Molecular Structure and 13C Chemical Shift Assignments of 10-(2'-Pyridyl)pyrido[3,2-b][1,4]benzothiazine Using 10-Phenylpyrido[3,2-b][1,4]benzothiazine as the Model Compound

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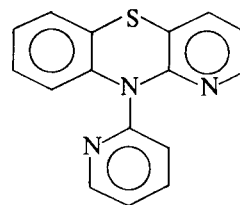Dallas, Texas 75275
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The crystal structure of 10-(2'-pyridyl)pyrido[3,2-b][1,4]benzothiazine, **6**, shows that orientation of the 10-pyridyl ring is in the plane bisecting the pyridobenzothiazine ring. This orientation is in contrast to that of 10-(2'-pyridyl)phenothiazine, **11**, in which the heterocyclic ring is perpendicular to the plane bisecting the phenothiazine nucleus. X-ray data also indicate that the resonance interaction between the lone pair of electrons of N_{10} in **6** with either the pyridine protons of the tricylcic ring or the 10-(2'-pyridyl) ring is not significant. The folding angle of 166.1° in **6** is the largest observed for the pyridobenzothiazine ring. The nmr spectral assignments of the titled compound, **6**, was accomplished using the structurally similar, 10-phenylpyrido-[3,2-b][1,4]benzothiazine, **9**, as the model compound. 10-(2'-Pyridyl)phenothiazine, **11**, was shown to be an inadequate model for such assigments.
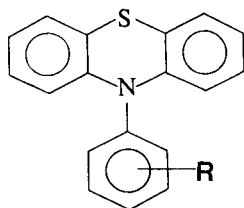
The orientation of the 10-phenyl ring in various 10-aryl- and 10-heteroarylphenothiazine compounds has been shown by x-ray diffraction studies to be dependent on the electronic nature of 4'-substituents or on the steric effects of 2'-substituents [1-6]. For example, the plane of the phenyl ring is nearly parallel to the plane bisecting the phenothiazine ring in compounds having electron-releasing groups in the 4'-position such as 10-(p-bromophenyl)phenothiazine, **1** [6], and 10-(o-methoxyphenyl)phenothiazine, **2** [5]. However, compounds having electron-withdrawing groups in the 4'-position, e.g. 4'-nitro-10-phenylphenothiazine, **3** [4] or a π- deficient heterocyclic ring, e.g. 10-(2'-pyrazyl)phenothiazine, **4** [2], the aromatic ring is nearly perpendicular to the plane bisecting the dihedral angle of the phenothiazine nucleus. Of these two orientations, only the latter permits delocalization of the lone pair of electrons on N_{10} into the 10-aromatic ring. The resonance interaction is revealed in the 13C nmr spectra of **3** and **4**; several of the chemical shifts of the phenothiazine ring carbon atoms in these compounds are significantly different than the corresponding ones of 10-phenylphenothiazine, **5** [7].

We have extended these studies to the pyrido[3,2-b]-[1,4]benzothiazine ring system and have shown that the plane of the 10-phenyl ring containing electron-releasing groups such as 4'-methoxy [8] and 4'-dimethylamino [9] are also nearly parallel to plane bisecting the pyridobenzothiazine ring. This paper reports on the effect of the electron-withdrawing 10-(2'-pridyl) ring on the structure and 13C nmr spectrum of 10-(2'-pyridyl)pyrido[3,2-b][1,4]benzothiazine, **6**. The knowledge of the structure of this compound is particularly important since it is the first biarylthiazine bidentate reported.

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Results and Discussion.

X-Ray Analysis.

The identification of the atoms and the configuration of the titled compound, **6**, are shown in ORTEP [10] drawing in Figure 1 (also see Experimental). The bond lengths and bond angles, with their standard deviations, are shown in Figure 2. The least-squares planes of the benzo and the

