

Structure of 10-(4-Nitrophenyl)pyrido[3,2-*b*]1,4]benzothiazine

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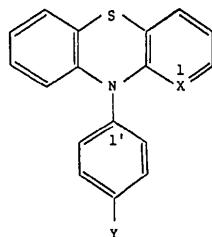
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**Abstract.** C<sub>17</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>S,  $M_r = 321.36$ , orthorhombic, *Pbcn*,  $a = 7.491$  (1),  $b = 15.030$  (2),  $c = 25.934$  (5) Å,  $V = 2919.9$  (9) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.462$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 2.24$  cm<sup>-1</sup>,  $F(000) = 1328$ ,  $T = 295$  K. Final  $R = 0.043$  for 1489 observed reflections. The central ring is in a boat conformation. The folding angle between the benzo and the pyrido planes is 149.1 (1)°. The 4-nitrophenyl substituent is in an equatorial position relative to the central ring and makes an angle of 19.1 (9)° with the plane S,N,C(1') bisecting the tricyclic ring.

**Introduction.** We have recently observed that in 10-(4-nitrophenyl)phenothiazine (Jovanovic, Biehl, de Meester & Chu, 1984), (I), the nitrophenyl group is almost perpendicular to the plane S,N,C(1') bisecting the tricyclic ring, whereas in 10-phenylphenothiazine, (II) (Klein, Conrad III & Morris, 1985), and in many other 10-phenyl-substituted phenothiazines, the phenyl ring is approximately parallel to the bisecting plane. The perpendicular conformation in (I) is attributed to the electron-withdrawing character of the nitro group. The object of the structural study of the title compound, (III), is to determine the conformation of the 10-(4-nitrophenyl) substituent with respect to the tricyclic ring system when the CH group at position 1 in (I) is replaced by an N atom. The conformation obtained in the solid state will also be compared with that deduced in solution by <sup>13</sup>C NMR spectroscopy.



- (I) X = CH, Y = NO<sub>2</sub>  
 (II) X = CH, Y = H  
 (III) X = N, Y = NO<sub>2</sub>  
 (IV) X = N, Y = OCH<sub>3</sub>

**Experimental.** Crystals of the title compound are orange flat needles. Lattice parameters from least-squares refinement of 15 reflections in range  $17 < 2\theta < 23^\circ$ , space group *Pbcn* from systematic absences ( $0kl$ ,  $k$  odd;  $h0l$ ,  $l$  odd; and  $hk0$ ,  $h + k$  odd). Crystal dimensions  $0.85 \times 0.32 \times 0.09$  mm. Automatic Syntex *P2*, diffractometer, graphite-monochromated Mo *K* $\alpha$  radiation,  $\theta/2\theta$  scanning mode, 2581 independent reflections in range  $3.5 < 2\theta < 50^\circ$ ,  $hkl$  range  $0 \leq h \leq 8$ ,  $0 \leq k \leq 17$ ,  $0 \leq l \leq 30$ , 1489 observed reflections with  $I > 3\sigma(I)$ ,  $\sigma(I)$  from counting statistics. Three standard reflections remeasured every 100 reflections showed no change in intensity greater than  $2.5\sigma(I)$ . Lorentz-polarization correction, no absorption or extinction corrections. Structure solved using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Refinement by full-matrix least squares using *SHELX76* (Sheldrick, 1976) using only observed reflections, anisotropic for non-H, isotropic for H atoms,  $w = 1/[\sigma^2(F) + 0.0003F^2]$ ,  $\sum w(|F_o| - |F_c|)^2$  minimized.  $R = 0.043$ ,  $wR = 0.043$  for 1489 observed reflections.  $(\Delta/\sigma)_{\max} = 0.02$ ,  $\Delta\rho_{\max} = 0.15$ ,  $\Delta\rho_{\min} = -0.23$  e Å<sup>-3</sup>. Atomic scattering factors for C, H, O, N and S and effects of anomalous dispersion for S those stored in *SHELX76*.

