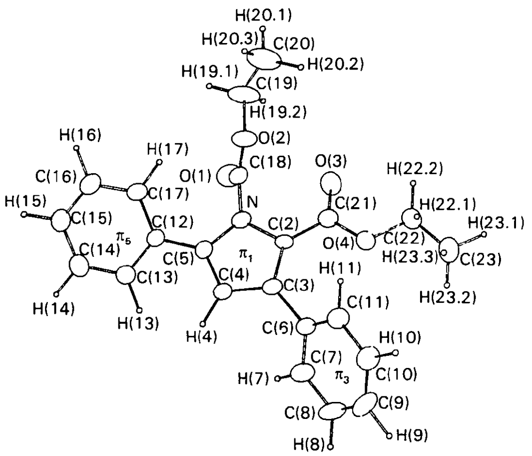


Fig. 1. Tracé *ORTEP* (Johnson, 1965) de la molécule 1: $C_{22}H_{21}NO_4$.

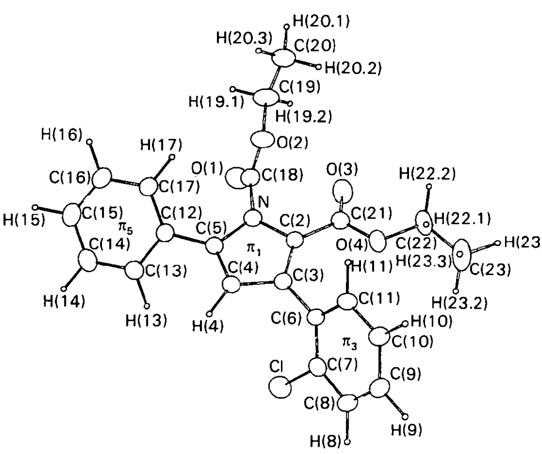


Fig. 2. Tracé *ORTEP* (Johnson, 1965) de la molécule 2: $C_{22}H_{20}ClNO_4$.

D'autre part, on remarque également une modification des déplacements chimiques des protons appartenant à la chaîne éthyle de la fonction carbamate de (2) par rapport à ceux de (1). Le déblindage observé peut s'expliquer par la variation des angles d'une part entre π_5 et π_1, et d'autre part entre celui de la chaîne et π_1, qui se traduit par un éloignement de l'ensemble éthoxy vis-à-vis du milieu M_5 du phényle en 5.

Les effets stériques son peu importants. La présence d'un atome de chlore en *ortho* du phényle en 3 ne provoque que de faibles contraintes stériques qui se traduisent par un léger accroissement de la valeur de l'angle entre les plans du phényle et du noyau pyrrole. Les protons de la chaîne ester voisine sont, de ce fait, davantage à proximité du cône de blindage et présentent un déplacement vers les champs forts. Ce phénomène est observé en RMN du proton pour tous les composés *ortho* substitués que nous avons synthétisés, démontrant par là une modification conformationnelle analogue. Mais, cette étude présente surtout l'intérêt de mettre en évidence un réarrangement qui survient lors de la déshydrogénation des dihydro-3,4 2*H*-pyrroles correspondantes au moyen du chloranile.

Les auteurs remercient M Sylvain Lecocq du Centre de Diffractométrie de l'Université de Lyon 1 pour les mesures des intensités des réflexions des deux cristaux.

Références

Birouk, M. (1981). DEA de Chimie Structurale, Faculté des Sciences, Besançon.

International Tables for X-ray Crystallography (1974). Tome IV. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Rapport ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Koch, J., Robert, J. F. & Panouse, J. J. (1978). *C.R. Acad. Sci. Sér. C*, **286**, 95–98.

Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. de York, Angleterre, et Louvain, Belgique.

Sheldrick, G. M. (1976). *SHELX*. Programme pour la détermination de structure. Univ. de Cambridge, Angleterre.