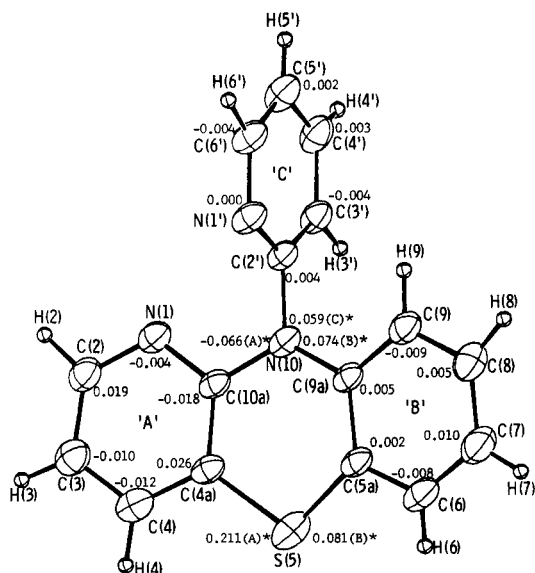|		
1	R = P-Br	
2	R = o-OCH₃	
3	R = P-NO₂	
4	R = 2'-PYRAZYL	
5	R = H	

Figure 1. ORTEP drawing of a molecule of **6** with the deviations of atoms from the least-squares planes shown in Å units. The equations for the planes are:

Plane 'A' 7.87(4)x - 4.977(9)y + 6.36(2)z = 2.219(6)
Plane 'B' 1.25(3)x - 5.032(7)y + 8.79(1)z = 1.700(1)
Plane 'C' 26.16(1)x + 2.73(1)y - 6.83(2)z = 2.189(6)

where x, y and z are in fractional coordinates. Dihedral angles between 'A' and 'B' 166.1(1)°, 'A' and 'C' 95.3(1)°, 'B' and 'C' 97.5(1)°. An asterisk indicates atoms excluded from the calculation of the least-squares planes. The lettering in parentheses indicates the plane that the deviation is from.
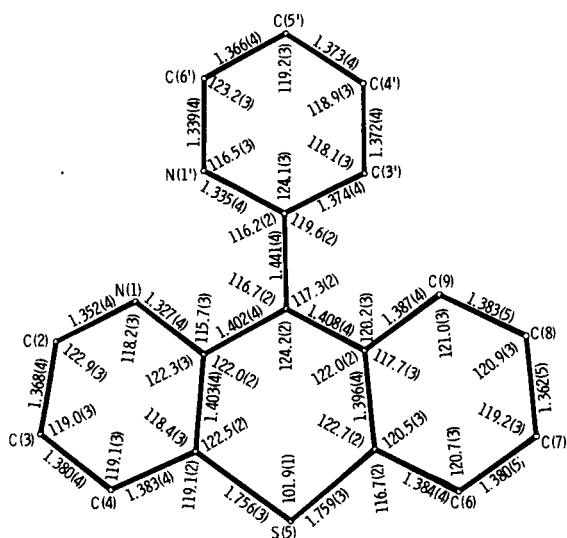

Figure 2. Bond lengths (Å) (a) and bond angles (°) (b) of **6** with e.s.d.'s in parentheses.

pyrido rings, together with the deviations of the atoms from the planes are shown also in Figure 1. The central ring is in a flattened boat conformation as shown by the small size of the torsion angles around the central ring and by the small Q value of the puckering parameters [11] in Table 3. The folding angle (dihedral angle) between the planes of the benzo and pyrido rings is 166.1(1)°. The 10-pyridyl ring is planar and is in a boat equatorial conformation with respect to the central ring of the pyridobenzothiazine ring system. The plane of the 10-pyridyl ring nearly bisects the pyridobenzothiazine ring with the dihedral angles of 95.3(1)° between the planes of pyridyl and benzo rings and 97.5(1)° between the planes of the two pyrido rings. The bisecting conformation can be shown also by the torsion angles about the N(10)-C(2') bond in Table 3 and in Figure 3. That the orientation of the 10-(2'-pyrido) ring in the pyrido[3,2-b][1,4]benzothiazine ring system is vastly different than the π-deficient rings in the phenothiazine compounds, **3** and **4**, is surprising. However, the perpendicular orientation of the 10-(2'-pyridyl)
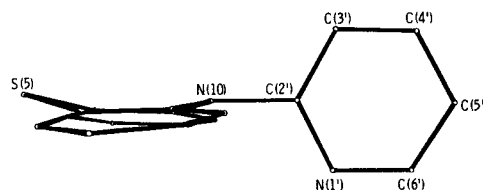

Figure 3. Side view of molecule **6**.

