

these result in the slightly shorter H(82)···C(2) and C(3) contacts in the present structure. Both six-membered rings have distorted half-chair conformations; C(4a) and C(8a) deviate by  $-0.45$  and  $+0.31$  Å from the mean plane of C(1) to C(4), and by  $+0.36$  and  $-0.41$  Å from the mean plane of C(5) to C(8) (e.s.d. of deviations =  $0.004$  Å). The carbonyl group is planar to within three standard deviations.

Molecules in the crystal are linked by hydrogen bonds, O(1)···O(4) =  $2.770$  (4) Å, O(4)—H(O4)···O(1) =  $164$  (9)°, to form chains along *a*. The molecular-packing diagram has been deposited.

### Photoproduct

The molecular structure of the polycyclic hemiacetal photoproduct (II) is shown in Fig. 1, where the atom numbering of the parent naphthoquinol (I) is retained. The structures allow the solid-state photoconversion (I) → (II) to be assigned as H abstraction from C(8) by C(3), C(2) to C(8) bonding (I'), and finally cyclization [C(1) to O(4) bonding] to form the hemiacetal (II) (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980).

The six-membered ring, C(4a), C(5), C(6), C(7), C(8), C(8a), is in a flattened half-chair conformation, with C(4a) and C(8a) displaced by  $+0.08$  and  $-0.49$  Å, respectively (e.s.d.'s  $0.005$  Å), from the plane of C(5) to C(8) (in comparison with  $+0.36$  and  $-0.41$  Å displacements in the naphthoquinol starting material, see above). The C(1), C(2), C(3), C(4), C(4a), C(8a) ring is a boat, with the oxygen-bridged C(1) and C(4) atoms displaced by  $1.07$  and  $0.75$  Å, respectively, from the C(2), C(3), C(4a), C(8a) plane; these four coplanar atoms, C(4), and C(8) form a chair-shaped ring [C(8) displaced by  $-1.06$  Å]. The two hetero-oxygen five-membered rings have envelope conformations with

O(4) displaced  $0.750$  (3) Å from the C(1), C(2), C(3), C(4) and  $0.766$  (3) Å from the C(1), C(4), C(4a), C(8a) planes. The four-membered ring is folded; C(8) is  $0.55$  Å out of the C(1), C(2), C(8a) plane.

The bond lengths and angles (Table 3) in the four-membered ring [formed from the starting material by C(2)—C(8) bonding] are indicative of the strain in the molecule. The internal angles in this ring range from  $86.8$  (4) to  $90.5$  (3)°, with C(2)—C(8) =  $1.595$  (7) Å. The angle at the bridging oxygen O(4) is  $94.7$  (3)°, with other angles in the five-membered hetero-rings ranging from  $98.8$  (4)° at C(3) to  $103.0$  (4)° at C(4). In view of the possibility of disorder no significance is attached to minor variations in bond distances and angles from expected values.

Molecules in the crystal are joined into centrosymmetric dimers by pairs of hydrogen bonds, O(1)—H(O)···O(4), with O···O =  $2.801$  (5), O(1)—H(O) =  $0.73$  (6), H(O)···O(4) =  $2.07$  (6) Å, O—H···O =  $173$  (6)°. Distances between dimers correspond to van der Waals interactions.

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## The Structures of 1-Oxo-1,2-dihydro-2,3-diazaphenothiazine and 1-Chloro-10-methyl-2,3-diazaphenothiazine

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### Abstract

The crystal and molecular structures of 1-oxo-1,2-dihydro-2,3-diazaphenothiazine [space group  $P\bar{1}$ ,  $a = 8.00$  (1),  $b = 14.03$  (1),  $c = 4.36$  (1) Å,  $\alpha = 87.7$  (2),

$\beta = 101.5$  (2),  $\gamma = 101.2$  (3)°] and of 1-chloro-10-methyl-2,3-diazaphenothiazine [space group  $Pbca$ ,  $a = 19.83$  (2),  $b = 15.29$  (2),  $c = 7.32$  (1) Å] have been determined by direct methods and refined by least squares to final residuals  $R$  of  $0.087$  and  $0.103$

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respectively. The two molecules are non-planar and the butterfly angles formed by the external rings are  $168.5^\circ$  and  $147.6^\circ$  respectively. In both molecules the central ring has a boat conformation and bond distances and angles are compared with those observed for other phenothiazine derivatives.

### Introduction

A series of 2,3-diazaphenothiazine derivatives were synthesized by Pappalardo, Condorelli & Raspagliesi (1966) in order to study the possible variations of the pharmacodynamic properties of the molecule with respect to 1,3- and 2,4-diaza-substituted derivatives.

The X-ray analyses of the present compounds were undertaken to compare these structures with those previously studied (Andreotti, Bocelli & Sgarabotto, 1974*a,b*) and with all other phenothiazine derivatives which have been analyzed by X-ray methods.

### Experimental

#### 1-Oxo-1,2-dihydro-2,3-diazaphenothiazine (I)

(I) crystallizes as brown prisms from an ethanol–benzene mixture. Weissenberg photographs indicated it to be triclinic. A Wilson (1942) plot suggested the centrosymmetric space group ( $P\bar{1}$ ), which was confirmed by the structure analysis. Cell parameters were determined by a least-squares analysis of the  $(\theta, \chi, \varphi)_{hkl}$  values of fifteen reflections measured on a Siemens single-crystal diffractometer.

*Crystal data.*  $C_{10}H_7N_3OS$ ,  $M_r = 217.4$ , triclinic, space group  $P\bar{1}$ ,  $a = 8.00$  (1),  $b = 14.03$  (1),  $c = 4.36$  (1) Å,  $\alpha = 87.7$  (2),  $\beta = 101.5$  (2),  $\gamma = 101.2$  (3)°,  $U = 470$  (1) Å<sup>3</sup>,  $Z = 2$ , Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å,  $\mu(\text{Cu } K\alpha) = 2.79$  mm<sup>-1</sup>.

