

Fig. 5. Position relative des différents plans moyens P_1 , P_2 , P_3 .

et des cycles A , B et C ainsi que les distances des atomes à ces plans. Les trois cycles A , B et C peuvent être considérés comme plans (respectivement P_1 , P_2 , P_3), par contre l'enchaînement précédent s'écarte légèrement de la planéité, ce qui pourrait s'expliquer par les substitutions sur les atomes de carbone C(5) et C(7). Les différents plans moyens P_1 , P_2 , P_3 (Fig. 5) calculés précédemment permettent d'évaluer les angles dièdres entre les cycles: $29,4^\circ$ entre B et C [en accord avec la valeur déterminée par Horwik & Kjøgh (1965) dans l'ion phényl-3 dithiole-1,2 ylium]; 76° entre A et B , valeur prévisible compte-tenu de l'encombrement stérique de l'atome S(1).

Les distances intermoléculaires les plus courtes sont $S(1)-S(1') = 3,85 \text{ \AA}$ et $S(1)-S(2') = 3,84 \text{ \AA}$, l'indice prime étant affecté à la molécule homologue se déduisant par le plan de glissement c . Ces valeurs sont proches de la somme des rayons de van der Waals.

Notre étude a permis d'établir la conformation du cyano-2 phényl-3 (phényl-5 dithiole-1,2 ylidène-3)-4 butène-2 nitrile, en désaccord avec le modèle proposé par Behringer & Falkenberg (1969), et en accord avec

l'un des deux modèles retenus par Catel (1975) et Catel & Mollier (1976).

Nos remerciements vont à J. M. Catel et Y. Mollier pour les discussions fructueuses et l'intérêt qu'ils ont manifesté pour ce travail, ainsi qu'à N. Rodier qui a effectué les mesures des intensités.

Références

- BEHRINGER, H. & FALKENBERG, J. (1969). *Chem. Ber.* **102**, 1580–1591.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
 CATEL, J. M. (1975). Thèse de Doctorat de Spécialité, Univ. de Caen.
 CATEL, J. M. & MOLLIER, Y. (1976). *C.R. Acad. Sci. Sér. C*, **282**, 361–363.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
 GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* **B24**, 91–96.
 HORWIK, A. & KJOGH, M. (1965). *Acta Chem. Scand.* **19**, 935–946.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.
 IWASAKI, F. & AIHARA, A. (1970). *Acta Cryst.* **B26**, 91–97.
 KEHL, W. L. & JEFFREY, G. A. (1958). *Acta Cryst.* **11**, 813–819.
 PHILLIPS, T. E., KISTENMACHER, T. J., BLOCH, A. N., FERRARIS, J. P. & COWAN, D. O. (1977). *Acta Cryst.* **B33**, 422–428.
 PINEL, R., MOLLIER, Y., LLAGUNO, E. C. & PAUL, I. C. (1971). *Chem. Commun.* pp. 1352–1353.

Acta Cryst. (1978). **B34**, 686–689

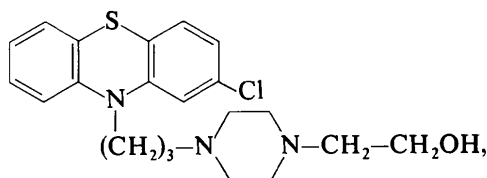
Perphenazine, a Phenothiazine Derivative

BY J. J. H. MCDOWELL

Department of Organic Chemistry, University of Cape Town, Rondebosch 7700, South Africa

(Received 1 September 1977; accepted 26 September 1977)

Abstract. C₁₈H₁₆N₂S, 2-chloro-10-[3-[4-(2-hydroxyethyl)piperazin-1-yl]propyl]phenothiazine,



monoclinic, Cc , $a = 20.930(2)$, $b = 11.900(2)$, $c = 8.140(2) \text{ \AA}$, $\beta = 90.26(8)^\circ$, $D_m = 1.30$, $D_c = 1.32 \text{ g cm}^{-3}$ for $Z = 4$. The structure of the potent tranquillizer drug perphenazine has been determined by direct methods and refined by full-matrix least squares to a final $R_w = 0.043$. In the tricyclic group, $C-S-C$ is $97.7(8)^\circ$, $C-S(\text{mean}) = 1.73(2)$, $C-N(\text{mean}) = 1.41(2)$, $C-O = 1.39(2)$ and $C-Cl = 1.75(2) \text{ \AA}$. The dihedral angle between the planes of the benzene rings