ring in **6** shows clearly the absence of resonance interactions between that ring and the lone pair of electrons on N_{10}. The folding angle in **6** (166.1°) is much larger than that in **3** (124.4°) [4] and **4** (132.2°) [2] indicating that the tricyclic ring is more planar in **6** than in **3** or **4**. Construction of a Drieding model of **6** reveals that the conformation necessary for resonance interactions between the 10-(2'-pyridyl) ring and N_{10} lone pair electrons, that is, with the ring bisecting the dihedral angle of the tricyclic nucleus, is prevented by unfavorable steric interactions between N_1 and C_9 of the tricyclic ring and $N_{1'}$ and $C_{6'}$ of the 10-(2'-pyridyl) ring.

Interestingly, the C(10a)-N(1) bond has considerably more double bond character than that of the C(10a)-N(10) bond in **6** indicating that resonance interactions between the lone pair of electrons of N(10) and N(1) is not significant. Also the former bond distance (1.327 Å) is significantly shorter than the corresponding one (1.344 Å) in 10-(4'-dimethylaminophenyl)pyrido[3,2-b][1,4]benzothiazine, **7**. The reason for these bond length differences is unclear at present but such differences may contribute, partly, to the disparate ease of oxidation of these two compounds. For example, attempts to oxidize **6** to its radical-
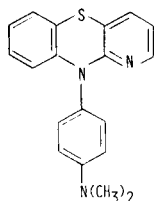
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cation in aqueous sulfuric acid were unsuccessful, however, **7**, as well as the phenothiazine analog, **4**, are readily oxidized under similar conditions [2,9]. The spin distribution of the radical cation of **7** has been shown to be pyridobenzothiazine-centered [9] whereas that of the corresponding 4'-dimethylaminophenothiazine derivative, **8**, is not phenothiazine-centered but located on the 10-aryl ring and on the dimethylamino group [12]. The resonance structure involving the 1-aza atom is shown in **7a** may
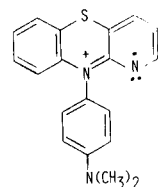
7A

contribute significantly to the stabilization of the radical cation of **3** to account for the location of the spin density in this compound. Such resonance stabilization of the radical cation of **6** is not likely due to the electron-withdraw-

ing nature of the 10-(2'-pyridyl) group which may account for the failure of **6** to undergo oxidation with aqueous mineral acids. We are studying other pyridobenzothiazines to see what relationships exist between the C(10a)-N(1) bond distance and the electronic nature of the 10-aromatic ring and the effect of such relationships on the chemical reactivities of these compounds.

Finally, the packing of the molecules in the unit cell is shown in the stereoscopic drawing in Figure 4. There is no intermolecular distance less than van der Waals separation.
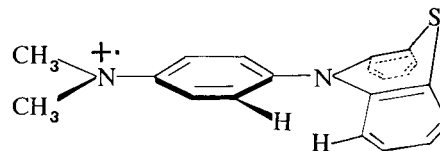
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NMR Analysis.

One method for assigning ^{13}C nmr chemical shifts to compounds as complex as **6** is the use of the model compounds. Preliminary x-ray data indicate that the orientation of the 10-phenyl ring in 10-phenylpyrido[3,2-b][1,4]-benzothiazine, **9**, is the same as that of the 10-pyridyl ring
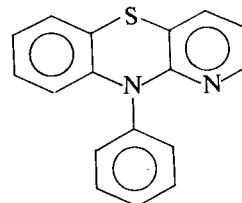
9

in **6** [13]. Further, we have shown that the chemical shifts of the tricyclic ring carbon atoms of 2'-nitro-10-phenyl-phenothiazine, **10**, which has a similar structure as **6** and also contains an electron withdrawing ring, are essentially
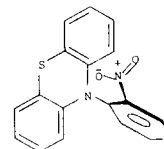
10

the same as those of unsubstituted 10-phenylphenothiazine, **5** [7]. Therefore, compound **9** might be a suitable model in the assignment of chemical shifts of **6**; the ^{13}C chemical shifts of the tricyclic ring carbons in both compounds should be similar.

Figure 4.   Stereoscopic drawing of molecular packing of **6**, excluding hydrogen atoms, in the unit cell.

