calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) using the sub-program *LSQPL* of X-RAY 72 and are given in Table 4, together with the individual displacements of atoms from the planes. The maximum deviation of the C atoms is 0·027 Å so that the benzene rings may be regarded as planar, within the limits of error. The S and N atoms however do not lie in the planes, which was also the case in chlorpromazine and thiethylperazine. C(14) is at −0·49 Å from plane I and −0·53 Å from plane II; thus atom N(3) in molecule I is situated at the apex of a flattened pyramid of which C(5), C(12) and C(14) form the base; in molecule II, C(114) is +0·33 Å from plane IV and +0·53 Å from plane V, so that N(1) occupies a similar position.

The molecules are folded along the line joining the S and N atoms and the dihedral angles between the

Table 4. *Mean plane parameters and deviations of atoms from the plane*

Atoms defining the plane: Equation of the plane	Deviation of atoms defining the plane		Distance of atoms not defining the plane	
I C(1) - C(6) $16.9437x + 0.9631y + 6.5061z = 3.6358$	C(1)	-0.0011 Å	S(4)	-0.0876 Å
	C(2)	-0.0114	N(3)	-0.0308
	C(3)	0.0129	S(3)	0.0096
	C(4)	-0.0016	H(2)	-0.2291
	C(5)	-0.0107	H(3)	-0.1024
	C(6)	0.0119	H(6)	-0.2236
II C(7) - C(12) $13.7040x - 5.9151y + 8.0611z = -2.0574$	C(7)	-0.0157	S(4)	-0.1394
	C(8)	0.0264	N(3)	-0.0616
	C(9)	-0.0135	H(8)	0.2677
	C(10)	-0.0100	H(9)	0.1874
	C(11)	0.0207	H(10)	0.2012
	C(12)	-0.0078	H(11)	0.0473
III C(16) - N(4) - C(17) - C(18) - C(19) - C(20) $17.0583x + 2.9612y + 4.8495z = 2.9129$	C(16)	-0.2434	C(15)	0.2361
	N(4)	0.2484	C(21)	-0.2446
	C(17)	-0.2453		
	C(18)	0.2402		
	C(19)	-0.2318		
	C(20)	0.2318		
IV C(101) - C(106) $16.4287x + 3.2302y + 6.2611z = 6.4990$	C(101)	0.0041	S(2)	0.1030
	C(102)	-0.0016	N(1)	-0.0645
	C(103)	-0.0007	S(1)	-0.0076
	C(104)	0.0004	H(102)	0.0306
	C(105)	0.0021	H(103)	0.1940
	C(106)	-0.0043	H(106)	-0.2096
V C(107) - C(112) $12.3485x - 5.550y + 10.2352z = 7.0430$	C(107)	0.0003	S(2)	0.0077
	C(108)	-0.0214	N(1)	0.0312
	C(109)	0.0272	H(108)	-0.4033
	C(110)	-0.0110	H(109)	-0.1215
	C(111)	-0.0096	H(110)	-0.1022
	C(112)	0.0146	H(111)	0.0416
VI C(116) - N(2) - C(117) - C(118) - C(119) C(120) $16.2075x + 4.4141y + 5.2925z = 8.0860$	C(116)	0.2439	C(115)	-0.2384
	N(2)	-0.2607	C(121)	0.1378
	C(117)	0.2552		
	C(118)	-0.2526		
	C(119)	0.2406		
	C(120)	-0.2264		

planes of the aromatic rings are 145·8° and 134·4° for molecules I and II respectively. The two molecules are oriented at an angle of approximately 10° to each other.

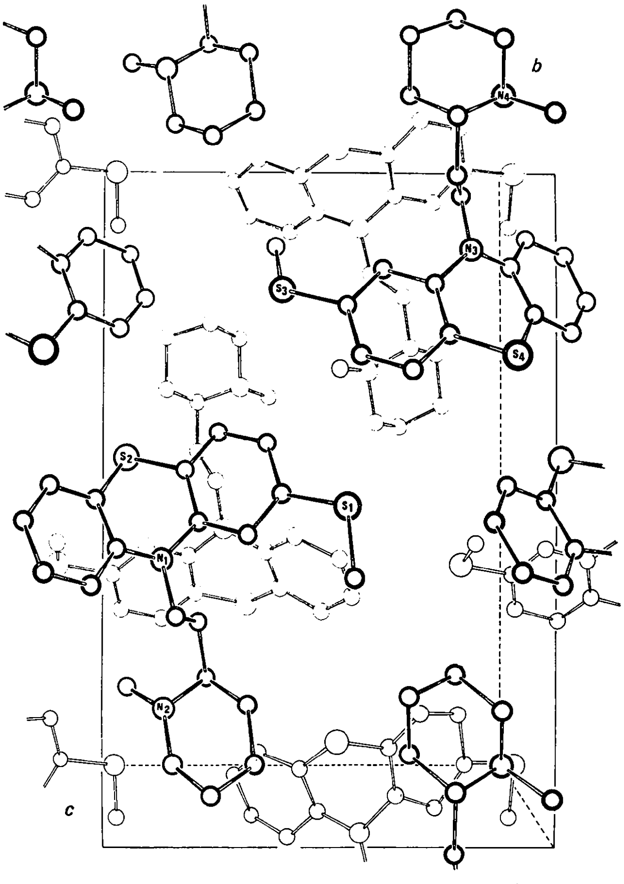


Fig. 2. The structure viewed down the *a* axis.