Table 1. Final atomic fractional coordinates ($\times 10^4$) with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
C1	-325 (3)	5172 (4)	1545 (7)
S	1069 (0)	558 (4)	2010 (0)
O	4388 (8)	3276 (13)	12244 (20)
N(1)	1280 (6)	2486 (10)	4263 (15)
N(2)	2349 (6)	3503 (9)	8372 (14)
N(3)	3626 (6)	3833 (12)	9585 (16)
C(1)	81 (8)	3888 (16)	1690 (21)
C(2)	-60 (7)	3072 (16)	526 (18)
C(3)	270 (8)	2029 (17)	578 (21)
C(4)	708 (7)	1859 (13)	1872 (19)
C(5)	846 (7)	2714 (15)	2998 (21)
C(6)	538 (7)	3725 (14)	2878 (18)
C(7)	1807 (9)	1008 (13)	2720 (19)
C(8)	2374 (10)	489 (15)	2284 (21)
C(9)	2960 (9)	808 (17)	2975 (25)
C(10)	2982 (11)	1669 (19)	4044 (25)
C(11)	2448 (7)	2243 (12)	4485 (19)
C(12)	1851 (8)	1914 (13)	3836 (17)
C(13)	1285 (7)	3240 (13)	5713 (18)
C(14)	1413 (7)	2564 (14)	7288 (17)
C(15)	1675 (7)	3338 (14)	8648 (17)
C(16)	2726 (7)	2570 (13)	9052 (20)
C(17)	3444 (8)	2794 (14)	8801 (23)
C(18)	3250 (7)	4769 (14)	9003 (20)
C(19)	2558 (7)	4526 (12)	9250 (19)
C(20)	4316 (8)	4039 (18)	9546 (22)
C(21)	4666 (9)	3381 (20)	10700 (28)
H(2)	-427 (7)	3214 (16)	-396 (18)
H(3)	193 (8)	1386 (17)	-338 (21)
H(6)	648 (7)	4400 (14)	3721 (18)
H(8)	2362 (10)	-207 (15)	1432 (21)
H(9)	3396 (9)	378 (17)	2649 (25)
H(10)	3441 (11)	1922 (19)	4525 (25)
H(11)	2472 (7)	2921 (12)	5365 (19)
H(131)	1668 (7)	3837 (13)	5553 (18)
H(132)	836 (7)	3683 (13)	5798 (18)
H(141)	973 (7)	2170 (14)	7668 (17)
H(142)	1768 (7)	1926 (14)	7047 (17)
H(151)	1589 (7)	2985 (14)	9849 (17)
H(152)	1435 (7)	4139 (14)	8547 (17)
H(161)	2629 (7)	2455 (13)	10343 (20)
H(162)	2591 (7)	1822 (13)	8386 (20)
H(171)	3550 (8)	2846 (14)	7505 (23)
H(172)	3712 (8)	2111 (14)	9342 (23)
H(181)	3385 (7)	5514 (14)	9679 (20)
H(182)	3345 (7)	4895 (14)	7713 (20)
H(191)	2283 (7)	5224 (12)	8778 (19)
H(192)	2468 (7)	4432 (12)	10548 (19)
H(201)	4403 (8)	4909 (18)	9852 (22)
H(202)	4485 (8)	3872 (18)	8319 (22)
H(211)	5141 (9)	3721 (20)	10841 (28)
H(212)	4695 (9)	2542 (20)	10200 (28)
H(213)	4257 (103)	3981 (169)	12439 (265)

is 140.7° . The piperazine ring has the chair configuration.

Introduction. The material was supplied by Sherag. Colourless transparent plate-like crystals were grown by repeated slow recrystallizations from a solution of perphenazine in 40–60°C petroleum spirit with a few drops of 60–80°C. Systematic absences noted on Weissenberg photographs were hkl , $h + k \neq 2n$, and $h0l$, $l \neq 2n$, indicating space groups Cc or $C2/c$.