The ^{13}C chemical shifts, in ppm, of compounds **6** and **9** are listed in Figure 5. The ^{13}C chemical shifts of 10-(2'-pyridyl)phenothiazine, **11**, are also shown in Figure 5 as an example of an unsatisfactory model for aiding the assignme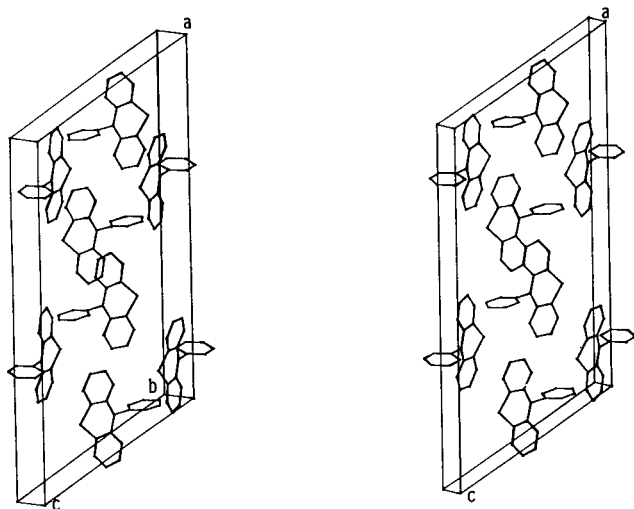nt of chemical shifts of **6**. The method for assigning chemical shifts for **9** and **11** has been reported previously [7].
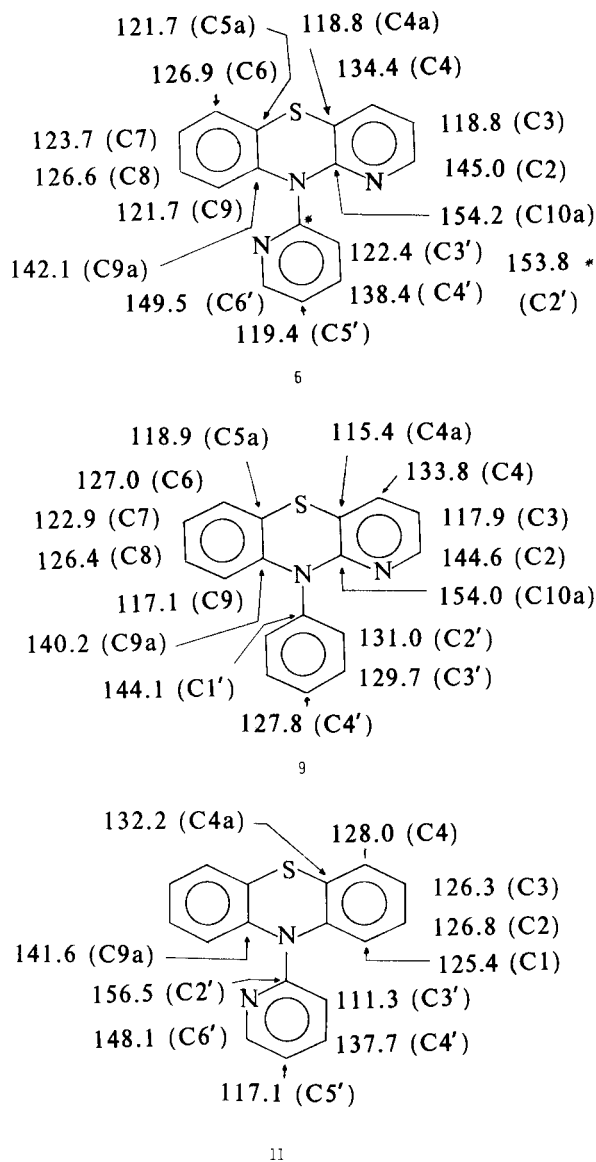
121.7 (C5a) — 118.8 (C4a)

126.9 (C6)   134.4 (C4)

123.7 (C7)   118.8 (C3)

126.6 (C8)   145.0 (C2)

121.7 (C9)   154.2 (C10a)

142.1 (C9a)   122.4 (C3')   153.8 *

149.5 (C6')   138.4 (C4')   (C2')

119.4 (C5')

6

118.9 (C5a)   115.4 (C4a)