A crystal with the approximate dimensions  $0.2 \times 0.1 \times 0.5$  mm was used for data collection. 1770 independent reflections were measured at room temperature on a Siemens diffractometer using Ni-filtered Cu  $K\alpha$  radiation and the  $\omega$ - $2\theta$  scan technique. Of these, 1122 were used in the crystal analysis, taking as unobserved the reflections whose intensities were less than twice their standard deviations (from counting statistics). No absorption correction was applied.

*Structure analysis and refinement.* The normalized structure amplitude, the absolute scale factor and the mean isotropic temperature factor were obtained by Wilson's (1942) method. For sign determination 194 reflections with  $|E| > 1.47$  were used. The structure was solved by direct methods using the basic set chosen by the program *MULTAN* (Main, Woolfson & Germain, 1974). A structure factor calculation with all the heavy atoms obtained by the  $E$  map computed using the most consistent set of signs gave  $R = 0.26$ .

The refinement was performed by block-diagonal least squares using initially isotropic and then anisotropic thermal parameters down to  $R = 0.124$ . A three-dimensional  $\Delta F$  map revealed the approximate positions of all the H atoms; these were refined isotropically to a final  $R = 0.087$ .\*

#### 1-Chloro-10-methyl-2,3-diazaphenothiazine (II)

(II) was recrystallized from a benzene–chloroform mixture as yellow prisms. Cell parameters were refined from a least-squares analysis of the  $(\theta, \chi, \varphi)_{hkl}$  values of fourteen reflections measured on a Siemens single-crystal diffractometer.

*Crystal data.*  $C_{11}H_8ClN_3S$ ,  $M_r = 249.7$ , orthorhombic, space group  $Pbca$ ,  $a = 19.83$  (2),  $b = 15.29$  (2),  $c = 7.32$  (1) Å,  $U = 2219$  (4) Å<sup>3</sup>,  $Z = 8$ , Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å,  $\mu(\text{Cu } K\alpha) = 4.61$  mm<sup>-1</sup>.

A crystal with dimensions  $0.2 \times 0.4 \times 0.7$  mm was used for the data collection. The intensities of 2076 independent reflections were measured as before and 635 of these were considered unobserved [ $I < 2\sigma(I)$ ] and were not used in the crystal analysis. No absorption correction was applied. During data collection a check reflection, measured periodically, revealed a little decomposition of the sample and intensities were accordingly rescaled.

*Structure analysis and refinement.* The structure was solved with the same methods as for (I) using 240 reflections with  $|E| > 1.49$ . The coordinates of all heavy atoms obtained from an  $E$  map computed using the most consistent set of signs gave  $R = 0.26$ . The refinement was carried out by full-matrix least squares with anisotropic thermal parameters down to  $R = 0.141$  using the program *SHELX* (Sheldrick, 1975). The atoms were then fixed at their theoretical positions (C–H 1.08 Å) with the isotropic thermal parameters of the heavy atoms to which they are bonded. The final conventional  $R$  factor was 0.103.

The final positional parameters (together with their standard deviations) for both compounds are given in Table 1.\* The atomic scattering factors were those of Cromer & Mann (1968) for all the heavy atoms and those of Stewart, Davidson & Simpson (1965) for H.

All the calculations were performed on the Cyber 76 computer of the Consorzio Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), with financial support from the University of Parma.

\* Lists of structure factors and thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35143 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) with e.s.d.'s in parentheses*

	Compound (I)			Compound (II)		
	x	y	z	x	y	z
Cl						
S	3574 (2)	3417 (1)	-4051 (5)	4987 (1)	2163 (2)	-1227 (3)
O	3420 (6)	-243 (3)	-3096 (12)	6845 (1)	-82 (1)	1716 (3)
N(1)	954 (6)	1073 (3)	-8831 (13)	4928 (3)	490 (5)	2670 (10)
N(2)	1657 (6)	364 (3)	-7110 (13)	4759 (3)	1065 (4)	1327 (8)
N(3)	4982 (6)	1612 (3)	-1020 (13)	6415 (2)	1268 (4)	-1062 (6)
C(1)	5548 (8)	3386 (4)	-1363 (15)	7349 (3)	795 (4)	901 (8)
C(2)	6637 (9)	4254 (4)	-454 (19)	7997 (4)	853 (5)	1471 (9)
C(3)	8137 (9)	4295 (5)	1844 (19)	8406 (3)	1489 (5)	747 (9)
C(4)	8517 (8)	3451 (5)	3129 (20)	8175 (3)	2076 (5)	-507 (10)
C(5)	7486 (8)	2562 (4)	2207 (18)	7520 (3)	2019 (5)	-1126 (8)
C(6)	5990 (8)	2513 (4)	-145 (16)	7091 (3)	1367 (4)	-435 (8)
C(7)	3681 (7)	1465 (4)	-3612 (15)	5912 (2)	1000 (4)	198 (7)
C(8)	2962 (7)	490 (4)	-4484 (15)	5244 (3)	1335 (5)	199 (9)
C(9)	1610 (8)	1946 (4)	-7895 (16)	5500 (4)	162 (5)	2938 (12)
C(10)	2940 (8)	2203 (4)	-5186 (16)	6050 (3)	431 (5)	1561 (8)
C(11)				6305 (3)	1567 (6)	-2823 (8)
H(1)	634 (7)	492 (4)	-141 (13)	819	42	251
H(2)	894 (7)	493 (4)	253 (13)	893	153	119
H(3)	957 (7)	348 (4)	488 (13)	851	257	-105
H(4)	775 (7)	192 (4)	315 (14)	733	249	-210
H(5)	526 (7)	101 (4)	18 (14)	585	121	-320
H(6)	109 (7)	-36 (4)	-787 (14)	674	123	-335
H(7)	115 (7)	246 (4)	-919 (14)	629	222	-339
H(8)				562	-27	407