**Discussion.** The final atomic parameters are given in Table 1.† The identification of the atoms and the conformation of the molecule are shown in the *ORTEP* (Johnson, 1965) drawing of Fig. 1. The bond lengths and bond angles are listed in Table 2. Comparison between the title compound (III) and 10-(4-nitrophenyl)phenothiazine, (I), shows that the main differences in the bond lengths and angles are centered on N(10). The angle C(9a)–N(10)–C(10a) of 120.1 (3)° in (III) has a larger value than those of 113.4 (2) and

† Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42824 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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114.4 (3)° found in the two independent molecules of (I). Also the distance N(10)–C(1') of 1.430 (4) Å in (III) is substantially larger than the distances of 1.383 (4) and 1.389 (4) Å in (I).

Table 1. Fractional atomic coordinates with equivalent isotropic thermal parameters for the non-H and isotropic for the H atoms (*e.s.d.*'s in parentheses)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> / <i>U</i> (Å <sup>2</sup> )*
N(1)	0.7680 (4)	0.5842 (2)	0.2783 (1)	0.0540 (7)
C(2)	0.7240 (5)	0.5709 (2)	0.2286 (1)	0.0597 (9)
C(3)	0.6965 (5)	0.6375 (2)	0.1939 (1)	0.0573 (9)
C(4)	0.7103 (4)	0.7239 (2)	0.2116 (1)	0.0519 (8)
C(4a)	0.7469 (4)	0.7402 (2)	0.2625 (1)	0.0448 (7)
S(5)	0.7299 (1)	0.84773 (5)	0.28756 (3)	0.0591 (2)
C(5a)	0.8887 (4)	0.8386 (2)	0.3370 (1)	0.0436 (7)
C(6)	0.9831 (5)	0.9131 (2)	0.3527 (1)	0.0523 (8)
C(7)	1.1010 (5)	0.9097 (2)	0.3925 (1)	0.0575 (9)
C(8)	1.1300 (5)	0.8304 (2)	0.4176 (1)	0.0576 (9)
C(9)	1.0391 (5)	0.7553 (2)	0.4021 (1)	0.0523 (8)
C(9a)	0.9171 (4)	0.7583 (2)	0.3623 (1)	0.0435 (7)
N(10)	0.8234 (4)	0.6802 (2)	0.3466 (1)	0.0490 (6)
C(10a)	0.7800 (4)	0.6673 (2)	0.2944 (1)	0.0434 (7)
C(1')	0.8245 (5)	0.6065 (2)	0.3815 (1)	0.0474 (8)
C(2')	0.7204 (5)	0.6120 (2)	0.4250 (1)	0.0534 (8)
C(3')	0.7161 (4)	0.5434 (2)	0.4603 (1)	0.0551 (8)
C(4')	0.8168 (4)	0.4691 (2)	0.4503 (1)	0.0463 (7)
C(5')	0.9213 (4)	0.4619 (2)	0.4074 (1)	0.0518 (8)
C(6')	0.9264 (4)	0.5309 (2)	0.3728 (1)	0.0511 (8)
N(4')	0.8080 (4)	0.3941 (2)	0.4864 (1)	0.0605 (8)
O(41')	0.7175 (4)	0.4015 (2)	0.5250 (1)	0.0909 (8)
O(42')	0.8934 (4)	0.3275 (2)	0.4760 (1)	0.0913 (9)
H(2)	0.714 (3)	0.510 (2)	0.218 (1)	0.052 (8)
H(3)	0.665 (4)	0.626 (2)	0.158 (1)	0.056 (8)
H(4)	0.690 (3)	0.769 (2)	0.190 (1)	0.036 (7)
H(6)	0.964 (3)	0.960 (2)	0.334 (1)	0.047 (7)
H(7)	1.161 (4)	0.962 (2)	0.406 (1)	0.059 (8)
H(8)	1.217 (4)	0.822 (2)	0.445 (1)	0.072 (10)
H(9)	1.059 (3)	0.702 (1)	0.418 (1)	0.039 (7)
H(2')	0.646 (4)	0.662 (2)	0.431 (1)	0.050 (8)
H(3')	0.634 (4)	0.543 (2)	0.487 (1)	0.069 (9)
H(5')	0.986 (4)	0.410 (2)	0.400 (1)	0.065 (9)
H(6')	1.002 (4)	0.527 (2)	0.342 (1)	0.054 (8)