127.0 (C6)   133.8 (C4)

122.9 (C7)   117.9 (C3)

126.4 (C8)   144.6 (C2)

117.1 (C9)   154.0 (C10a)

140.2 (C9a)   131.0 (C2')

144.1 (C1')   129.7 (C3')

127.8 (C4')

9

132.2 (C4a) — 128.0 (C4)

              126.3 (C3)

              126.8 (C2)

141.6 (C9a)   125.4 (C1)

156.5 (C2')   111.3 (C3')

148.1 (C6')   137.7 (C4')

117.1 (C5')

11

Figure 5

Figure 6 shows the expanded aromatic region of the ^{13}C coupled spectrum for compound **6**; its ^{13}C-H coupling constants are given (in Hz) in Figure 7. The pyridyl carbon atoms, C_2, C_3, C_4, C_{4a}, and C_{10a} are slightly deshielded when compared to **9**, possibly due to the inductive effect of the 10-(2'-pyridyl) group. All quaternary carbon atoms in **6** (C_{4a}, C_{5a}, C_{9a}, C_{10a}, and $C_{2'}$) showed only long-range coup-
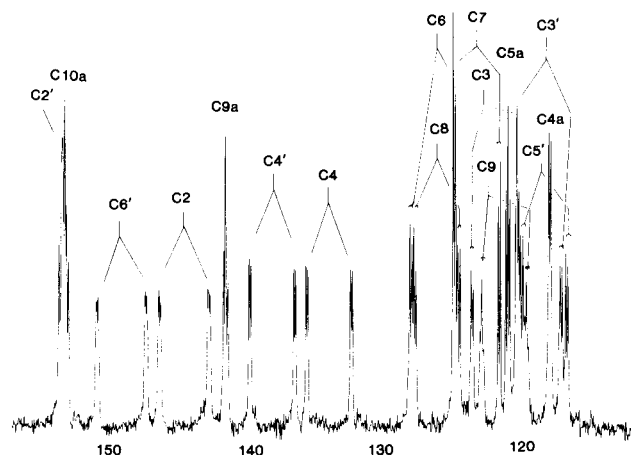
Figure 6. 1500 Hz expansion of the aromatic region of the proton coupled ^{13}C nmr spectrum of **6**.

ling, have larger relaxation times, and their resonances appeared lower in intensity than those of the protonated carbon atoms. The bridgehead carbons next to nitrogen (N_{10}) are shifted further downfield than those next to sulfur, and the same is true for pyridyl carbons C_{10a}, $C_{2'}$ when compared to C_{9a}. The upfield signals were properly identified as C_{4a} and C_{5a}. The latter is a triplet ($^3J_{C_{5a}H_7}$ = $^3J_{C_{5a}H_9}$) and the former is a narrow double due to the absence of $^3J_{C_{4a}H_1}$ allylic coupling (Figure 7) [7]. The triplet at 142.1 ppm is unmistakably C_{9a} ($^3J_{C_{9a}H_6}$ = $^3J_{C_{9a}H_8}$) whereas the two overlapping multiplets at 154 ppm (see Figure 6) are identified as C_{10a} and $C_{2'}$. Presently, we cannot distinguish between the two resonances. However, C_{10a} should appear in the ^{13}C coupled spectrum of **6** as a nar-

Table 1

Crystal and Experimental Data 1

Chemical formula	$C_{16}H_{11}N_3S$
Formula weight	277.35
Crystal system	Monoclinic
Space Group	C2/c
Unit cell dimensions	a = 27.887(2)Å
	b = 7.982(1)
	c = 14.252(1)
	β = 124.04(1)°
	V = 2628.4( )Å^3
Number of molecules per unit cell	8
Density (calculated)	1.209 g cm^{-1}
X-radiation used for data collection	$\lambda(CuK_\alpha)$ = 1.5418Å
Linear absorption coefficient	$\mu(CuK_\alpha)$ = 19.93 cm^{-1}
Total number of reflections with $2\theta < 130°$	2195
Number of reflections with I > 3 σ(I)	1860
Maximum residue electron density	0.46 eÅ^{-3}
Disagreement index, R for 1860 observed reflections	0.060
Weighted disagreement index, R$_w$ for 1860 observed reflections	0.069
Crystal size	0.67 × 0.57 × 0.23 mm

Table 2

Fractional Atomic Coordinates and Thermal Paramaters ($\times 10^4$) for Non-hydrogen and ($\times 10^3$) for Hydrogen Atoms.
(The estimated standard deviations are given in parentheses and refer to the last positions of respective values.)

