relative des cycles aromatiques apparaît tout à fait comparable à celle des triphényléthylènes, la conformation globale de la molécule est néanmoins très différente. En effet si les atomes C(7) et C(33) devraient être dans le plan C(6)—C(19)—C(13) pour un triphényléthylène, ils sont ici observés de part et d'autre de ce plan à des distances importantes, respectivement égales à 1,141 (4) et 1,157 (5) Å.

La chaîne acétamidométhyle ne présente pas un allongement maximum. Sa conformation peut être expliquée par la présence d'une liaison hydrogène N(34)(x, y, z)—O(54)($\frac{1}{2}+x, y, \frac{1}{2}-z$); la distance N—O est égale à 2,817 (7) Å.

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

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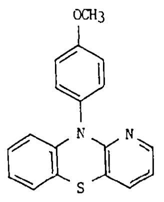
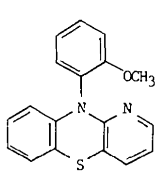
Abstract. $M_r = 306\cdot38$, triclinic, $P\bar{1}$, $a = 13\cdot680$ (4), $b = 10\cdot982$ (2), $c = 11\cdot782$ (3) Å, $\alpha = 101\cdot63$ (2), $\beta = 116\cdot24$ (2), $\gamma = 70\cdot97$ (2)°, $V = 1497\cdot4$ (7) Å^3, $Z = 4$, $D_x = 1\cdot359$, $D_m = 1\cdot35$ g cm^{-3} (by flotation), λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 2\cdot09$ cm^{-1}, $F(000) = 640$, $T = 295$ K, final $R = 0\cdot051$ for 3529 observed reflections. There are two crystallographically independent molecules in an asymmetric unit of the unit cell. The pyridobenzothiazine ring is folded with the central ring in a boat conformation. The folding angles are 157·1 (1) and 155·2 (1)° for the two crystallographically independent molecules. The 10-(4-methoxyphenyl) substituent is in a boat-equatorial conformation with respect to the central ring of the tricyclic ring system.

Introduction. The determination of the title compound (I) is one of a series of heteroarylphenothiazines under study in this laboratory. The purpose of this study is to determine the effects of the different substituents on the conformation and reactivity (Chiou, Reeves & Biehl, 1976) of the heteroarylphenothiazines. The crystal structure of 10-(2-methoxyphenyl)pyrido[3,2-*b*][1,4]benzothiazine (II) has been determined (de Meester, Chu, Jovanovic & Biehl, 1984). The objective of the present study is to provide information on the effect of the methoxy substituent occupying different positions of the 10-phenyl ring.



(I)



(II)

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 in range 20–34° measured on the diffractometer, $P\bar{1}$ confirmed from

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structure analysis, Syntex $P2_1$ automatic diffractometer, crystal 0·59 × 0·36 × 0·15 mm, $\theta/2\theta$ scanning mode, graphite-monochromated Mo $K\alpha$ radiation, 6832 independent reflections with $2\theta < 55°$, range of *hkl*: h $-16\rightarrow15$, k ±14, l $0\rightarrow15$, 3529 observed, $I > 3\sigma(I)$; three standard reflections measured repeatedly after every 50 reflections showed no significant variation 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, hydrogen positions located in successive difference Fourier syntheses, isotropic temperature factors for hydrogen atoms, two crystallographically independent molecules in an asymmetric unit cell. The methoxy carbon, C(7′), of molecule *B* is disordered from difference Fourier analysis. 50% occupancy factor for each of the two disordered methoxy carbon atoms was assigned since the two disordered carbon atoms have nearly the same electron densities in the difference Fourier synthesis; hydrogen atoms for the disordered methoxy carbon atoms were not located; $w = 1{\cdot}609/[\sigma^2(F) + kF^2]$, $\sigma(F)$ from counting statistics, $k = 8{\cdot}29 \times 10^{-4}$ from least-squares refinement, 496 variables, $\sum w(|F_o| - |F_c|)^2$ minimized, $R = 0{\cdot}051$, $wR = 0{\cdot}057$, $(\Delta/\sigma)_{\max} = 0{\cdot}51$, max. height in final difference Fourier synthesis 0·36 e Å^{-3} at a distance of 0·48 Å from disordered methoxy carbon C(7′)*B*, min. height −0·22 e Å^{-3}, atomic scattering factors for S, O, N, C, and H from *International Tables for X-ray Crystallography* (1974), anomalous-scattering factors for S included in refinement (Sheldrick, 1976).