\*  $U_{eq} = (U_{11} + U_{22} + U_{33})/3$ . The standard deviations of  $U_{eq}$ 's were calculated according to Schomaker & Marsh (1983).

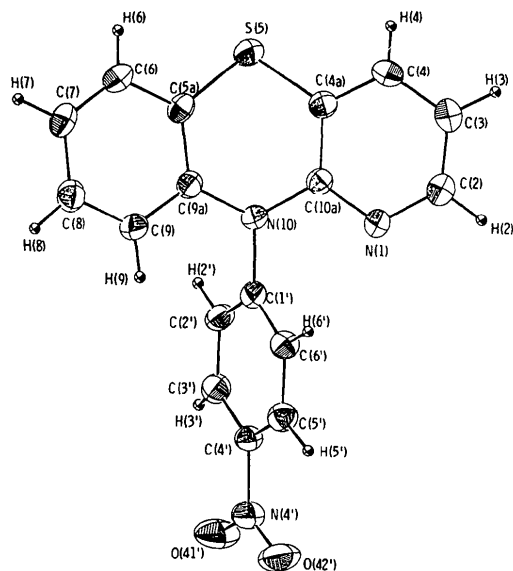


Fig. 1. ORTEP drawing of the molecule. Thermal ellipsoids are scaled at the 50% probability level. H atoms are represented as spheres of arbitrary radii.

Table 2. Bond lengths (Å), bond angles (°) and selected torsion angles (°) with *e.s.d.*'s in parentheses