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Cl—C(8)	(I) 1.776 (7)	(II) 1.776 (6)	C(1)—C(2)	(I) 1.375 (8)	(II) 1.354 (9)	H(1)—C(2)	(I) 1.06 (6)
S—C(1)	1.743 (6)	1.764 (6)	C(1)—C(6)	1.395 (9)	1.408 (8)	H(2)—C(3)	1.01 (5)
S—C(10)	1.251 (8)		C(2)—C(3)	1.395 (10)	1.373 (10)	H(3)—C(4)	1.01 (5)
O—C(8)	1.362 (7)	1.361 (9)	C(3)—C(4)	1.351 (11)	1.363 (10)	H(4)—C(5)	1.02 (6)
N(1)—N(2)	1.284 (7)	1.256 (10)	C(4)—C(5)	1.382 (9)	1.378 (8)	H(5)—N(3)	1.01 (6)
N(1)—C(9)	1.379 (8)	1.333 (8)	C(5)—C(6)	1.405 (9)	1.405 (9)	H(6)—N(2)	1.07 (5)
N(2)—C(8)	1.385 (7)	1.425 (7)	C(7)—C(8)	1.414 (8)	1.420 (7)	H(7)—C(9)	0.98 (6)
N(3)—C(6)	1.368 (8)	1.419 (6)	C(7)—C(10)	1.383 (9)	1.352 (8)		
N(3)—C(7)		1.385 (7)	C(9)—C(10)	1.429 (9)	1.541 (10)		
N(3)—C(11)							
C(1)—S—C(10)	(I) 101.1 (7)	(II) 98.4 (6)	C(2)—C(3)—C(4)	(I) 118.1 (14)	(II) 121.9 (12)	Cl—C(8)—N(2)	(I) 113.0 (8)
N(2)—N(1)—C(9)	115.5 (9)	126.4 (13)	C(3)—C(4)—C(5)	122.1 (13)	119.8 (11)	Cl—C(8)—C(7)	122.8 (7)
N(1)—N(2)—C(8)	126.8 (13)	118.0 (11)	C(4)—C(5)—C(6)	120.1 (13)	119.8 (10)	O—C(8)—C(7)	125.6 (12)
C(6)—N(3)—C(7)	123.3 (12)	118.9 (8)	N(3)—C(6)—C(1)	123.3 (11)	120.0 (9)	O—C(8)—N(2)	119.0 (11)
C(6)—N(3)—C(11)		114.4 (9)	N(3)—C(6)—C(5)	118.9 (11)	122.0 (9)	N(2)—C(8)—C(7)	115.5 (10)
C(7)—N(3)—C(11)		126.1 (9)	C(1)—C(6)—C(5)	117.8 (12)	118.1 (10)	N(1)—C(9)—C(10)	124.8 (13)
S—C(1)—C(2)	118.2 (10)	118.7 (8)	N(3)—C(7)—C(8)	116.8 (11)	123.5 (8)	S—C(10)—C(7)	123.2 (9)
S—C(1)—C(6)	121.7 (10)	119.9 (7)	N(3)—C(7)—C(10)	123.6 (13)	121.6 (9)	S—C(10)—C(9)	119.3 (10)
C(2)—C(1)—C(6)	120.2 (11)	121.2 (11)	C(8)—C(7)—C(10)	119.3 (11)	114.9 (10)	C(7)—C(10)—C(9)	117.6 (12)
C(1)—C(2)—C(3)	121.5 (13)	119.2 (11)					120.8 (11)

### Molecular geometries

Table 2 lists the bond distances and angles of the two compounds.

#### Compound (I)

The stereochemistry of the molecule is illustrated in Fig. 1 which shows the arbitrary numbering scheme

used in the analysis. Table 3 contains the equations of some mean planes. The molecule as a whole is not planar and the butterfly angle formed between the benzene ring and the mean pyridazone ring is  $168.5^\circ$ . The S and N atoms of the central ring are displaced from the benzene plane by 0.164 (7) and -0.028 (8) Å respectively.

The central ring has a flattened boat conformation with N(1) and S out of the basal plane formed by C(1),

Table 3. Analysis of the planarity of compounds (I) and (II)

(a) Distances ( $\text{\AA} \times 10^3$ ) of atoms from least-squares planes

## Compound (I)

Plane (1): C(1)–C(6)

C(1) 25 (9), C(2)–13 (10), C(3)–8 (10), C(4) 11 (10),  
C(5) 6 (10), C(6)–23 (9), S 164 (7), N(3)–28 (8)

Plane (2): S, C(10), C(7), N(3)

S 0(7), C(10)–1 (10), C(7) 1 (9), N(3)–2 (9)

Plane (3): C(7), C(8), O, N(2)

C(7) –1 (10), C(8) 2 (10), O –1 (9), N(2) –1 (9)

Plane (4): C(8), N(2), N(1), C(9)

C(8) 2 (10), N(2) –4 (9), N(1) 4 (9), C(9) –2 (10),  
O 44 (9), C(7) –51 (10), C(10) 32 (10)

## Compound (II)

Plane (1): C(1)–C(6)

C(1) –9 (6), C(2) 1 (7), C(3) 12 (7), C(4) –12 (8),  
C(5) –1 (7), C(6) 9 (6), S 107 (3), N(3) 53 (5)

Plane (2): N(1), N(2), N(3), C(7), C(9), C(10)

N(1) 2 (8), N(2) –1 (6), N(3) –4 (6), C(7) 5 (6),  
C(9) –11 (8), C(10) 7 (7), C(8) –61 (7), S 150 (2)