Table 2. Bond lengths (Å) and angles ($^\circ$) with e.s.d.'s

C(1)–C(2)	1.388 (22)	N(1)–C(13)	1.482 (17)
C(2)–C(3)	1.422 (23)	C(13)–C(14)	1.537 (20)
C(3)–C(4)	1.408 (21)	C(14)–C(15)	1.538 (19)
C(4)–C(5)	1.399 (21)	C(15)–N(2)	1.443 (16)
C(5)–C(6)	1.368 (21)		
C(6)–C(1)	1.371 (20)	N(2)–C(16)	1.470 (17)
C(1)–C1	1.752 (18)	C(16)–C(17)	1.541 (21)
		C(17)–N(3)	1.441 (19)
C(7)–C(8)	1.386 (22)	N(3)–C(18)	1.443 (19)
C(8)–C(9)	1.399 (24)	C(18)–C(19)	1.493 (17)
C(9)–C(10)	1.345 (26)	C(19)–N(2)	1.477 (18)
C(10)–C(11)	1.359 (25)		
C(11)–C(12)	1.410 (18)	N(3)–C(20)	1.465 (19)
C(12)–C(7)	1.414 (20)	C(20)–C(21)	1.423 (24)
		C(21)–O	1.392 (24)
C(4)–S	1.726 (17)	O–H(213)	0.897 (195)
C(7)–S	1.731 (17)		
C(5)–N(1)	1.397 (18)		
C(12)–N(1)	1.419 (17)		
C(6)–C(1)–C(2)	121.9 (16)	C(3)–C(4)–S	121.4 (12)
C(1)–C(2)–C(3)	119.2 (15)	C(8)–C(7)–S	122.7 (14)
C(2)–C(3)–C(4)	117.6 (15)	C(6)–C(5)–N(1)	121.9 (15)
C(3)–C(4)–C(5)	121.2 (16)	C(11)–C(12)–N(1)	121.4 (13)
C(4)–C(5)–C(6)	119.8 (14)	C(5)–N(1)–C(13)	118.1 (12)
C(5)–C(6)–C(1)	120.1 (15)	C(12)–N(1)–C(13)	118.9 (11)
C1–C(1)–C(2)	117.5 (14)		
C1–C(1)–C(6)	120.5 (14)	N(1)–C(13)–C(14)	110.4 (12)
		C(13)–C(14)–C(15)	110.3 (12)
C(12)–C(7)–C(8)	116.8 (16)	C(14)–C(15)–N(2)	108.3 (11)
C(7)–C(8)–C(9)	121.8 (17)	C(15)–N(2)–C(16)	111.3 (11)
C(8)–C(9)–C(10)	119.6 (17)	C(15)–N(2)–C(19)	108.9 (11)
C(9)–C(10)–C(11)	121.9 (20)		
C(10)–C(11)–C(12)	119.3 (16)	C(19)–N(2)–C(16)	106.4 (10)
C(11)–C(12)–C(7)	120.6 (14)	N(2)–C(16)–C(17)	110.0 (12)
		C(16)–C(17)–N(3)	110.2 (12)
C(4)–S–C(7)	97.7 (8)	C(17)–N(3)–C(18)	112.0 (12)
S–C(7)–C(12)	120.4 (13)	N(3)–C(18)–C(19)	109.5 (12)
C(7)–C(12)–N(1)	121.4 (13)	C(18)–C(19)–N(2)	112.3 (12)
C(12)–N(1)–C(5)	117.3 (11)		
N(1)–C(5)–C(4)	118.3 (14)	C(17)–N(3)–C(20)	113.1 (15)
C(5)–C(4)–S	121.4 (12)	C(18)–N(3)–C(20)	113.5 (13)
		N(3)–C(20)–C(21)	113.5 (16)
		C(20)–C(21)–O	115.4 (17)
		C(21)–O–H(213)	101.8 (143)

Intensities were collected on a Philips PW 1100 four-circle diffractometer with graphite-monochromated $\text{Mo } K\alpha$ ($\lambda = 0.7107 \text{ \AA}$) radiation at a temperature of 20°C . The ω -scan mode was used with a scan rate of $0.04^\circ \text{ s}^{-1}$ and a scan width of 1.2° in θ . Background counts of 15 s on each side of the reflexion were taken. 1006 reflexions, including 75 systematically extinct and 204 rated as unobserveds [$I < 1.65\sigma(I)$], were measured within a sphere $\theta_{\text{max}} = 20^\circ$. The lattice constants were obtained by least-squares refinement of 2θ , χ and φ angles for 25 reflexions. Only Lorentz–polarization corrections were applied as μr for the crystal ($0.4 \times 0.4 \times 0.3 \text{ mm}$) was < 0.07 .

