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Acta Cryst. (1984). C**40**, 1753–1756

10-(2-Methoxyphenyl)pyrido[3,2-*b*][1,4]benzothiazine, $C_{18}H_{14}N_2OS$

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Abstract. $M_r = 306{\cdot}38$, monoclinic, $P2_1/c$, $a = 11{\cdot}859\,(1)$, $b = 8{\cdot}121\,(1)$, $c = 16{\cdot}016\,(1)$ Å, $\beta = 101{\cdot}59\,(1)^\circ$, $V = 1511{\cdot}0\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}347$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 18{\cdot}07$ cm^{-1}, $F(000) = 640$, $T = 295$ K. Final $R = 0{\cdot}050$ for 1708 observed reflections. The central ring of the tricyclic ring system is in a boat conformation. The folding angle between the planes of the pyrido and benzo rings is 158·7 (1)°. The plane of the 10-phenyl ring, almost perpendicular to the plane of the central ring [dihedral angle 95·4 (1)°], nearly bisects the tricyclic ring system.

Introduction. During the continuous search for biologically active phenothiazines, a series of substituted phenothiazines (Chiou, Reeves & Biehl, 1976; Biehl, Patrizi, Lapis & Reeves, 1974), heteroarylphenothiazines (Jovanovic & Biehl, 1983; Jovanovic, Biehl, Rosenstein & Chu, 1984), and their pyridobenzothiazine analogs (Jovanovic & Biehl, 1983) have been prepared. One of the interesting findings of these studies was the significant electronic interactions between the phenothiazine tricyclic ring and electron-withdrawing 10-aryl substituents. The examination of the interaction in the solid state by X-ray analysis can be used to compare the study of the same effects in solution by NMR spectroscopy (Jovanovic & Biehl, 1983, 1984).

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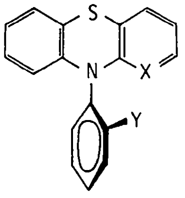
The *ortho*-substituted 10-arylphenothiazines have been used as the model compounds for assessing the relationship between resonance interactions as a function of the torsion angle between the two ring systems (Jovanovic & Biehl, 1984; Chu, Yang & van der Helm, 1976). The structure of 10-(2-methoxyphenyl)pyrido[3,2-*b*][1,4]benzothiazine (I) is reported in this paper as a reference compound for similar studies of 10-aryl-1-azaphenothiazines.



(I) X = N, Y = OCH_3
(II) X = CH, Y = OCH_3
(III) X = N, Y = H

Experimental. Colorless, flat needles of (I) recrystallized from a solution of 15% CH_2Cl_2–85% absolute ethanol, unit-cell parameters by least-squares analysis of 15 reflections with 2θ values measured on the diffractometer, $P2_1/c$ deduced from systematic absences ($h0l$ absent with l odd, $0k0$ absent with k odd), Syntex $P2_1$ automatic diffractometer, crystal 0·43 × 0·37 × 0·07 mm, $\theta/2\theta$ scanning mode, graphite-monochromated Cu $K\alpha$ radiation, 2529 independent reflections with $2\theta < 130°$, range of hkl: $h \pm 13$, k 0→9, l 0→18, 1708 observed, $I > 3\sigma(I)$; three standard reflections measured repeatedly after every 50 reflections showed a random variation of less than 4% in intensity; Lorentz–polarization corrections, no absorption or extinction corrections; direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refinement by full-matrix least squares using *SHELX*76 (Sheldrick, 1976), anisotropic, H positions located in successive difference Fourier syntheses, isotropic temperature factors for H atoms, $w = 1/[\sigma(F)]^2$, $\sigma(F)$ from counting statistics, $\sum w(|\,|F_o| - |F_c|\,|)^2$ minimized, $R = 0{\cdot}050$, $R_w = 0{\cdot}062$, $(\Delta/\sigma)_{\max} = 0{\cdot}06$, max. height in final difference Fourier synthesis 0·21 e Å^{-3}, atomic scattering factors for S, O, N, C and H from *International Tables for X-ray Crystallography* (1974).

Discussion. Final parameters are given in Table 1.* The identification of the atoms and the configuration of the molecule are shown in the *ORTEP* (Johnson, 1965) drawing in Fig. 1. The bond lengths and bond angles, with their standard deviations, are shown in Fig. 2. The bond lengths and bond angles of the title compound are in good agreement with those of 10-(*o*-methoxyphenyl)phenothiazine (II) (Chu *et al.*, 1976).