Plane (3): N(1), N(2), C(8), C(9), C(10)

N(1) –3 (8), N(2) 18 (6), C(8) –23 (7), C(9) –22 (8),  
C(10) 18 (7), C(7) 39 (6), S 154 (2), N(3) 51 (6)

Plane (4): C(7), C(8), C(9), C(10)

C(7) 7 (6), C(8) –5 (7), C(9) 7 (8), C(10) –10 (7),  
N(1) 66 (8), N(2) 81 (6), Cl –192 (3), S 68 (2)

Plane (5): N(1), N(2), C(8), C(9)

N(1) –9 (8), N(2) 5 (6), C(8) –4 (7), C(9) 5 (8),  
C(7) 99 (6), C(10) 82 (7), Cl –207 (3)

Plane (6): C(7), C(8), C(9), C(10), N(1), N(2)

C(7) 15 (6), C(8) –39 (7), C(9) –20 (8), C(10) 2 (7),  
N(1) 5 (8), N(2) 18 (6), S 129 (2), N(3) 10 (6)(b) Angles ( $^\circ$ ) between planes

## Compound (I)

(1)–(2) 14.4 (3)–(4) 2.3 (2)–(4) 4.2

## Compound (II)

(1)–(6) 147.6 (1)–(4) 145.9 (4)–(5) 4.0

C(6), C(7), C(10) by 0.277 (9) and 0.233 (7)  $\text{\AA}$  respectively. The pyridazone ring is non-planar; however, the two portions formed by C(7), C(8), O, N(2) and C(8), N(2), N(1), C(9) are planar. Bond distances in the pyridazone ring are of the same order of those observed in 6-aminocarbonyl-3-pyridazone (Cucka, 1963).

Molecules are arranged in zigzag chains running along [100] joined by  $N(3)\cdots O^i = 2.88 (1) \text{\AA}$  [ $H(5)\cdots O^i = 1.92 (6) \text{\AA}$ ; (i)  $-1 - x, -y, -z$ ] and by  $N(2)\cdots N(1)^{ii} = 2.96 (1) \text{\AA}$  [ $H(6)\cdots N(1)^{ii} = 2.07 (6) \text{\AA}$ ; (ii)  $-x, -y, 2 - z$ ] hydrogen bonds (see Fig. 2). Other contacts are consistent with van der Waals interactions; packing distances less than 3.50  $\text{\AA}$  are reported in Table 4.

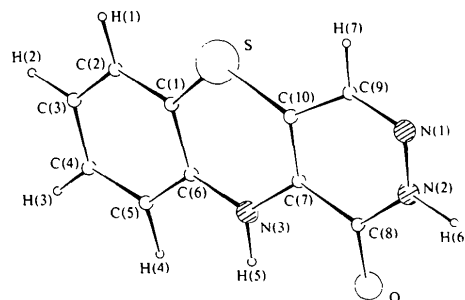


Fig. 1. Perspective view and numbering of the atoms for a molecule of (I).

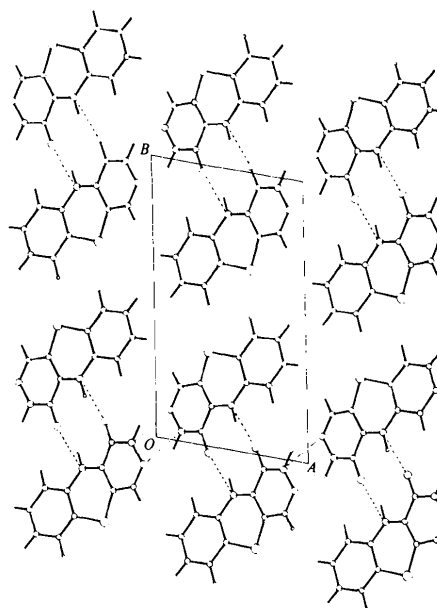


Fig. 2. Packing of (I).

Table 4. Contacts less than 3.5  $\text{\AA}$ 

## Compound (I)

N(3)–C(9) <sup>i</sup>	3.37 (1)	N(1)–N(3) <sup>iv</sup>	3.48 (1)
C(7)–C(9) <sup>i</sup>	3.41 (1)	C(10)–N(3) <sup>iv</sup>	3.49 (1)
N(3)–C(10) <sup>i</sup>	3.49 (1)	N(1)–C(7) <sup>iv</sup>	3.27 (1)
O–O <sup>ii</sup>	3.30 (1)	C(9)–C(7) <sup>iv</sup>	3.41 (1)
N(3)–O <sup>ii</sup>	2.88 (1)	N(1)–C(8) <sup>iv</sup>	3.40 (1)
C(5)–O <sup>ii</sup>	3.22 (1)	N(2)–N(2) <sup>v</sup>	3.49 (1)
H(4)–O <sup>ii</sup>	2.36 (5)	N(1)–N(1) <sup>vi</sup>	3.21 (1)
H(5)–O <sup>ii</sup>	1.92 (6)	N(2)–N(1) <sup>vi</sup>	2.96 (1)
O–O <sup>iii</sup>	3.25 (1)	N(2)–N(2) <sup>vi</sup>	3.31 (1)
C(8)–O <sup>iii</sup>	3.35 (1)	H(6)–N(2) <sup>vi</sup>	2.77 (5)
N(2)–O <sup>iv</sup>	3.41 (1)	N(1)–H(6) <sup>vi</sup>	2.07 (5)

## Compound (II)

Cl–N(2) <sup>vii</sup>	3.28 (1)
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Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at  $x, y, z$ :

(i)	$x, y, z - 1$	(v)	$-x, -y, 1 - z$
(ii)	$-x - 1, -y, -z$	(vi)	$-x, -y, 2 - z$
(iii)	$-x - 1, -y, 1 - z$	(vii)	$x, \frac{1}{2} - y, -\frac{1}{2} + z$
(iv)	$x, y, 1 + z$		