Analysis of the $|E|$ statistics and distribution emphatically indicated the noncentrosymmetric space group Cc , which was confirmed by the refinement. Using the program *SHELX 76* (Sheldrick, 1976), which incorporates a multiresolution tangent-formula

Table 3. Mean-plane parameters and deviations of atoms from the plane (Å)

Deviations of atoms defining the plane		Distances of atoms not defining the plane	
(I) C(1)–C(6)			
$15.0468x + 4.2300y - 4.8886z = 0.9578$			
C(1)	-0.0165	S	-0.0960
C(2)	-0.0061	N(1)	-0.0637
C(3)	0.0244	C(13)	-0.4468
C(4)	-0.0209	Cl	-0.0140
C(5)	-0.0016	H(2)	-0.0431
C(6)	0.0207	H(3)	0.0847
		H(6)	0.0584
(II) C(7)–C(12)			
$2.7274x + 7.5997y - 6.1781z = -0.4092$			
C(7)	-0.0125	S	-0.1173
C(8)	0.0171	N(1)	0.0137
C(9)	-0.0073	C(13)	-0.3074
C(10)	-0.0070	H(8)	0.0115
C(11)	0.0109	H(9)	-0.0137
C(12)	-0.0013	H(10)	0.0131
		H(11)	-0.0113
(III) N(2)–C(16)–C(17)–N(3)–C(18)–C(19)			
$-3.5278x - 1.1287y + 7.9924z = 5.7322$			
N(2)	-0.2651	C(15)	0.2118
C(16)	0.2509	C(20)	-0.0807
C(17)	-0.2290		
N(3)	0.2171		
C(18)	-0.2216		
C(19)	0.2477		

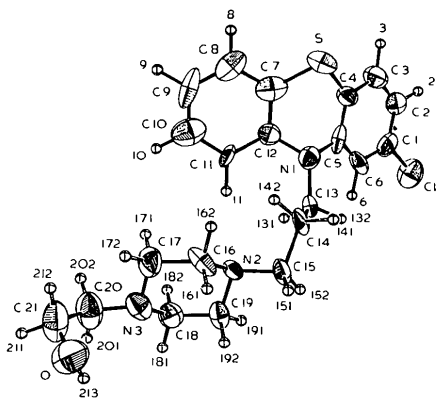
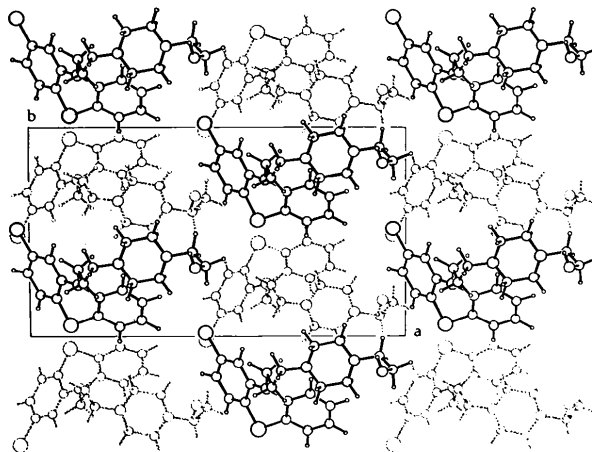


Fig. 1. Thermal-vibration ellipsoids and atomic numbering.

phasing procedure, five reflexions were hand-selected from 187 with $E \geq 1.2$. The E map with the highest figure of merit located 23 of the non-H atoms; the remaining four were found on the first Fourier map. Using the XRAY system (1972), three cycles of full-matrix least-squares refinement of coordinates and individual isotropic B 's of all non-H atoms, followed by two cycles with anisotropic β 's, reduced R to 0.076 where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. The function

Fig. 2. The structure viewed down the c axis.

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; later $w(hkl) = k / (\sigma^2 |F_o| + |g| F_o^2)$ with a final $k = 0.76$ and $g = 0.0002$. The scattering factors of Cromer & Mann (1968) were used for Cl, S, O, N and C, and those of Stewart, Davidson & Simpson (1965) for H. The H atoms were located on successive difference Fourier syntheses but the ratio of reflexions to variables (931 to 320) was considered inadequate for satisfactory convergence. Therefore, with the exception of H(213) which was allowed to refine freely, the H atoms were placed in idealized positions and constrained to 'ride' on the C atoms to which they are attached. They were assigned isotropic thermal parameters equal to those of the carrier atoms; six further cycles converged to final R and R_w values for observed reflexions of 0.051 and 0.043 respectively. (R and R_w for all reflexions = 0.071 and 0.051 respectively.) Positional parameters are given in Table 1.*

Discussion. Perphenazine is a potent tranquillizer with actions and uses similar to chlorpromazine, but it is effective in much smaller doses and rarely produces undesirable effects (*British Pharmaceutical Codex*, 1973). The bond lengths and angles of the molecule are presented in Table 2 and agree well with values for other phenothiazine derivatives, except for C–S which at 1.728 (17) Å has more double-bond character (20%)

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33033 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Selected torsion angles