Discussion. Final parameters are given in Table 1.* The identification of the atoms and the configuration of the two crystallographically independent molecules 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. There is good agreement in the bond lengths and bond angles between the two crystallographically independent molecules. However, C(7′)—O(4′) bond lengths of the methoxy group are 1·327 (12) and 1·307 (10) Å in the disordered molecule *B* as compared to that of 1·415 (8) Å in molecule *A*. The short C—O bond lengths in *B* are most likely due to the refinement since the methoxy group is disordered and, furthermore, it has large thermal motions as indicated in Fig. 1(*b*). There is an apparent short intermolecular separation of 2·72 (2) Å between the C(7″)*B* at (x, y, z) and the C(7″)*B* at ($2-x$, $-y$, $1-z$), and the two positions are related by a center of

Table 1. *Fractional atomic coordinates* (×10^4 *for non-hydrogen,* ×10^3 *for hydrogen atoms*) *with equivalent isotropic thermal parameters for non-hydrogen* (×10^3) *and isotropic for hydrogen atoms* (×10^2) (*e.s.d.'s given in parentheses*)

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

	x	y	z	U_{eq}/U(Å^2)
N(1)*A*	6109 (2)	6906 (2)	9455 (2)	53 (1)*
C(2)*A*	6593 (3)	7828 (3)	10242 (3)	61 (1)
C(3)*A*	7727 (3)	7667 (3)	10832 (3)	68 (1)
C(4)*A*	8433 (3)	6486 (3)	10657 (3)	62 (1)
C(4a)*A*	7969 (2)	5503 (3)	9900 (3)	49 (1)
S(5)*A*	8859 (1)	3950 (1)	9871 (1)	60 (1)
C(5a)*A*	8021 (2)	3315 (3)	8401 (3)	48 (1)
C(6)*A*	8560 (3)	2305 (3)	7784 (4)	62 (1)
C(7)*A*	7951 (3)	1701 (3)	6681 (3)	67 (1)
C(8)*A*	6796 (3)	2122 (3)	6181 (3)	60 (1)
C(9)*A*)	6250 (3)	3152 (3)	6758 (3)	51 (1)
C(9a)*A*	6848 (2)	3766 (3)	7874 (3)	43 (1)
N(10)*A*	6272 (2)	4831 (2)	8465 (2)	44 (1)
C(10a)*A*	6790 (2)	5764 (3)	9279 (3)	43 (1)
C(1′)*A*	5042 (2)	5131 (3)	7928 (3)	43 (1)
C(2′)*A*	4376 (3)	5993 (3)	6987 (3)	50 (1)
C(3′)*A*	3225 (3)	6212 (3)	6452 (3)	50 (1)
C(4′)*A*	2725 (2)	5565 (3)	6851 (3)	57 (1)
C(5′)*A*	3379 (3)	4714 (3)	7792 (3)	67 (1)
C(6′)*A*	4541 (3)	4512 (3)	8323 (3)	57 (1)
O(4′)*A*	1576 (2)	5830 (3)	6240 (2)	86 (1)
C(7′)*A*	1021 (5)	5242 (8)	6653 (6)	160 (3)
N(1)*B*	3969 (2)	2513 (2)	3551 (2)	50 (1)
C(2)*B*	3452 (3)	3715 (3)	3888 (3)	56 (1)