## Compound (II)

Fig. 3 shows a projection of the molecule and the atomic numbering scheme. In Table 3 the least-squares analysis of some planar parts of the molecule is reported. The molecule is not planar and the butterfly angle formed between the benzene plane and the mean pyridazine ring is  $147.0^\circ$ . S and N of the thiazine ring are out of the benzene plane by 0.107 (3) and 0.053 (5) Å respectively. The central ring has a boat conformation with N(3) and S out of the plane formed by C(1), C(6), C(7), C(10) by 0.361 (6) and 0.559 (2) Å respectively. The pyridazine ring is slightly distorted, but lies in a plane: for that part of the plane formed by N(1), N(2), C(7), C(9) and C(10), C(8) is out by 0.066 (7) Å; for N(1), N(2), C(8), C(9) and C(10), C(7) is out by 0.039 (6) Å; and for N(1), N(2), C(8) and C(9), C(7) and C(10) are out by 0.099 (6) and 0.082 (7) Å respectively. The Cl—C(8) bond distance [1.718 (7) Å] is slightly shorter than that observed in chlorpromazine [1.74 (1) Å; McDowell (1969)].

Van der Waals interactions less than 3.50 Å between the molecules are listed in Table 4 and a picture of the packing is given in Fig. 4.

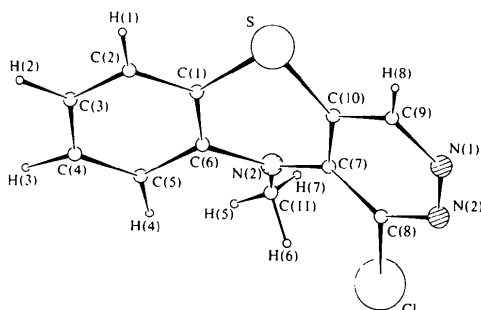


Fig. 3. Perspective view and numbering of the atoms for a molecule of (II).

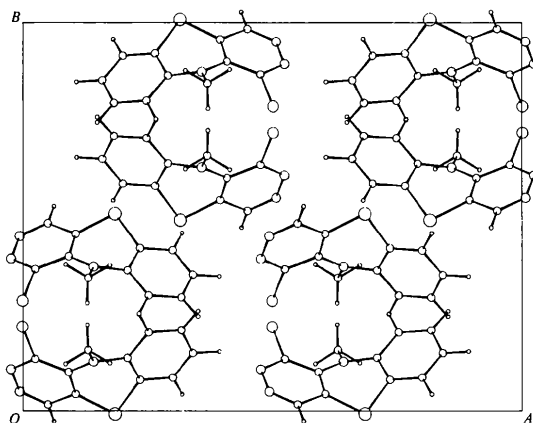


Fig. 4. Packing of (II).

## Discussion

In Table 5 are reported some geometrical and conformational parameters concerning diazaphenothiazines and phenothiazines which have been published so far.

With the exception of the methylene blue thiocyanate (Kahn-Harari, Ballard & Norris, 1973), all the molecules are non-planar, with the thiazine ring in a boat conformation and with 'butterfly' angles (the dihedral angle formed by the external rings) ranging from  $134.4$  to  $173.6^\circ$ . Butterfly angles greater than  $168^\circ$  are observed only when the molecules are cations or when the substituents of the external ring, at a carbon  $\beta$  with respect to S or N, could interact by 'one-way'  $\pi$  delocalization with these atoms [compound (I); Andreotti *et al.* (1974*a,b*)].

Molecular features to be discussed are (a) S—C bond lengths and C—S—C bond angles; (b) N—C bond lengths and C—N—C bond angles; (c) displacements of the S and N atoms from the mean plane of the two external rings; (d) pyramidalicity of the N atom in the thiazine ring and the orientation of the substituents at N; (e) conformation of the thiazine ring.

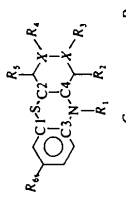
(a) For structures reported in Table 5 with butterfly angles less than  $168^\circ$  and with e.s.d.'s  $\leq 0.006$  Å, the mean C—S bond length is 1.762 (1) Å\* with a very limited spread, while in the case of compounds with butterfly angles greater than  $168^\circ$ , the S—C bond length decreases slightly to 1.742 (3) Å. As has already been pointed out (Ammon, Watts & Stewart, 1970), unsymmetric conjugation involving S seems to be favored and the variation of S—C bond length with the amount of conjugation is always very small and at the limit of significance. C—S—C bond angles range from  $94.4^\circ$  in 2-methoxyphenothiazine (Phelps & Cordes, 1975) to  $104^\circ$  in a complex of phenothiazine with 7,7,8,8-tetracyano-*p*-quinodimethane (Kobayashi, 1974) with a mean value of  $98.5$  (2) $^\circ$  (considering only the values with reported e.s.d.'s). Larger values are usually observed when the molecules are nearly planar, but some exceptions are observed in 4-oxo-3,4-dihydro-2,3-diazaphenothiazine monohydrate (Andreotti *et al.*, 1974*a,b*) and in simple phenothiazine (McDowell, 1976).

(b) N—C bond distances range from 1.329 (20) Å in methylene blue thiocyanate (Kahn-Harari *et al.*, 1973) to 1.47 (2) Å in triflupromazine (Phelps & Cordes, 1974). The shortest values are observed for molecules with butterfly angles greater than  $168^\circ$  [compound (I); 4-oxo-3,4-dihydro-2,3-diazaphenothiazine monohydrate (Andreotti *et al.*, 1974*a,b*); methylene blue thiocyanate (Kahn-Harari *et al.*, 1973)] with the exception of the ion radical molecular complex

\* The formulas used to calculate the mean values are:  $\bar{x} = \frac{\sum_{i=1}^N (x_i/\sigma_i^2)}{\sum_{i=1}^N (1/\sigma_i^2)}$ ;  $\bar{\sigma}_m = \left\{ \frac{\sum_{i=1}^N [(x_i - \bar{x}_m)^2/\sigma_i^2]}{(N-1) \times \sum_{i=1}^N (1/\sigma_i^2)} \right\}^{1/2}$ .