Table 1. *Fractional atomic coordinates* (×10^4 *for non*-H, ×10^3 *for* H *atoms*) *with equivalent isotropic thermal parameters for non*-H (×10^4) *and isotropic for* H *atoms* (×10^3) (*e.s.d.'s are in parentheses*)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}/U(Å^2)
C(1)	2017 (3)	79 (4)	8858 (2)	580 (8)*
C(2)	1183 (4)	616 (5)	9275 (3)	821 (11)
C(3)	221 (4)	1419 (5)	8844 (3)	849 (12)
C(4)	99 (3)	1683 (5)	7988 (3)	739 (11)
S(5)	827 (1)	1784 (1)	6486 (1)	750 (2)
C(6)	1534 (3)	−88 (5)	5283 (2)	634 (9)
C(7)	2260 (4)	−1144 (5)	4990 (2)	741 (10)
C(8)	3152 (4)	−1811 (5)	5564 (2)	720 (10)
N(9)	3319 (3)	−1528 (4)	6419 (2)	686 (7)
N(10)	2784 (2)	−220 (3)	7592 (2)	502 (6)
C(4a)	949 (3)	1194 (4)	7562 (2)	562 (8)
C(5a)	1690 (3)	274 (4)	6141 (2)	547 (7)
C(9a)	2579 (2)	−500 (4)	6710 (2)	485 (7)
C(10a)	1908 (2)	346 (4)	8007 (2)	496 (7)
C(1′)	3764 (2)	−1014 (4)	8111 (2)	504 (7)
C(2′)	3738 (3)	−2700 (4)	8278 (2)	525 (7)
C(3′)	4690 (3)	−3441 (5)	8775 (2)	665 (9)
C(4′)	5643 (3)	−2512 (6)	9097 (3)	761 (11)
C(5′)	5680 (3)	−864 (6)	8930 (3)	817 (12)
C(6′)	4729 (3)	−103 (5)	8426 (2)	685 (9)
O′	2748 (2)	−3504 (3)	7934 (1)	643 (6)
C(7′)	2751 (6)	−5254 (6)	7935 (4)	932 (15)
H(1)	260 (3)	−50 (5)	916 (2)	114 (16)
H(2)	133 (3)	26 (5)	984 (2)	80 (12)
H(3)	−33 (5)	178 (6)	916 (3)	141 (19)
H(4)	56 (3)	212 (5)	771 (2)	85 (12)
H(6)	95 (3)	37 (4)	493 (2)	72 (11)
H(7)	211 (3)	−145 (4)	439 (2)	72 (10)
H(8)	370 (4)	−249 (6)	537 (3)	94 (13)
H(3′)	467 (3)	−449 (5)	886 (2)	67 (11)
H(4′)	619 (4)	−299 (5)	945 (3)	91 (13)
H(5′)	630 (4)	−9 (6)	911 (3)	110 (15)
H(6′)	474 (3)	122 (5)	825 (2)	84 (11)
H(71′)	205 (2)	−545 (8)	763 (4)	178 (27)
H(72′)	288 (4)	−562 (7)	848 (3)	116 (19)
H(73′)	329 (4)	−554 (5)	759 (3)	99 (15)

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

The tricyclic ring system is folded with the central ring in a boat conformation as shown by the torsion angles in Fig. 2 and the puckering parameters (Cremer & Pople, 1975). The puckering parameters are $q_2 = 0{\cdot}500$, $q_3 = 0{\cdot}001$, $Q = 0{\cdot}501$ Å, $\varphi_2 = 4{\cdot}0$ and $\theta = 101{\cdot}0°$. For ideal boat conformation, these values are $q_2 = Q$, $q_3 = 0$ Å, $\varphi_2 = 0$ and $\theta = 90°$. The 10-(2-methoxyphenyl) substituent is in a boat-equatorial conformation with respect to the central ring. The least-squares planes of the pyrido, benzo, and phenyl rings together with the deviations of atoms from the planes are shown in Fig. 1. The folding angle between the planes of the pyrido and benzo rings is 158·7 (1)° in (I) compared with the folding angle of 157·5° in (II). The phenyl ring nearly bisects the tricyclic ring system and the plane of the phenyl ring is nearly perpendicular to the plane of the central ring [C(4a), C(5a), C(9a) and C(10a)] with a dihedral angle of 95·4 (1)°. The dihedral angles between the plane of the phenyl ring and the planes of the benzo and pyrido rings are 95·3 (1) and 106·0 (1)° respectively. These data indicate that the substitution of the benzo ring in (II) by the pyrido ring does not have any significant effect on

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39564 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