C(3)*B*	2318 (3)	4220 (3)	3460 (3)	54 (1)
C(4)*B*	1646 (3)	3437 (3)	2647 (3)	54 (1)
C(4a)*B*	2135 (2)	2186 (3)	2312 (3)	49 (1)
S(5)*B*	1284 (1)	1139 (1)	1467 (1)	80 (1)
C(5a)*B*	2130 (2)	42 (3)	732 (3)	55 (1)
C(6)*B*	1602 (3)	−623 (3)	−385 (3)	66 (1)
C(7)*B*	2230 (3)	−1558 (3)	−956 (4)	67 (1)
C(8)*B*	3376 (3)	−1794 (3)	−416 (3)	62 (1)
C(9)*B*	3917 (3)	−1119 (3)	688 (3)	49 (1)
C(9a)*B*	3306 (2)	−188 (3)	1287 (3)	45 (1)
N(10)*B*	3866 (2)	520 (2)	2417 (2)	45 (1)
C(10a)*B*	3319 (2)	1763 (3)	2765 (3)	43 (1)
C(1′)*B*	5091 (2)	109 (3)	2978 (3)	43 (1)
C(2′)*B*	5718 (3)	612 (3)	2642 (3)	49 (1)
C(3′)*B*	6882 (3)	172 (3)	3155 (3)	58 (1)
C(4′)*B*	7425 (3)	−789 (3)	3989 (3)	54 (1)
C(5′)*B*	6800 (3)	−1294 (3)	4331 (3)	59 (1)
C(6′)*B*	5632 (3)	−835 (3)	3826 (3)	55 (1)
O(4′)*B*	8582 (2)	−1219 (3)	4486 (3)	99 (1)
C(7′)*B*	9244 (7)	−2019 (8)	5378 (9)	97 (3)
C(7″)*B*	9374 (7)	−859 (12)	4382 (10)	137 (4)
H(2)*A*	603 (3)	865 (3)	1034 (3)	8 (1)
H(3)*A*	803 (3)	838 (3)	1143 (3)	8 (1)
H(4)*A*	921 (3)	628 (3)	1104 (3)	6 (1)
H(6)*A*	928 (3)	204 (3)	812 (3)	6 (1)
H(7)*A*	831 (3)	102 (3)	631 (3)	9 (1)
H(8)*A*	631 (3)	176 (3)	540 (3)	7 (1)
H(9)*A*	549 (2)	337 (3)	639 (3)	5 (1)
H(2′)*A*	467 (2)	640 (3)	670 (3)	5 (1)
H(3′)*A*	276 (2)	682 (3)	581 (3)	6 (1)
H(5′)*A*	310 (3)	423 (3)	817 (3)	9 (1)
H(6′)*A*	496 (3)	391 (3)	899 (4)	9 (1)
H(71′)*A*	28 (5)	553 (6)	617 (6)	20 (3)
H(72′)*A*	123 (4)	543 (5)	770 (5)	15 (2)
H(73′)*A*	135 (5)	433 (1)	668 (6)	16 (1)
H(2)*B*	394 (3)	418 (3)	438 (3)	7 (1)
H(3)*B*	203 (3)	504 (3)	372 (3)	7 (1)
H(4)*B*	87 (3)	377 (3)	232 (3)	6 (1)
H(6)*B*	82 (2)	−44 (3)	−70 (3)	6 (1)
H(7)*B*	191 (3)	−199 (3)	−177 (3)	9 (1)
H(8)*B*	384 (2)	−238 (3)	−83 (3)	6 (1)
H(9)*B*	470 (3)	−127 (3)	102 (3)	6 (1)
H(2′)*B*	537 (2)	126 (3)	208 (3)	5 (1)
H(3′)*B*	729 (3)	51 (3)	288 (3)	6 (1)
H(5′)*B*	714 (3)	−200 (3)	495 (3)	7 (1)
H(6′)*B*	519 (2)	−122 (3)	403 (3)	6 (1)

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

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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 42212 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

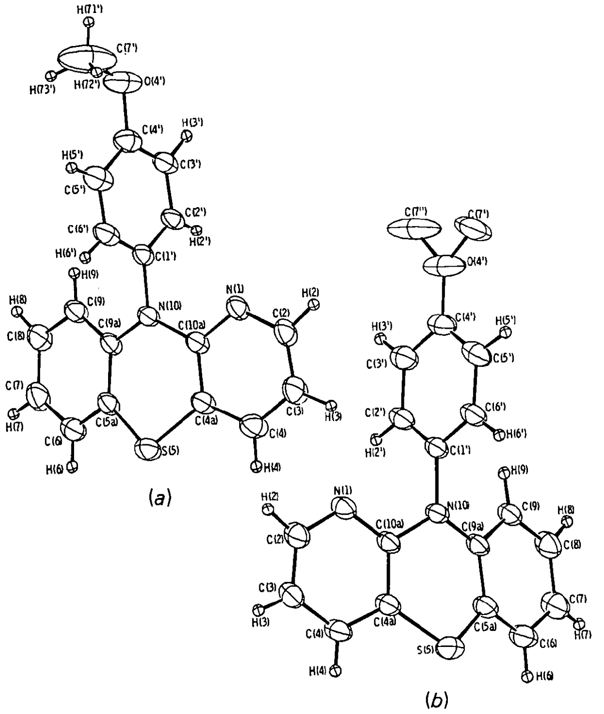

Fig. 1. *ORTEP* drawing of (*a*) molecule *A* and (*b*) molecule *B*.