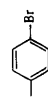
Table 5. Comparison of geometrical features in phenothiazine derivatives

In the first four references X = N; in all other references, X = C; the substituents R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, and R<sub>6</sub> are H atoms unless indicated differently.



	A	B	C	D	E	F	G	H	I	L	M	N	O	P
	1-776 (7)	1-743 (6)	1-385 (7)	1-368 (8)	101-1 (7)	123.3 (12)	0.15	0.23	168.5	0.032	0.23	0.15	169.6	Compound (I)
	1-776 (6)	1-764 (6)	1-425 (7)	1-419 (6)	98.4 (6)	118.9 (8)	-0.11	-0.05	147.6	0.065	0.56	0.36	153.7	Compound (II)
	1-769 (4)	1-747 (4)	1-394 (4)	1-361 (4)	100.5 (4)	125.4 (7)	0.13	-0.05	173.6	0.065	0.13	0.01	166.5	Andreotti <i>et al.</i> (1974a)
	1-789 (4)	1-763 (4)	1-423 (2)	1-408 (3)	100.2 (2)	120.6 (3)	0.08	-0.06	146.4	0.18	0.52	0.35	168.1	Andreotti <i>et al.</i> (1974b)
	1-76 (2)		1-39 (2)		101 (1)	123 (1)	0.01	0.02	156					Fritche & Trus (1968)
	1-770 (3)		1-406 (2)		99.6	121.5	0.18	0.03	153.3					Bell <i>et al.</i> (1968)
	1-76		1-40		102	126	-0.01	0.01						Fritche (1969)
	1-75 (1)	1-75 (1)	1-41 (1)	1-40 (1)	97.3 (3)	118.4 (5)	0.14	0.01	139.4	0.206	0.61	0.45	162.8	McDowell (1969)
	1-78 (2)	1-78 (2)	1-46 (2)	1-39 (2)	99.0 (7)	118.1 (10)	0.02	0.06	139.0	0.208	0.60	0.46	163.0	McDowell (1970)
							0.14	0.05						Wakayama (1971)
	1-820 (17)		1-430 (26)		97 (77)	120 (2.5)	0.18	0.07	151					Marseau (1971)
	1-765	1-767	1-41	1-42	97.5	116.4	0.09	0.00	138	0.219	0.65	0.48	162.7	Marseau & Casas (1971)
	1-767 (4)	1-765 (3)	1-421 (5)	1-418 (4)	98.2 (2)	117.6 (3)	-0.02	0.03	138.5	0.195	0.60	0.46	161.6	Marseau & Cordes (1972)
	1-79 (1)	1-75 (1)	1-43 (2)	1-43 (2)	98.5 (7)	115.4 (11)	0.36	0.13	136.5	0.210	0.61	0.48	162.5	Malmstrom & Cordes (1972)
	1-73						-0.01	0.03						Kobayashi (1973)
	1-75 (2)	1-77 (1)	1-41 (2)	1-43 (2)	98.7 (7)	118.1 (9)	-0.03	0.02	135.4	0.210	0.61	0.48	162.0	Malmstrom & Cordes (1973)
	1-765 (6)	1-777 (6)	1-409 (7)	1-412 (8)	98.0 (3)	117.2 (5)	0.06	0.06	135.6	0.197	0.67	0.47	159.5	Marseau & Cam (1973)
	1-766 (5)	1-766 (5)	1-419 (6)	1-408 (6)	98.8 (2)	118.5 (4)	0.14	-0.08	140.6	0.15	0.60	0.32	150.6	Marseau & Busetta (1973)
	1-750 (7)	1-766 (7)	1-416 (8)	1-409 (7)	99.8 (3)	122.3 (5)	0.02	0.00	157.7	0.138	0.48	0.27	169.6	Marseau & Gauthier (1973)
	1-742 (16)	1-736 (16)	1-329 (20)	1-353 (22)	103.45	122.4	0.19	0.03	180.0					Kahn-Harari <i>et al.</i> (1973)
							0.0	0.0						Without substituent at N <sub>3</sub>
	1-73		1-36		104	134	-0.05	0.04						Complex
	1-764 (2)		1-402 (2)		97.4 (1)	118.0 (2)	-0.05	0.04	143.7	0.207	0.66	0.4	166.4	Kobayashi (1974)
	1-766 (8)	1-746 (8)	1-42 (2)	1-47 (2)	97.9 (4)	115 (1)	0.13	0.03	134.4	0.202	0.66	0.46	162.2	Chu & van der Helm (1974)
	1-738 (8)	1-729 (8)	1-41 (2)	1-40 (2)	96.5 (4)	117 (1)	0.22	0.06	141.0	0.205	0.59	0.44	164.5	Phepys & Cordes (1974)
	1-72 (1)	1-74 (1)	1-38 (2)	1-44 (2)	102.8 (7)	121 (1)	0.06	0.10	172.2					Complex
	1-765 (3)	1-767 (3)	1-427 (4)	1-406 (4)	97.4 (1)	116.7 (2)	0.01	0.01	135.0	0.211	0.66	0.48	161.9	Singhbandhu <i>et al.</i> (1975)
	1-786 (8)	1-762 (9)	1-423 (9)	1-399 (9)	99.0 (4)	118.9 (5)	-0.09	0.03	145.8	0.131	0.55	0.39	159.3	Chu & van der Helm (1975)
	1-776 (8)	1-761 (7)	1-400 (9)	1-413 (9)	97.8 (4)	118.1 (5)	0.14	0.06	134.4	0.189	0.66	0.45	159.6	McDowell (1975)
	1-78	1-77	1-40	1-39	94.4	121.0	0.01	0.03	149.4	0.195	0.52	0.36	174	Phepys & Cordes (1975)
							-0.11	0.00	158.5					McDowell (1976)
	1-763 (1)	1-761 (1)	1-410 (2)	1-410 (2)	100.9 (3)	124.4 (5)	0.17	0.02	136.1	0.112	0.65	0.43	152.7	Chu & van der Helm (1976)
	1-756 (1)	1-760 (1)	1-414 (2)	1-414 (2)	98.1 (1)	118.6 (1)	-0.11	0.08	146.8	0.098	0.58	0.39	154.6	Chu & van der Helm (1976)
	1-754 (2)	1-759 (2)	1-414 (2)	1-423 (2)	100.7 (1)	122.5 (1)	0.23	0.06	157.5	0.171	0.47	0.26	175.3	Chu, Yang & van der Helm (1976)
							0.19	0.25						Complex
	1-770 (3)	1-768 (3)	1-400 (3)	1-427 (3)	98.4 (1)	117.2 (2)	0.21	-0.18	138.7	0.169	0.62	0.47	157.5	McDowell (1977)
	1-775 (2)	1-758 (2)	1-406 (3)	1-412 (3)	98.9 (1)	120.4 (2)	0.04	0.00	148.2	0.125	0.56	0.33	163.0	Chu & van der Helm (1977)
	1-758 (2)	1-762 (2)	1-413 (3)	1-406 (2)	99.1 (1)	120.7 (2)	-0.05	0.01	150.1	0.132	0.57	0.34	162.5	Chu & Yang (1977)
	1-764 (4)	1-753 (4)	1-411 (5)	1-428 (5)	98.9 (2)	120.0 (3)	0.22	0.00	144.9	0.023	0.14	0.09	163.1	
	1-766 (4)	1-763 (4)	1-421 (5)	1-425 (5)	99.1 (2)	120.8 (3)	0.04	0.00	150.8	0.026	0.08	0.04	178.2	
							-0.01	0.03						