Acta Cryst. (1984). C**40**, 1281–1283

1-Isopropyl-10-methylphenothiazine, $C_{16}H_{17}NS$

By Shirley S. C. Chu, S. V. L. Narayana and Robert D. Rosenstein

School of Engineering and Applied Science, Southern Methodist University, Dallas, Texas 75275, *USA*

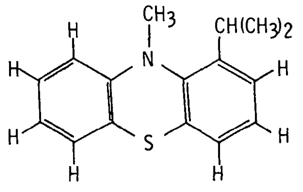
(*Received* 20 *January* 1984; *accepted* 27 *March* 1984)

Abstract. $M_r = 255{\cdot}37$, monoclinic, $P2_1/c$, $a = 12{\cdot}273\,(1)$, $b = 7{\cdot}998\,(1)$, $c = 14{\cdot}926\,(1)$ Å, $\beta = 111{\cdot}395\,(1)°$, $V = 1364{\cdot}2\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}243$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}875$ mm^{-1}, $F(000) = 544$, $T = 298$ K. Final $R = 0{\cdot}047$ for 2135 observed reflections. The central ring of the phenothiazine ring system is in a boat conformation. The folding angle between the least-squares

0108-2701/84/071281-03$01.50

planes of the two benzo rings is 143·0 (1)°. The 10-methyl group is in a quasi-axial conformation with respect to the central ring of the phenothiazine ring system due to the interaction with the 1-isopropyl group.

Introduction. The determination of the structure of the title compound (I) is part of a continuous study of 1-substituted, 10-substituted and 1,10-disubstituted phenothiazines. The crystal structures of a number of 1- and 10-substituted phenothiazines have been determined in this laboratory (Chu & van der Helm, 1974, 1975, 1976; Chu & Yang, 1977; Chu, Napoleone, Ternay & Chang, 1982*a*,*b*). The crystal structure of 1-isopropyl-10-methylphenothiazine is reported in this paper to determine the effect of 1,10-disubstituents on the conformation and configuration of the phenothiazine ring system.



(I)

Experimental. Single crystals obtained through the courtesy of Dr A. L. Ternay Jr of the Department of Chemistry, University of Texas at Arlington, unit-cell parameters by least-squares analysis of 15 reflections with 2θ from 20 to 80°, space group $P2_1/c$ determined from systematic absences ($h0l$ absent with l odd, $0k0$ absent with k odd), automatic diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, crystal $0{\cdot}11 \times 0{\cdot}32 \times 0{\cdot}08$ mm, $\theta/2\theta$ scanning mode, 2276 independent reflections, $2\theta < 130°$, range of hkl: $0\rightarrow14$, $0\rightarrow9$, $-17\rightarrow16$, 2135 observed, $I > 3\sigma(I)$, three standard reflections measured after every 50 reflections with a random variation of less than 4% in intensity, Lorentz–polarization corrections, no absorption or extinction corrections; direct methods (*MULTAN*, Germain, Main & Woolfson, 1971), refinement by block-diagonal least squares (Shiono, 1971), anisotropic, H positions located in a difference Fourier synthesis, isotropic temperature factors for H atoms, $w = 1/[\sigma(F)]^2$, $\sigma(F)$ from counting statistics, $\sum w(|F_o| - |F_c|)^2$ minimized; $R = 0{\cdot}047$, $R_w = 0{\cdot}054$, $S = 0{\cdot}90$; $(\Delta/\sigma)_{\max} = 0{\cdot}15$, max. and min. heights in final ΔF map 0·2 and $-0{\cdot}3$ e Å^{-3}; atomic scattering factors for S, N and C from *International Tables for X-ray Crystallography* (1962), for H from Stewart, Davidson & Simpson (1965).

Table 1. *Fractional atomic coordinates for non*-H ($\times10^4$) *and for* H *atoms* ($\times10^3$), *with equivalent isotropic thermal parameters for non*-H ($\times10^4$) *and isotropic for* H *atoms* ($\times10^3$)

E.s.d.'s are given in parentheses.