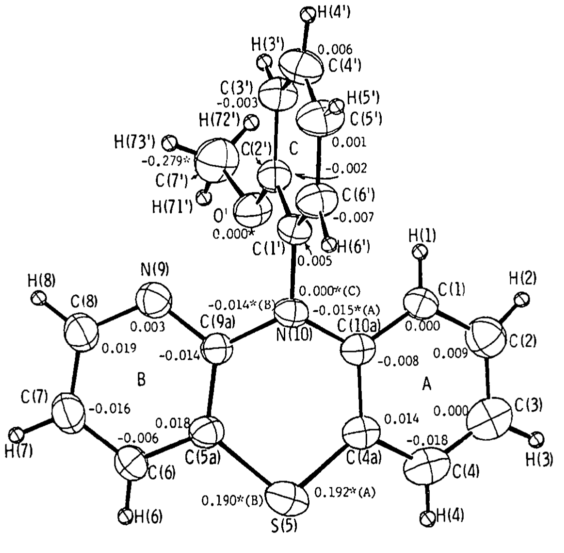

Fig. 1. *ORTEP* drawing of a molecule of (I) with the deviations of atoms from least-squares planes shown in Å (e.s.d.'s ~ 0·005 Å). The equations for the planes are:

Plane *A* $0{\cdot}445\,(2)x+0{\cdot}8737\,(8)y+0{\cdot}103\,(2)z=2{\cdot}58\,(2)$
Plane *B* $0{\cdot}629\,(1)x+0{\cdot}770\,(1)y-0{\cdot}232\,(2)z=-0{\cdot}87\,(2)$
Plane *C* $-0{\cdot}538\,(1)x+0{\cdot}196\,(2)y+0{\cdot}9111\,(7)z=9{\cdot}27\,(2)$

where *x*,*y*, and *z* are in Å. Dihedral angles: between *A* and *B* 158·7 (1), *A* and *C* 95·3 (1), *B* and *C* 106·0 (1)°. An asterisk indicates atoms excluded from the calculation of the least-squares planes. The letter in parentheses indicates the plane from which the atom deviates.

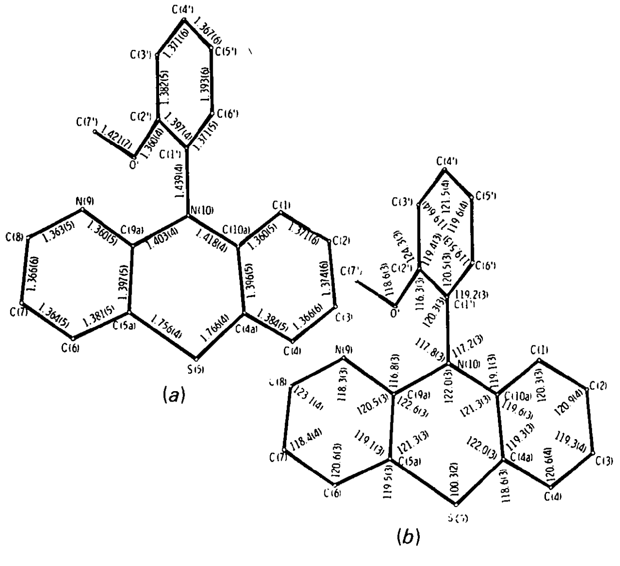

Fig. 2. (*a*) Bond lengths (Å) and (*b*) bond angles (°) of (I) with e.s.d.'s in parentheses. The torsion angles (°) around the central ring are: C(4a)–S(5)–C(5a)–C(9a) −26·1 (3), S(5)–C(5a)–C(9a)–N(10) 4·9 (4), C(5a)–C(9a)–N(10)–C(10a) 23·8 (5), C(9a)–N(10)–C(10a)–C(4a) −23·0 (4), N(10)–C(10a)–C(4a)–S(5) −6·0 (4), C(10a)–C(4a)–S(5)–C(5a) 26·7 (3).

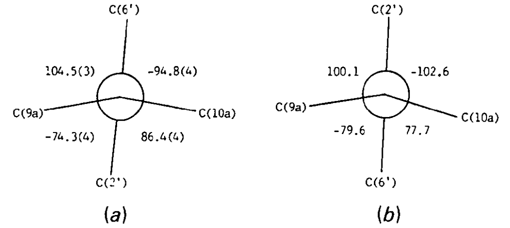

Fig. 3. Torsion angles (°) about the N(10)–C(1′) bond in (*a*) (I) and (*b*) (II). The methoxy group is bonded to C(2′).