(L) Sum of the bond angles around the N atom (°)  
(M) Displacement of the S and N atoms from the plane formed by the four C atoms of the thiazine ring (Å)  
(N) Angle S...N...R<sub>1</sub> (°)  
(O) Substituents or comments  
(P) References

Complex  
R<sub>1</sub> = (CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>; R<sub>2</sub> = Cl  
R<sub>3</sub> = (CH<sub>2</sub>)<sub>2</sub>-N(CH<sub>2</sub>)<sub>2</sub>  
R<sub>4</sub> = SC<sub>2</sub>H<sub>5</sub>  
R<sub>5</sub> = CH<sub>3</sub>  
R<sub>6</sub> = (CH<sub>2</sub>)<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
R<sub>1</sub> = (CH<sub>2</sub>)<sub>2</sub>COOH  
R<sub>1</sub> = (CH<sub>2</sub>)<sub>2</sub>CN  
R<sub>1</sub> = (CH<sub>2</sub>)<sub>2</sub>CH(CH<sub>2</sub>)N(CH<sub>2</sub>)<sub>2</sub>  
R<sub>1</sub> = CH<sub>2</sub>CH(CH<sub>2</sub>)N(CH<sub>2</sub>)<sub>2</sub>; HBr  
R<sub>1</sub> = (CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>  
R<sub>2</sub> = OCH<sub>3</sub>  
Without substituent at N<sub>3</sub>  
R<sub>3</sub> = N(CH<sub>2</sub>)<sub>2</sub>  
Complex  
R<sub>1</sub> = CH<sub>3</sub>  
R<sub>1</sub> = (CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>, HCl  
R<sub>1</sub> = CF<sub>3</sub>  
Complex  
R<sub>1</sub> = C<sub>2</sub>H<sub>5</sub>  
R<sub>1</sub> = (CH<sub>2</sub>)<sub>2</sub>; R<sub>2</sub> = SCH<sub>3</sub>  
R<sub>1</sub> = OCH<sub>3</sub>  
R<sub>1</sub> = CH(CH<sub>2</sub>)<sub>2</sub>  
R<sub>1</sub> = (CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>; R<sub>2</sub> = Cl; R<sub>3</sub> = OH  
R<sub>1</sub> = CH<sub>2</sub>Ph  
R<sub>1</sub> = 

of *cis*-bis[bis(trifluoromethyl)ethylene-1,2-dithiolato]-nickel with phenothiazine (Singhabhandhu, Robinson, Fang & Geiger, 1975).

The average of the N—C bond distances for compounds with butterfly angles  $\leq 168^\circ$  and with e.s.d.'s  $\leq 0.006 \text{ \AA}$  is  $1.413 (2) \text{ \AA}$ , and for compounds with butterfly angles greater than  $168^\circ$  and with e.s.d.'s  $\leq 0.006 \text{ \AA}$  the average value is  $1.393 (5) \text{ \AA}$  [for compound (I) and for 4-oxo-3,4-dihydro-2,3-diazaphenothiazine monohydrate (Andreotti *et al.*, 1974*a,b*) only the distances towards the ring with conjugative ability have been taken into account].

The C—N—C bond angles range from  $115 (1)^\circ$  in triflupromazine (Phelps & Cordes, 1974) to  $134^\circ$  in 7-hydroxychlorpromazine (McDowell, 1977); an enlargement of this angle roughly corresponds to a flattening of the molecule, even if the relationship is not quantitative.