The expression for th ethermal parameters with U values in Å^2 is:

$$T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^3c^{*2} + 2U_{12}hka^*b^* + 2U_{13}h^9a^*c^* + 2U_{23}k\ell b^*c^*\}$$

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
N(1)	343(1)	−2880(3)	232(2)	467(11)	443(11)	422(10)	−25(8)	293(9)	−48(8)
C(2)	−86(1)	−2735(3)	402(2)	455(13)	512(13)	478(13)	0(11)	297(12)	−54(11)
C(3)	−93(1)	−1515(3)	1068(2)	553(15)	541(15)	544(14)	74(12)	394(13)	56(12)
C(4)	367(1)	−417(3)	1629(1)	634(16)	442(13)	459(13)	33(10)	393(13)	60(11)
C(4a)	823(1)	−590(3)	1508(2)	483(13)	377(11)	328(11)	17(9)	245(10)	28(9)
S(5)	1443(1)	651(1)	2341(1)	646(4)	799(5)	556(4)	−361(4)	382(4)	−216(4)
C(5a)	1788(1)	442(3)	1625(2)	396(12)	444(12)	307(10)	10(9)	135(9)	−16(10)
C(6)	2234(1)	1549(4)	1924(2)	521(15)	555(16)	436(13)	−111(12)	175(12)	−127(13)
C(7)	2551(1)	1414(4)	1454(3)	513(16)	729(20)	627(18)	−104(15)	262(14)	−258(15)
C(8)	2411(1)	199(4)	669(3)	506(16)	816(20)	574(16)	−49(15)	333(14)	−152(15)
C(9)	1960(1)	−898(4)	346(2)	448(13)	564(15)	420(13)	−35(11)	258(11)	−68(11)
C(9A)	1644(1)	−813(3)	826(2)	365(11)	390(11)	277(10)	24(8)	145(9)	13(9)
N(10)	1210(1)	−2005(2)	539(2)	434(11)	437(10)	384(10)	−114(8)	257(9)	−72(8)
C(10a)	783(1)	−1816(3)	762(2)	417(12)	358(11)	299(10)	25(8)	215(9)	14(9)
N(1')	782(1)	−2853(3)	−1354(2)	512(12)	501(12)	379(10)	−54(9)	250(10)	−26(9)
C(2')	1113(1)	−3284(3)	−263(2)	395(11)	420(12)	351(11)	−68(9)	240(10)	−57(9)
C(3')	1371(1)	−4824(3)	121(2)	420(12)	455(13)	438(12)	−15(11)	231(11)	6(10)
C(4')	1291(1)	−5988(3)	−663(3)	479(14)	437(13)	650(16)	−80(13)	334(13)	−8(11)
C(5')	953(1)	−5574(3)	−1791(2)	548(15)	570(16)	575(16)	−258(13)	372(13)	−44(12)
C(6')	707(1)	−4019(4)	−2101(2)	524(15)	657(17)	374(12)	−116(12)	246(11)	−114(13)
H(2)	−39(1)	−364(4)	1(2)	57(7)					
H(3)	−41(2)	−147(4)	115(3)	83(10)					
H(4)	36(1)	43(4)	215(2)	55(7)					
H(6)	231(1)	232(4)	241(3)	51(7)					
H(7)	286(2)	215(4)	173(3)	68(9)					
H(9)	190(1)	−185(4)	−14(3)	59(8)					
H(3')	161(1)	−508(3)	95(2)	50(7)					
H(4')	146(1)	−702(4)	−39(3)	57(8)					
H(5')	92(2)	−636(4)	−225(3)	72(9)					
H(6')	48(2)	−385(5)	−295(3)	88(11)					

row doublet of doublets as in **9** ($^3J_{C_{10a}H_2} > {}^3J_{C_{10a}H_4}$) with the larger coupling (11-13 Hz) assigned to the coupling across the heterocyclic nitrogen N_1 ($C_{10a}H_2$). Similar ^{13}C-^1H couplings have been described [14-16].