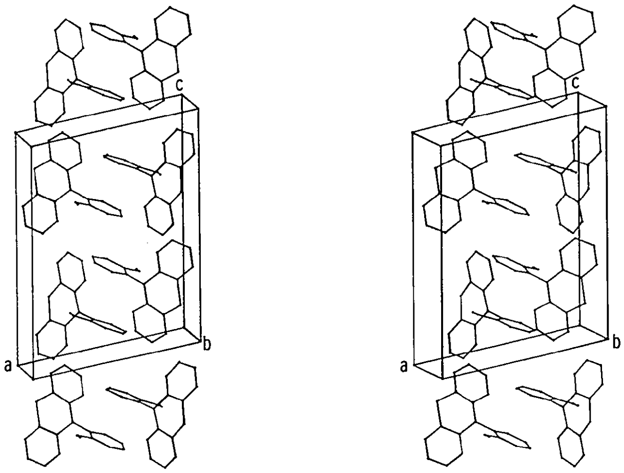

Fig. 4. Stereoscopic drawing of the molecular packing of (I), excluding H atoms, in the unit cell.

the conformation and configuration of the tricyclic ring system. The oxygen of the methoxy group is coplanar with the phenyl ring; however, the methyl carbon deviates from the plane of the phenyl ring by 0·279 (9) Å. In (II), both the oxygen and the methyl carbon are nearly coplanar with the phenyl ring. One major difference between the structures of (I) and (II) is that the methoxy group in (I) extends to the concave side of the tricyclic ring system while in (II) it extends to the convex side (Fig. 3). The difference in the conformation of the methoxy group between (I) and (II) is due to the substitution of C(9) in (II) by N(9) with the absence of H(9). The nonbonded intramolecular distance between N(9) and O′(methoxy oxygen) is 3·095 (5) Å.

The packing of the molecules in the unit cell is shown in the stereoscopic drawing in Fig. 4. There are no intermolecular contacts less than the van der Waals distances.

The ^{13}C NMR spectrum and assignments for the title compound (I) have been reported (Jovanovic & Biehl, 1984). Several of the *ipso* ^{13}C–H and *ortho* ^{13}C–H coupling constants are influenced significantly by the *o*-methoxy group when compared with those of unsubstituted 10-phenylpyrido[3,2-*b*][1,4]benzothiazine (III). However, the largest differences observed are for the C atoms in the pyridine ring. This is supported by the conformation of the 10-(2-methoxyphenyl) substituent observed in the solid state. The *o*-methoxy group is tilted toward the pyrido ring as shown by the dihedral angles in Fig. 1 and the torsion angles about the N(10)—C(1′) bond in Fig. 3. Furthermore, all of the *ortho* ^{13}C—H couplings were too small to be observed in (III); however, the coupling constants in (I) have been observed and they are 3·10, 2·93, and 2·90 Hz, between C(8)—H(7), C(6)—H(7), and C(1)—H(2), respectively. These coupling changes indicate that there is an increase in the folding angle of the pyridobenzothiazine ring in (I) as compared to the unsubstituted 10-phenyl derivative (III). The crystal structure of (III) will be investigated to determine if the folding angle of (III) is smaller than that of (I) as predicted by NMR studies in solution.

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Thuriferin Monohydrate, $C_{21}H_{34}O_4.H_2O$

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Abstract. $M_r = 368·52$, monoclinic, $P2_1$, $a = 7·131$ (1), $b = 21·310$ (3), $c = 7·033$ (1) Å, $\beta = 110·93$ (1)°, $V = 998·2$ (3) Å^3, $Z = 2$, $D_x = 1·226$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0·697$ mm^{-1}, $F(000) = 404$, room temperature, $R = 0·046$ for 1257 unique reflections with $I \geq 2\sigma(I)$. Thuriferin is a kaurane-type diterpene isolated from *Robinsonia thurifera* (Mol.) D.C. (tribe Senecioneae of family Compositae). It contains three six-membered rings in chair conformations, a five-membered ring in an envelope conformation, and an unusual methyl hemiacetal functionality.

Introduction. The concept of the tribe Senecioneae (Bentham, 1873) was generally accepted and remained basically unchanged for almost a century. During recent years there has been some disagreement concerning the number of subtribes, and a number of genera have even been shifted from tribes such as Helenieae into an expanded concept of Senecioneae (Nordenstam, 1977). Others have narrowed the concept and have excluded anomalous genera and even the entire subtribe Liabinae (Turner & Powell, 1977). In an attempt to provide chemical data for use as additional taxonomic markers, we have investigated *Robinsonia thurifera*. The genus *Robinsonia* contains approximately six species of rosette trees or epiphytic plants on tree ferns.

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