Table 2. *Torsion angles and puckering parameters*

The torsion angles and puckering parameters refer to the molecule with atomic parameters shown in Table 1.

Torsion angles (°)		
Around the central ring:	Molecule *A*	Molecule *B*
C(4a)–S(5)–C(5a)–C(9a)	−26·8 (3)	27·9 (3)
S(5)–C(5a)–C(9a)–N(10)	4·4 (4)	−4·8 (4)
C(5a)–C(9a)–N(10)–C(10a)	24·5 (5)	−25·2 (4)
C(9a)–N(10)–C(10a)–C(4a)	−22·2 (5)	23·2 (4)
N(10)–C(10a)–C(4a)–S(5)	−8·7 (4)	8·5 (4)
C(10a)–C(4a)–S(5)–C(5a)	29·1 (3)	−30·0 (3)
About the N(10)–C(1′) bond:		
C(9a)–N(10)–C(1′)–C(2′)	−90·8 (4)	89·9 (4)
C(9a)–N(10)–C(1′)–C(6′)	86·5 (4)	−87·7 (4)
C(10a)–N(10)–C(1′)–C(2′)	72·8 (4)	−71·8 (4)
C(10a)–N(10)–C(1′)–C(6′)	−109·9 (4)	110·7 (4)
About the C(4′)–O(4′) bond:		
C(3′)–C(4′)–O(4′)–C(7′)	−177·1 (4)	172·4 (6)
C(5′)–C(4′)–O(4′)–C(7′)	3·6 (6)	−6·5 (8)
C(3′)–C(4′)–O(4′)–C(7″)		3·5 (9)
C(5′)–C(4′)–O(4′)–C(7″)		−175·5 (8)

Puckering parameters	Molecule *A*	Molecule *B*	Ideal boat conformation
Q(Å)	0·391	0·406	
q_2(Å)	0·382	0·397	Q
q_3(Å)	0·083	−0·086	0
θ(°)	77·7	102·2	90
φ_2(°)	183·5	2·7	0 or 180

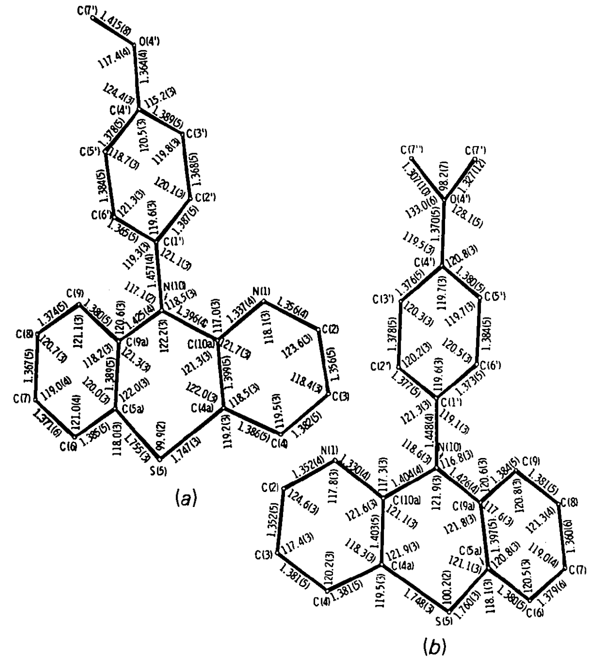

Fig. 2. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses of (*a*) molecule *A* and (*b*) molecule *B*.

symmetry. The close contact can be eliminated if the *B* molecules are paired with one methoxy in the single-prime position to the one (across the center of symmetry) in the double-prime position. Each of the two positions will have 50% occupancy and the structure will still be disordered if there is no correlation between the methoxy orientation in one pair and those in translationally related pairs. The large thermal vibrations of the methoxy groups demonstrated by the NMR data show that there is a free rotation of the methoxy carbon in solution. However, the methoxy carbon in (II) does not have this freedom due to the steric effect.