	x	y	z	U_{eq}*/U_{iso}(Å^2)
S(5)	8655 (1)	6667 (1)	5283 (<1)	536 (2)
N(10)	7113 (2)	9539 (3)	4218 (1)	458 (5)
C(1)	6734 (2)	8356 (3)	2616 (2)	483 (6)
C(2)	6899 (2)	7051 (<1)	2066 (2)	582 (7)
C(3)	7576 (2)	5670 (3)	2462 (2)	613 (7)
C(4)	8126 (2)	5560 (3)	3446 (2)	566 (7)
C(6)	9869 (2)	9278 (3)	6378 (2)	542 (7)
C(7)	10023 (2)	10937 (4)	6653 (2)	578 (7)
C(8)	9234 (2)	12117 (3)	6120 (2)	595 (7)
C(9)	8293 (2)	11655 (3)	5311 (2)	525 (6)
C(11)	7266 (2)	8223 (3)	3619 (2)	443 (6)
C(12)	7961 (2)	6837 (3)	4024 (2)	466 (6)
C(13)	8900 (2)	8804 (3)	5577 (2)	454 (6)
C(14)	8111 (2)	9984 (3)	5040 (2)	442 (5)
C(15)	6011 (2)	9566 (4)	4363 (2)	661 (8)
C(16)	6044 (2)	9886 (3)	2136 (2)	535 (7)
C(17)	4824 (3)	9446 (4)	1427 (3)	855 (10)
C(18)	6701 (3)	10885 (4)	1618 (3)	984 (12)
H(2)	660 (2)	713 (3)	140 (2)	72 (8)
H(3)	771 (2)	477 (3)	207 (2)	74 (8)
H(4)	865 (3)	459 (4)	378 (2)	93 (10)
H(6)	1048 (2)	850 (3)	678 (2)	79 (9)
H(7)	1071 (2)	1132 (3)	724 (2)	74 (8)
H(8)	933 (2)	1331 (4)	629 (2)	96 (10)
H(9)	779 (2)	1254 (3)	493 (2)	74 (8)
H(15)1	591 (2)	1056 (3)	474 (2)	85 (9)
H(15)2	542 (3)	951 (4)	380 (2)	96 (10)
H(15)3	590 (3)	845 (4)	481 (2)	124 (12)
H(16)	602 (2)	1069 (3)	261 (2)	70 (8)
H(17)1	447 (3)	879 (5)	183 (2)	149 (14)
H(17)2	441 (3)	1048 (4)	117 (2)	115 (11)
H(17)3	491 (3)	879 (5)	83 (2)	158 (14)
H(18)1	690 (4)	1015 (6)	110 (3)	230 (21)
H(18)2	735 (3)	1126 (4)	224 (2)	143 (13)
H(18)3	633 (3)	1192 (5)	140 (3)	152 (15)

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

Discussion. The final parameters are given in Table 1.[*] The identification of the atoms and the configuration of the molecules are shown in Fig. 1. The bond lengths and bond angles with their standard deviations are shown in Fig. 2. The mean C—S bond length and C—S—C bond angle have similar magnitudes to those in 1- and 10-substituted phenothiazines (Chu & van der Helm, 1974, 1975, 1976; Chu *et al.*, 1982*a*,*b*). However, the bond angles of C(15)—N(10)—C(11) [116·5 (2)°] and C(16)—C(1)—C(11) [121·9 (2)°] are larger than those of C(15)—N(10)—C(14) [115·0 (2)°] and C(16)—C(1)—C(2) [120·4 (2)°], respectively. The differences in the bond angles are due apparently to the non-bonded interaction between the 1-isopropyl and 10-methyl substituents. The closest non-bonded intramolecular distance between the 1-isopropyl and 10-methyl groups is 2·36 (4) Å for H(15)2—H(16) and the closest non-bonded intramolecular distance on the side of the benzo ring without any substituent is

---

[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39357 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2·73 (4) Å between H(15)1 and H(9). All the C—H bond lengths and C—C—H and H—C—H bond angles are within reasonable ranges of magnitudes.