N(1)–C(2)	1.345 (4)	C(9)–C(9a)	1.379 (4)
N(1)–C(10a)	1.320 (4)	C(9a)–N(10)	1.427 (4)
C(2)–C(3)	1.362 (4)	N(10)–C(10a)	1.406 (4)
C(3)–C(4)	1.381 (4)	N(10)–C(1')	1.430 (4)
C(4)–C(4a)	1.370 (4)	C(1')–C(2')	1.374 (4)
C(4a)–S(5)	1.747 (3)	C(1')–C(6')	1.387 (4)
C(4a)–C(10a)	1.395 (4)	C(2')–C(3')	1.379 (4)
S(5)–C(5a)	1.754 (3)	C(3')–C(4')	1.372 (4)
C(5a)–C(6)	1.386 (4)	C(4')–C(5')	1.365 (4)
C(5a)–C(9a)	1.390 (4)	C(4')–N(4')	1.467 (4)
C(6)–C(7)	1.359 (4)	C(5')–C(6')	1.372 (4)
C(7)–C(8)	1.375 (4)	N(4')–O(41')	1.214 (4)
C(8)–C(9)	1.378 (4)	N(4')–O(42')	1.218 (4)
C(2)–N(1)–C(10a)	117.4 (3)	C(9a)–N(10)–C(1')	117.0 (3)
N(1)–C(2)–C(3)	124.1 (3)	C(10a)–N(10)–C(1')	120.3 (3)
C(2)–C(3)–C(4)	117.4 (3)	N(1)–C(10a)–C(4a)	122.9 (3)
C(3)–C(4)–C(4a)	120.2 (3)	N(1)–C(10a)–N(10)	116.8 (3)
C(4)–C(4a)–S(5)	120.7 (2)	C(4a)–C(10a)–N(10)	120.3 (3)
C(4)–C(4a)–C(10a)	117.8 (3)	N(10)–C(1')–C(2')	118.0 (3)
S(5)–C(4a)–C(10a)	121.2 (2)	N(10)–C(1')–C(6')	122.3 (3)
C(4a)–S(5)–C(5a)	98.7 (1)	C(2')–C(1')–C(6')	119.7 (3)
S(5)–C(5a)–C(6)	119.9 (2)	C(1')–C(2')–C(3')	120.9 (3)
S(5)–C(5a)–C(9a)	121.1 (2)	C(2')–C(3')–C(4')	118.0 (3)
C(6)–C(5a)–C(9a)	119.0 (3)	C(3')–C(4')–C(5')	122.3 (3)
C(5a)–C(6)–C(7)	121.6 (3)	C(3')–C(4')–N(4')	118.7 (3)
C(6)–C(7)–C(8)	119.6 (3)	C(5')–C(4')–N(4')	119.0 (3)
C(7)–C(8)–C(9)	119.6 (3)	C(4')–C(5')–C(6')	119.3 (3)
C(8)–C(9)–C(9a)	121.3 (3)	C(1')–C(6')–C(5')	119.8 (3)
C(5a)–C(9a)–C(9)	118.9 (3)	C(4')–N(4')–O(41')	118.7 (3)
C(5a)–C(9a)–N(10)	120.3 (3)	C(4')–N(4')–O(42')	117.8 (3)
C(9)–C(9a)–N(10)	120.8 (3)	O(41')–N(4')–O(42')	123.4 (3)
C(9a)–N(10)–C(10a)	120.1 (3)		
C(4a)–S(5)–C(5a)–C(9a)	–32.2 (4)	C(10a)–C(4a)–S(5)–C(5a)	34.9 (4)
S(5)–C(5a)–C(9a)–N(10)	3.3 (5)	C(9a)–N(10)–C(1')–C(2')	73.9 (5)
C(5a)–C(9a)–N(10)–C(10a)	33.4 (5)	C(9a)–N(10)–C(1')–C(6')	–106.0 (4)
C(9a)–N(10)–C(10a)–C(4a)	–30.7 (5)	C(10a)–N(10)–C(1')–C(2')	–124.4 (4)
N(10)–C(10a)–C(4a)–S(5)	–8.3 (5)	C(10a)–N(10)–C(1')–C(6')	55.7 (5)

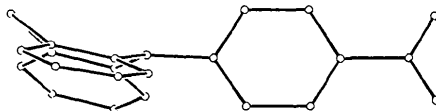


Fig. 2. Side view of the molecule. The H atoms have been omitted for clarity.

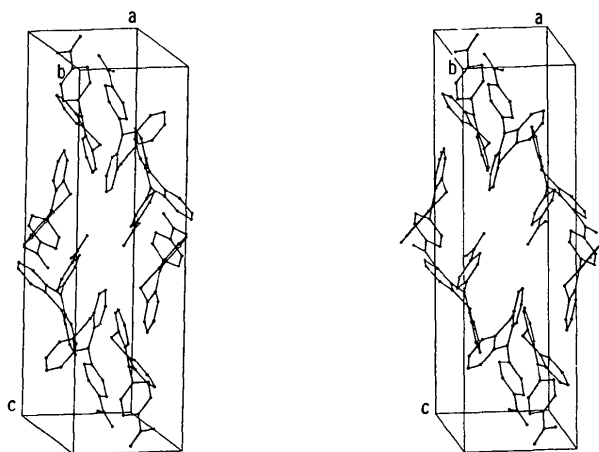


Fig. 3. Stereoscopic drawing of the molecular packing in the cell (H atoms excluded).