The tricyclic ring is folded with the central ring in a boat conformation as shown by the torsion angles and the puckering parameters (Cremer & Pople, 1975) in Table 2. The 10-(4-methoxyphenyl) substituent is in a boat-equatorial conformation with respect to the central ring in both *A* and *B*. The pyrido, benzo, and phenyl rings are planar and the atomic deviations from the plane range from 0·001 to 0·018 Å. The deviations of the methoxy group from the phenyl ring are −0·030 (6) and 0·026 (11) Å for O(4′) and C(7′), respectively, in molecule *A*, and 0·000 (6) 0·126 (12), and 0·075 (15) Å for O(4′), C(7′), and C(7″), respectively, in molecule *B*. The folding angles between the planes of the pyrido and benzo rings are 157·1 (1) and 155·2 (1)° for *A* and *B* respectively. These are similar to the magnitude of 158·7 (1)° observed in (II). The plane of the phenyl ring nearly bisects the tricyclic ring system. The dihedral angles between the planes of the phenyl ring and pyrido ring are 111·3 (1) and

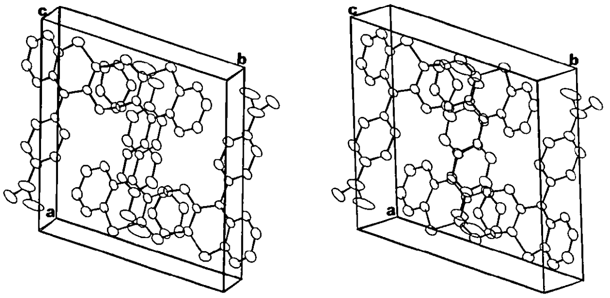

Fig. 3. Stereoscopic drawing of the molecular packing of *A* and *B* excluding hydrogen atoms, in the unit cell.

112·2 (1)° for *A* and *B* respectively and those between the planes of the phenyl ring and benzo ring are 92·4 (1) and 91·2 (1)° for *A* and *B* respectively. In (II), the dihedral angle between the planes of the phenyl ring and pyrido ring is 106·0 (1)° and that between the planes of the phenyl ring and benzo ring is 95·3 (1)°. The torsion angles about the N(10)—C(1′) link between the two ring systems and about the C(4′)—O(4′) of the methoxy group are also shown in Table 2. The torsion angles about the N(10)—C(1′) link between the two ring systems in (II) also have similar values. Therefore, there is no significant difference in the conformation of the two ring systems whether the methoxy substituent is at the C(2′) or C(4′) position.

The packing of the molecules in the unit cell is shown in the stereoscopic drawing in Fig. 3. Except for the close intermolecular contacts involving the methoxy carbon atoms, there are no other contacts less than van der Waals distances.

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Structure of a Polymorph of the 1/1 Addition Compound Between Benzoic Acid and 2,4-Diamino-5-(3,4,5-trimethoxybenzyl)pyrimidinium Benzoate (Trimethoprim Monobenzoate–Benzoic Acid 1/1 Complex, Form II), $C_{14}H_{19}N_4O_3^+.C_7H_5O_2^-.C_7H_6O_2$

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Abstract. $M_r = 534·57$, triclinic, $P\bar{1}$, $a = 10·192$ (1), $b = 14·595$ (1), $c = 9·457$ (1) Å, $\alpha = 97·41$ (1), $\beta = 89·69$ (1), $\gamma = 104·57$ (1)°, $V = 1349·6$ (2) Å^3, $Z = 2$, $D_m = 1·307$ (6), $D_x = 1·315$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·89$ cm^{-1}, $F(000) = 564$, $T = 296$ K, $R = 0·037$ for 2881 observed reflections. The trimethoprim cation is bonded to the benzoate anion through two N—H···O hydrogen bonds [N···O = 2·673 (2), 2·870 (2) Å], the other benzoic acid molecule being linked through a short O—H···O hydrogen bond [2·531 (2) Å] involving its carboxyl OH and an oxygen atom of the anion. The trimethoprim cation is in a twist conformation, as in the trimethoprim benzoate salt. Cyclic centrosymmetrical N—H···N and linear N—H···O hydrogen bonds are responsible for molecular packing.

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