The phenothiazine carbons C_6, C_7, C_8, and C_9 of **6** were assigned resonances at 126.9 ppm, 123.7 ppm, 126.6 ppm, and 121.7 ppm, respectively. They do not deviate much from the original assignments made for other 10-arylpyridobenzothiazines [7]. Small deshielding of C_{9a} (+1.9 ppm), C_{4a} (+2.8 ppm), C_7 (+0.8 ppm), and C_9 (+4.6 ppm) for **6** compared to derivative **9** is due to the inductive effect of the 10-(2'-pyridyl) group as is the case with C_2, C_3, C_4, C_{4a}, and C_{10a}.

The assignment of resonances C_3' and C_5' was based on a smaller *ipso* coupling for $C_3'H_3'$ (159.4 Hz) as compared to 165.6 Hz for $C_5'H_5'$ [7,14]. Similar differences are observed for C_9H_9 and C_7H_7 (Figure 7).

Table 3

Torsion Angles and Ring Puckering Parameters

Torsion angles around the central pyridobenzothiazine ring

C(4a)-S(5)-C(5a)-C(9a)	−15.9(3)°
S(5)-C(5a)-C(9a)-N(10)	−0.1(4)
C(5a)-C(9a)-N(10)-C(10a)	18.0(4)
C(9a)-N(10)-C(10a)-C(4a)	−14.1(4)
N(10)-C(10a)-C(4a)-S(5)	−7.2(4)
C(10a)-C(4a)-S(5)-C(5a)	19.4(3)

Torsion angles about the N(10)-C(2') bond

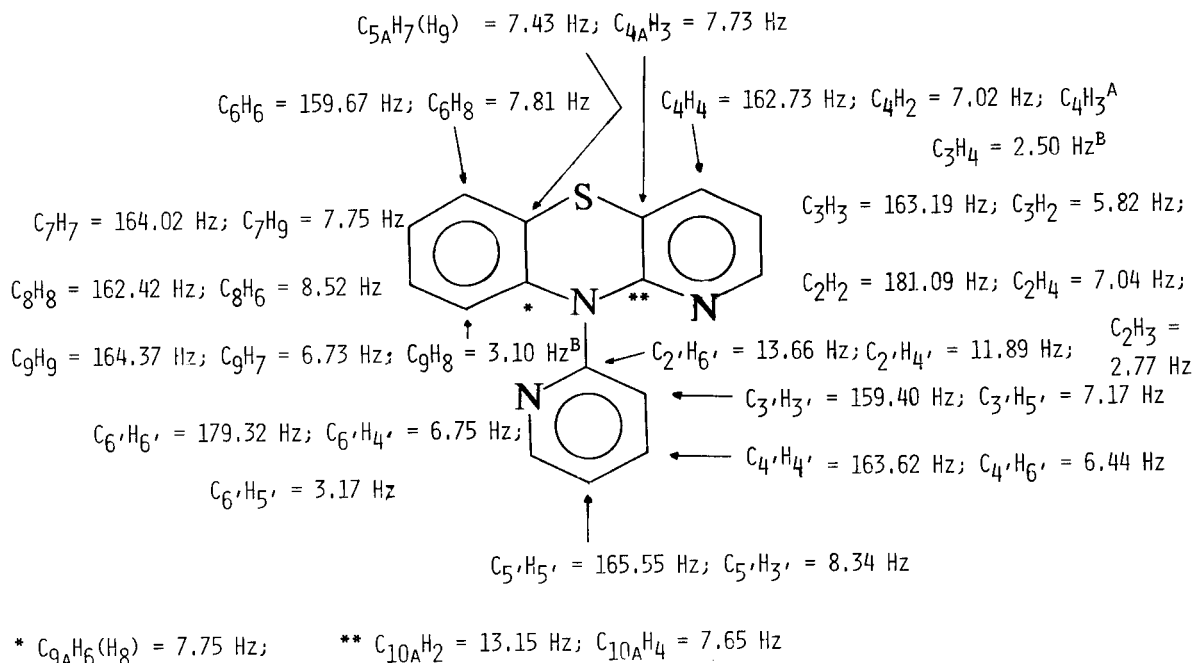|	
C(9a)-N(10)-C(2')-N(1')	−81.6(3)°
C(9a)-N(10)-C(2')-C(3')	96.6(3)
C(10a)-N(10)-C(2')-N(1')	84.0(3)
C(10a)-N(10)-C(2')-C(3')	−97.8(3)