The central ring is in a boat conformation as shown in Fig. 2 and also by the torsion angles (Table 2) and the puckering parameters (Cremer & Pople, 1975)  $q_2 = 0.489$  (3),  $q_3 = -0.083$  (3),  $Q = 0.496$  (3) Å,  $\varphi_2 = 116.9$  (3) and  $\theta = 99.7$  (3)°. In the ideal boat conformation, these parameters are  $q_2 = Q$ ,  $q_3 = 0$  Å,  $\varphi_2 = 120$  and  $\theta = 90$ °. The tricyclic ring is folded along the line S(5)···N(10). The folding angle of 149.1 (1)° in (III) has a value comparable to those of 155.2 and 157.1° found in the two independent molecules of 10-(4-methoxyphenyl)pyrido[3,2-*b*][1,4]benzothiazine, (IV) (de Meester, Chu, Jovanovic & Biehl, 1985), and those of 150.7 (5) and 162.6 (5)° observed in the two independent molecules of (II) (Klein *et al.*, 1985), but is considerably larger than those found in (I) (120.8 and 124.4° for the two independent molecules). The smaller folding angles in (I) are apparently due to the different orientation of the 10-phenyl substituent with respect to the tricyclic ring system.

The 10-phenyl substituent is in an equatorial position with respect to the central ring as shown in Fig. 2. The orientation of the phenyl ring relative to the plane formed by the three atoms S(5), N(10) and C(1') (bisecting the tricyclic ring) is given by the angle of 19.1 (9)° between these two planes, a value similar to those found in many 10-phenyl-substituted phenothiazines (where these two planes are approximately parallel). However, the values of 80.5 and 79.3° were found in the two independent molecules of (I) where the 4-nitrophenyl group is approximately perpendicular to the plane bisecting the tricyclic ring. The perpendicular conformation in (I) indicates that there is an electronic interaction between the two ring systems since the 4-nitrophenyl is an electron-withdrawing substituent as evidenced by the short N(10)—C(1') distance. The electronic interaction between the two ring systems cannot take place when the 10-aryl is an electron-

releasing substituent as in (IV) or is an electron-neutral substituent as in (II). In the case of the title compound, (III), the 4-nitrophenyl is an electron-withdrawing substituent; however, the electronic interaction cannot take place when there is also an electron-withdrawing group in the tricyclic ring system [the replacement of CH in (I) by N in (III)]. The conformation of the 4-nitrophenyl substituent in (III) has been studied by <sup>13</sup>C NMR spectroscopy. The conformation deduced in solution agrees with that observed in the solid state.

The packing of the molecules of (III) in the cell is shown in Fig. 3. There is no intermolecular distance shorter than the van der Waals separations. The shortest intermolecular contact is C(3)···O(41') of 3.374 (4) Å.

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#### References

- CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 JOVANOVIĆ, M. V., BIEHL, E. R., DE MEESTER, P. & CHU, S. S. C. (1984). *J. Heterocycl. Chem.* **21**, 1793–1800.  
 KLEIN, C. L., CONRAD, J. M. III & MORRIS, S. A. (1985). *Acta Cryst.* **C41**, 1202–1204.  
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 MEESTER, P. DE, CHU, S. S. C., JOVANOVIĆ, M. V. & BIEHL, E. R. (1985). *Acta Cryst.* **C41**, 1246–1249.  
 SCHOMAKER, V. & MARSH, R. E. (1983). *Acta Cryst.* **A39**, 819–820.  
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1986). **C42**, 879–881

## Structural Chirality of the Insecticide (–)-2,2-Dichloro-1-(4-ethoxyphenyl)-1-cyclopropanecarboxylic Acid

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**Abstract.** C<sub>12</sub>H<sub>12</sub>Cl<sub>2</sub>O<sub>3</sub>,  $M_r = 275.131$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.594$  (1),  $b = 8.167$  (2),  $c = 23.443$  (4) Å,  $V = 1262$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.443$ ,  $D_x = 1.448$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu =$

$44.3$  cm<sup>-1</sup>,  $F(000) = 568$ , room temperature. Final  $R = 0.039$  for all 2452 intensities. There are no unusual bond lengths or angles in the molecule. The configuration of the biologically active isomer is *S*. The