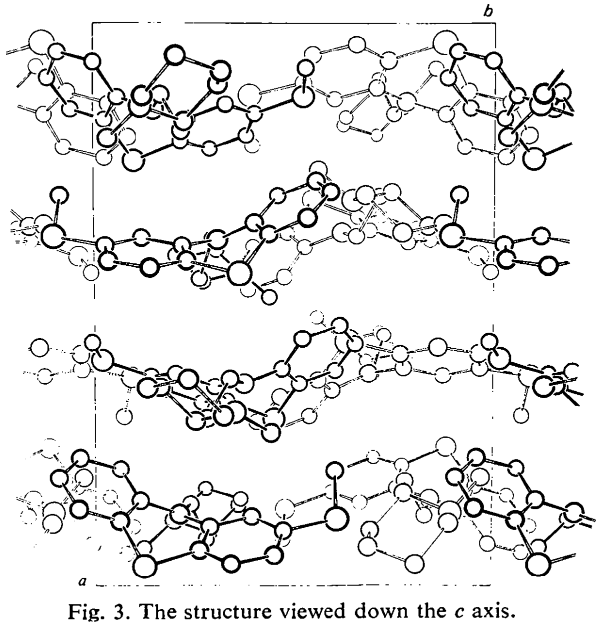


Fig. 3. The structure viewed down the *c* axis.

From Table 4 (planes III and VI) it can be seen that the piperidine rings have the chair configuration. The angles in the rings and angles around the methylated nitrogens N(2) and N(4) are all close to the tetrahedral value (109°). Similar results were found in indolealkylamines studied by Falkenberg & Carlström (1971). The C–N bond lengths in the piperidine ring in molecule I are all close to the three-covalent C–N standard bond of 1·472 Å (Sutton, 1965). However in molecule II, the very high thermal motion of the atoms constituting the piperidine ring renders the bond angles less reliable than those of molecule I.

The molecular configurations are illustrated in Fig. 1, in which the hydrogen atoms are represented by spheres of diameter 0·1 Å; the ellipsoids of the other atoms represent contour surfaces of equal probability density (Johnson, 1970).

Fig. 1 clearly shows that the thermal motion of the two molecules is not identical. In molecule I the librations increase along a direction nearly parallel to **b**, *i.e.* from a point in the central ring outward towards C(9) at one end and C(13) at the other, with S(3) and C(13) having the greatest motion; whereas in molecule II, the librations become increasingly larger from the central ring along the **c** direction towards the piperidine ring, with C(117), C(118), C(119) having extremely large anisotropic vibrations. In addition, the average temperature factor for molecule II is higher than for molecule I. It appears that the environments of the two molecules are not identical, but further calculations and models are still in progress in order to explain the variances.

Fig. 2 is a perspective drawing of one-half the contents of the unit cell (from 0 to *a*/2) viewed down the *a* axis; the view down the *c* axis in Fig. 3 shows the folded molecules in parallel corrugated layers which resemble the arrangement of the molecules in thiethylperazine. Unlike thiethylperazine, but as in chlorpromazine, four of the molecules in the unit cell are 'left-handed', while the other four are 'right-handed' enantiomorphs.

Most of the calculations were performed on a Univac 1106 computer, except for the full refinement cycles of 606 variables, which were carried out on an IBM 360/65 computer. The author is indebted to the CSIR for computing grants and thanks Dr G. Gafner, head of the crystallography division of the Council of Scientific and Industrial Research, for his encouragement and for setting up the crystal and collecting the data on the diffractometer.

References

ABRAHAMS, S. C. (1956). *Quart. Rev.* **10**, 407–436.

BELL, J. D., BLOUNT, J. F., BRISCOE, O. V. & FREEMAN, H. C. (1968). *Chem. Commun.* pp. 1656–1657.

British Pharmaceutical Codex (1973). London, p. 507.

COX, E. G., CRUICKSHANK, D. W. J. & SMITH, J. A. S. (1958). *Proc. Roy. Soc.* A**247**, 1–21.

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

Extra Pharmacopoeia (1972). pp. 1853–1855. London: Martindale.

Falkenberg, G. & Carlström, D. (1971). *Acta Cryst.* B**27**, 411–418.