τ_1	C(4)–C(5)–N(1)–C(13)	–162.1°	τ_9	C(15)–N(2)–C(16)–C(17)	–177.7°
τ_2	C(7)–C(12)–N(1)–C(13)	165.1	τ_{10}	C(15)–N(2)–C(19)–C(18)	–179.0
τ_3	C(5)–N(1)–C(13)–C(14)	143.4	τ_{11}	C(19)–N(2)–C(16)–C(17)	–59.2
τ_4	C(12)–N(1)–C(13)–C(14)	–64.1	τ_{12}	C(16)–N(2)–C(19)–C(18)	60.9
τ_5	N(1)–C(13)–C(14)–C(15)	158.0	τ_{13}	N(2)–C(16)–C(17)–N(3)	58.7
τ_6	C(13)–C(14)–C(15)–N(2)	–80.8	τ_{14}	N(2)–C(19)–C(18)–N(3)	–59.3
τ_7	C(14)–C(15)–N(2)–C(16)	–83.1	τ_{15}	C(16)–C(17)–N(3)–C(20)	173.8
τ_8	C(14)–C(15)–N(2)–C(19)	159.9	τ_{16}	C(19)–C(18)–N(3)–C(20)	–174.2
			τ_{17}	C(16)–C(17)–N(3)–C(18)	–56.4
			τ_{18}	C(19)–C(18)–N(3)–C(17)	56.3

than is generally found, the range of C–S bonds in this group of compounds lying between 1.75 and 1.78 Å. However, a value of 1.734 (8) Å was reported for trifluorpromazine (Phelps & Cordes, 1974) and short C–S bonds [mean 1.733 (3) Å] were also observed in one member of the thioxanthone series, 2-chlorothioxanthone (Chu & Yang, 1976). The sum of the angles about N(1) is 354.3°; thus N(1) forms the apex of a flattened pyramid with C(6), C(12), C(13) as the base.

The molecular configuration and atomic numbering are illustrated in Fig. 1, drawn by *ORTEP* (Johnson, 1970). Table 3 shows that the benzene rings are planar within the limits of precision whereas S and N(1) lie asymmetrically out of the planes. The dihedral angle between the planes is 140.7°. Table 4 lists selected torsion angles, calculated by the method of Allen & Rogers (1969). It is interesting to note that τ_3 and τ_4 are close to the values found in 7-hydroxychlorpromazine (McDowell, 1977) but the remaining angles in the first column of Table 4 clearly relate the molecule to chlorpromazine. The values of τ_9 – τ_{18} demonstrate the symmetry of the piperazine ring. Fig. 2 (drawn by *PLUTO*, a program written by Dr W. D. S. Motherwell) illustrates the packing of the molecules in the unit cell. There are no abnormally short intermolecular contacts.

The author is indebted to the South African Council of Scientific and Industrial Research for a running-expenses grant and sincerely thanks Dr G. Gafner of the CSIR for the data-collection service.

References

- ALLEN, F. H. & ROGERS, D. (1969). *Acta Cryst.* B25, 1326–1330.
British Pharmaceutical Codex (1973). P. 358. London: The Pharmaceutical Press.
 CHU, S. S. C. & YANG, H. T. (1976). *Acta Cryst.* B32, 2248–2250.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
 JOHNSON, C. K. (1970). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 MCDOWELL, J. J. H. (1977). *Acta Cryst.* B33, 771–774.
 PHELPS, D. W. & CORDES, A. W. (1974). *Acta Cryst.* B30, 2812–2816.
 SHELDRIK, G. M. (1976). *SHELX 76. A 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.
 XRAY system (1972). Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, revised 1974.

Acta Cryst. (1978). B34, 689–691

Réexamen de la Structure du Complexe Hexaméthylènetétrathiofulvalène–Tétracyanoquinodiméthane

PAR D. CHASSEAU, G. COMBERTON, J. GAULTIER ET C. HAUW

Laboratoire de Cristallographie, Université de Bordeaux I, 351 cours de la Libération, 33405 Talence, France

(Reçu le 19 septembre 1977, accepté le 6 octobre 1977)

Abstract. HMTTF–TCNQ, orthorhombic, *Pmna*, $a = 12.462$ (4), $b = 3.901$ (2), $c = 21.597$ (6) Å, $Z = 2$, $D_x = 1.54$ g cm⁻³; in agreement with previously published work by Greene, Mayerle, Schumaker, Castro,

Chaikin, Etemad & La Placa [*Solid State Commun.* (1976), 20, 943–946]. The cell constants and intensity data were collected with an Enraf–Nonius CAD-4 automatic diffractometer, Cu $K\alpha$ radiation and a