(c) With the exception of methylene blue thiocyanate (Kahn-Harari *et al.*, 1973) a significant feature of the majority of phenothiazines studied up to now is the out-of-plane bending of the hetero-atoms from the mean planes of the external rings. The effect is greater for S than for N and it has been shown by Domenicano, Vaciego & Coulson (1975) to be related to the hybridization changes induced by substitution at the benzene ring. In the case of phenothiazines the displacements are not constant; sometimes both are in the same direction, sometimes opposite, even if the nature of the substituents, in most cases at the thiazine N, is similar as regards electron-withdrawing or -releasing properties. It seems probable that the electronic effects of the substituents, mainly at N, influencing the conformation of the molecule, as we will see in (d), perturb the hetero-atoms which behave as though they had different abilities to modify the *s* or *p* character of the C atom  $\sigma$ -bonded to them (Del Buttero, Maiorana, Andreotti, Bocelli & Sgarabotto, 1975).

(d) In all cases [apart from the perfectly planar methylene blue thiocyanate; Kahan-Arari *et al.* (1973)] the substituents at N are quasi-equatorial and the angles S...N—C, which give their orientation with respect to the thiazine ring, range from  $150.6$  to  $178.2^\circ$ . The pyramidality of N is a constant feature of all phenothiazines, though it varies significantly from compound to compound. Usually, but not always, there is a relationship between the pyramidality of N and the butterfly angle: in fact, when N (see column I of Table 5) is more than  $0.18 \text{ \AA}$  out-of-plane the butterfly angle is never greater than  $140^\circ$ , the only exception being *N*-methylphenothiazine (Chu & van der Helm, 1974). It can be deduced that the electronic situation at N is an important factor that controls the conformation of the molecule even if, in the solid state, packing forces could slightly influence the 'frozen' conformation. This

has already been pointed out by Malmstrom & Cordes (1972).

(e) The thiazine ring always has a boat conformation with the four basal atoms quite often significantly deviating from the least-squares plane (column M of Table 5). So for the tricyclic system there is no plane of symmetry through the S—N axis even in the unsubstituted phenothiazine (Bell, Blount, Briscoe & Freeman, 1968).

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## The Structures of Four Reaction Products of 1,2,2a,3,4,5-Hexahydropyrrolo-[3,2,1-*jk*]carbazole with *p*-Chlorobenzenesulphonyl Azide

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### Abstract

The crystal structures of 12-(*p*-chlorophenylsulphonylamino)-6,7,10,11-tetrahydroazocino[1,2-*a*]indol-8(9*H*)-one, C<sub>20</sub>H<sub>19</sub>ClN<sub>2</sub>O<sub>3</sub>S (I) [monoclinic,  $a = 10.404$  (3),  $b = 9.091$  (4),  $c = 10.213$  (1) Å,  $\beta = 102.48$  (2)°,  $Z = 2$ , space group  $P2_1$ , 2050 reflexions,  $R_w = 0.043$ ], 14-(*p*-chlorophenyl)-8-(*p*-chlorophenylsulphonylamino)-13-oxa-14-thia-1,15-diazapentacyclo[10.4.2.0<sup>2,7</sup>.0<sup>8,16</sup>.0<sup>12,16</sup>]octadeca-2,4,6,14-tetraene *S*-oxide, C<sub>26</sub>H<sub>23</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub> (II) [triclinic,  $a = 8.127$  (2),  $b = 12.476$  (4),  $c = 12.732$  (5) Å,  $\alpha = 100.73$  (3),  $\beta = 90.77$  (3),  $\gamma = 94.93$  (3)°,  $Z = 2$ , space group  $P\bar{1}$ , 2378 reflexions,  $R_w = 0.054$ ], 6-(*p*-chlorophenylsulphonylamino)-2,2a,3,4,5,6-hexahydro-2a,6-methano-1*H*-azeto[1,2-*a*][1]benzazocin-12-one, C<sub>20</sub>H<sub>19</sub>ClN<sub>2</sub>O<sub>3</sub>S (III) [triclinic,  $a = 6.781$  (2),  $b = 9.781$  (2),  $c = 14.151$  (2) Å,  $\alpha = 98.88$  (2),  $\beta = 97.85$  (2),  $\gamma = 96.74$  (2)°,  $Z = 2$ , space group  $P\bar{1}$ , 2386 reflexions,  $R_w = 0.044$ ], and 8-(*p*-chlorophenylsulphonylamino)-4-hydroxyimino-1,2,3,4,5,6,7,8-octahydro-1,8-methano[1]benzazecin-13-one pyridine solvate, C<sub>20</sub>H<sub>20</sub>ClN<sub>3</sub>O<sub>4</sub>S.C<sub>5</sub>H<sub>5</sub>N (IV) [triclinic,  $a = 9.981$  (2),  $b = 11.624$  (2),  $c = 13.088$  (2) Å,  $\alpha =$

$65.46$  (1),  $\beta = 71.74$  (1),  $\gamma = 63.34$  (2)°,  $Z = 2$ , space group  $P\bar{1}$ , 2112 reflexions,  $R_w = 0.057$ ] have been determined.

### Introduction

*p*-Chlorobenzenesulphonyl azide reacts with 1,2,2a,3,4,5-hexahydropyrrolo[3,2,1-*jk*]carbazole in CCl<sub>4</sub> in accordance with the scheme on page 1847 (Bailey, Scott & Vandrevala, 1980). The structures of the products (I–IV) were determined by X-ray methods.

### Experimental

Transparent plate-like crystals of all four compounds were prepared. After survey photography by Weissenberg and precession techniques, the crystals were set up on a Nonius CAD-4F, PDP8-controlled  $\kappa$ -geometry diffractometer which used Mo  $K\alpha$  radiation from a graphite monochromator. Cell dimensions and the orientation matrix were obtained by least squares from the setting angles of 25 reflexions.