The phenothiazine ring is folded, with the central ring in a boat conformation as shown by the torsion angles in Fig. 1. The Cremer & Pople (1975) puckering parameters for the central ring are: $q_2 = 0{\cdot}527$, $q_3 = 0{\cdot}054$, $Q = 0{\cdot}530$ Å, $\varphi_2 = 358{\cdot}6$ and $\theta = 84{\cdot}2°$. For ideal boat conformation, these parameters are: $q_2 = Q$, $q_3 = 0$, $\varphi_2 = 360$ and $\theta = 90°$. The 10-methyl group is in a quasi-axial conformation with respect to the central ring instead of the equatorial conformation as observed in 1- or 10-substituted phenothiazines. The quasi-axial conformation can also be shown by the sum of the three C—N—C bond angles of 348·4° in the title compound. In all 1- or 10-substituted phenothiazines, the three N—C bonds are nearly planar in configuration. The more pyrimidal characteristics of the three N—C bonds in the title compound can be attributed to the non-bonded interactions between the 1-isopropyl and 10-methyl substituents. The two benzo rings are planar; the equations of the least-squares planes are $0{\cdot}8806\,(5)x + 0{\cdot}0472\,(1)y - 0{\cdot}364\,(1)z = 8{\cdot}999\,(6)$ and $0{\cdot}8089\,(7)x - 0{\cdot}128\,(1)y - 0{\cdot}8295\,(6)z = 2{\cdot}84\,(1)$ for rings *A* and *B* respectively. The deviations of atoms range from 0·001 to 0·011 Å for plane *A* and from 0·004 to 0·012 Å for plane *B* with an e.s.d. of 0·003 Å. The folding angle between the planes of the two benzo rings is 143·0 (1)°, which is similar to the 143·7° in 10-methylphenothiazine (Chu & van der Helm, 1974). The deviation of C(16) of the 1-isopropyl substituent from the least-squares plane of ring *A* is 0·103 (4) Å as compared with that of 0·098 Å in 1-isopropylphenothiazine (Chu *et al.*, 1982*a*). The conformation of the 1-isopropyl substituent with respect to the benzo ring in the title compound is different from that in 1-isopropylphenothiazine as indicated by the torsion angles about the C(1)—C(16) bond. The torsion angles of C(2)—C(1)—C(16)—C(17) and C(2)—C(1)—C(16)—C(18) in the title compound are 54·7 (3) and −67·8 (3)° respectively. The corresponding torsion angles are 31·7 (6) and 94·2 (5)° in 1-isopropylphenothiazine. The different conformation in the title compound is the consequence of the non-bonded intramolecular interaction between the 1-isopropyl and 10-methyl substituents. Since the size of the 10-methyl substituent is small, the non-bonded interaction is minimized by the change of conformation of the 10-methyl and the 1-isopropyl substituents. The effects on the folding angle and on the conformation of the phenothiazine ring system are negligible.

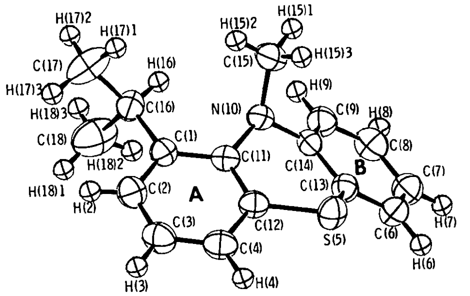


Fig. 1. *ORTEP* drawing (Johnson, 1965) of one molecule of the title compound. The torsion angles around the central ring are: S(5)—C(13)—C(14)—N(10) −2·8 (3), N(10)—C(11)—C(12)—S(5) 0·7 (3), C(13)—C(14)—N(10)—C(11) −37·2 (3), C(11)—C(12)—S(5)—C(13) −32·0 (2), C(14)—N(10)—C(11)—C(12) 38·1 (3), C(12)—S(5)—C(13)—C(14) 33·1 (2)°.

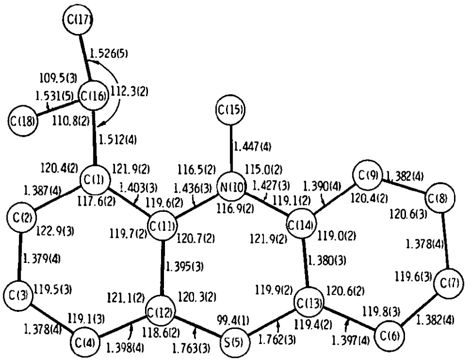


Fig. 2. Bond lengths (Å) and bond angles (°) of the title compound with e.s.d.'s in parentheses.

The packing of the molecules in the unit cell is determined by the van der Waals interactions. There are no intramolecular contacts less than 3·5 Å between non-H atoms.

This research was supported by a grant from the Robert A. Welch Foundation, Houston, Texas.

References

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.

Chu, S. S. C., Napoleone, V., Ternay, A. L. Jr & Chang, S. (1982*a*). *Acta Cryst.* B**38**, 2506–2508.

Chu, S. S. C., Napoleone, V., Ternay, A. L. Jr & Chang, S. (1982*b*). *Acta Cryst.* B**38**, 2508–2511.

Chu, S. S. C. & Yang, H. T. (1977). *Acta Cryst.* B**33**, 1892–1896.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Schomaker, V. & Marsh, R. E. (1983). *Acta Cryst.* A**39**, 810–820.

Shiono, R. (1971). Tech. Rep. 49. Crystallography Department, Univ. of Pittsburgh.

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