Hosoya, S. (1966). *Acta Cryst.* **20**, 429–432.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210–214.

Johnson, C. K. (1970). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

Lynton, H. & Cox, E. G. (1956). *J. Chem. Soc.* pp. 4886–4895.

McDowell, J. J. H. (1969). *Acta Cryst.* B**25**, 2175–2181.

McDowell, J. J. H. (1970). *Acta Cryst.* B**26**, 954–964.

Marsau, P. & Busetta, B. (1973). *Acta Cryst.* B**29**, 986–991.

Marsau, P. & Calas, M. R. (1971). *Acta Cryst.* B**27**, 2058–2062.

Marsau, P. & Cam, Y. (1973). *Acta Cryst.* B**29**, 980–986.

Maslen, E. N. (1967). *Acta Cryst.* **22**, 945–946.

Schomaker, V., Waser, J., Marsh, R. E. & Bergman, G. (1959). *Acta Cryst.* **12**, 600–604.

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

Sutton, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Spec. Publ. No. 18, S16s. London: The Chemical Society.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.

X-RAY (1972). X-RAY System, version of June 1972, Technical Report TR-192 of the Computer Science Centre, Univ. of Maryland, U.S.A.

Acta Cryst. (1975). B**31**, 2264

Structure Cristalline du Trimétaphosphate d'Argent Monohydraté, $Ag_3P_3O_9.H_2O$

Par M. Bagieu-Beucher, A. Durif et J. C. Guitel

Laboratoire des Rayons X, CNRS, B.P. 166, *Centre de Tri*, 38042 *Grenoble-Cedex, France*

(*Reçu le* 13 *février* 1975, *accepté le* 8 *avril* 1975)

Silver trimetaphosphate monohydrate, $Ag_3P_3O_9.H_2O$, is triclinic ($P\bar{1}$) with $a=7{\cdot}800$ (5), $b=7{\cdot}796$ (5), $c=9{\cdot}276$ (5) Å, $\alpha=115{\cdot}15$ (5), $\beta=115{\cdot}15$ (5), $\gamma=88{\cdot}93$ (5)°, and $Z=2$. The crystal structure has been determined from 1874 independent reflexions collected with an automatic diffractometer (Mo $K\alpha_1,\alpha_2$). The final R value is 0·048. The P_3O_9 cyclic anion has the chair configuration and possesses a pseudo-mirror plane.

Introduction

Les caractéristiques cristallographiques et la préparation chimique du trimétaphosphate d'argent monohydraté: $Ag_3P_3O_9.H_2O$ ont été précisées par Fleitmann & Henneberg (1848), Eanes (1960) et Grenier (1973). L'intérêt de ce sel réside dans le fait qu'il est la matière première de base de la préparation de nombreux trimétaphosphates (Boullé, 1938).

Techniques expérimentales

Le cristal utilisé était un prisme triclinique choisi suffisamment petit pour qu'aucune correction d'absorption ne soit nécessaire ($\mu R=0{,}2$ pour la dimension maximale). A l'aide d'un diffractomètre automatique Philips PW 1100, 2154 réflexions indépendantes ont été mesurées à l'aide de la longueur d'onde $K\alpha_1,\alpha_2$.

Les conditions expérimentales de mesure étaient les suivantes: vitesse de balayage 0,03° s^{-1}; largeur de balayage 1,20°; type de balayage ω.

Un affinement par moindres carrés de quelques valeurs angulaires relevées à l'aide du diffractomètre automatique conduit à une maille: $a=7{,}800(5)$, $b=7{,}796(5)$, $c=9{,}276(5)$ Å; $\alpha=115{,}15(5)$, $\beta=115{,}15(5)$, $\gamma=88{,}93(5)$°, renfermant deux unités formulaires.

Détermination de la structure

La structure cristalline a été résolue par la méthode de l'atome lourd. L'examen de la synthèse de Patterson tridimensionnelle révèle les trois sites d'argent. Leurs positions font apparaître une pseudo-symétrie par rapport au plan diagonal $\mathbf{a}+\mathbf{b},\mathbf{c}$, que laissaient prévoir l'examen des dimensions de la maille et la comparaison des intensités $I(h,k,l)$ et $I(k,h,l)$. Une synthèse de Fourier effectuée à l'aide de la contribution des seuls atomes d'argent révèle alors la totalité des atomes de phosphore et d'oxygène de l'anion P_3O_9. Un affinement de ces sites suivi d'une synthèse de Fourier-différence permet alors de mettre en évidence la molécule d'eau, de confirmer la centrosymétrie de cet arrangement et l'existence d'un pseudo-miroir $\mathbf{a}+\mathbf{b},\mathbf{c}$ dans la maille.

A ce stade, quelques cycles d'affinement conduisent rapidement à une valeur finale de $R=0{,}048$ pour les