Puckering parameters

Central		Ideal boat conformation	
$Q = 0.254$ Å		$q_2 = Q$	
$q_2 = 0.249$		$q_3 = 0$	
$q_3 = -0.049$			
$\theta = 101.1°$		$v = 90°$	
$\phi_2 = 351.2°$		$\phi_2 = 360°$	

$C_{5A}H_7(H_9) = 7.43$ Hz; $C_{4A}H_3 = 7.73$ Hz

$C_6H_6 = 159.67$ Hz; $C_6H_8 = 7.81$ Hz

$C_4H_4 = 162.73$ Hz; $C_4H_2 = 7.02$ Hz; $C_4H_3^A$

$C_3H_4 = 2.50$ Hz^B

$C_7H_7 = 164.02$ Hz; $C_7H_9 = 7.75$ Hz

$C_3H_3 = 163.19$ Hz; $C_3H_2 = 5.82$ Hz;

$C_8H_8 = 162.42$ Hz; $C_8H_6 = 8.52$ Hz

$C_2H_2 = 181.09$ Hz; $C_2H_4 = 7.04$ Hz;

$C_9H_9 = 164.37$ Hz; $C_9H_7 = 6.73$ Hz; $C_9H_8 = 3.10$ Hz^B

$C_2'H_6' = 13.66$ Hz; $C_2'H_4' = 11.89$ Hz;

$C_2H_3 = 2.77$ Hz

$C_3'H_3' = 159.40$ Hz; $C_3'H_5' = 7.17$ Hz

$C_6'H_6' = 179.32$ Hz; $C_6'H_4' = 6.75$ Hz;

$C_4'H_4' = 163.62$ Hz; $C_4'H_6' = 6.44$ Hz

$C_6'H_5' = 3.17$ Hz

$C_5'H_5' = 165.55$ Hz; $C_5'H_3' = 8.34$ Hz

* $C_{9A}H_6(H_8) = 7.75$ Hz;   ** $C_{10A}H_2 = 13.15$ Hz; $C_{10A}H_4 = 7.65$ Hz

A) COUPLING TOO SMALL TO BE DETECTED. B) ESTIMATED VALUE.

Figure 7. ^{13}C-^1H coupling constants of **6**.

EXPERIMENTAL

Crystal Data.

The crystals of **6**, whose preparation has been reported previously [1], are yellow prisms. A crystal of 0.67 × 0.57 × 0.23 nm in dimensions was selected for the determination of unit cell parameters were obtained from a least-squares analysis of 15 reflections with 2_v values measured on a Syntex P2$_1$ automatic diffractometer with graphite monochromatized CuKα radiation. The space group, C2/c, was deduced from systematic absences (hkl absent with h + k = 2n + 1, H01 absent with l = 2n + 1) and from the structure analysis. The crystal data are summarized in Table 1. The intensity data were collected with the $\theta/2\theta$ scanning mode. A total of 2195 independent reflections were measured with 2θ values below 130°, of which 1860 reflections were considered as observed by the criterion I > $3\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were deduced to structure amplitudes by the application of Lorentz and polarization factors, and no absorption corrections were applied.

The structure was solved by the application of direct methods with the weighed multisolution tangent-refinement program, MULTAN 78 [17]. The E map showed the position of all non-hydrogen atoms. The refinements were carried out by full-matrix least-squares method using the SHELX system of programs [18]. The anisotropic temperature factors were used for non-hydrogen atoms. All hydrogen atoms were located in a difference Fourier synthesis and the isotropic temperature factors were used for hydrogen atoms in the refinement. The weight of the reflection was assigned as $1/[\sigma(F)]^2$, where $\sigma(F)$ was calculated from counting statistics. The quantity $\Sigma w(|F_o|-|F_c|)^2$ was minimized. The final R index, $\Sigma \|F_o\| - |F_c\|/\Sigma |F_o|$, was 0.060 and the weight disagreement index was 0.069 for 1860 observed reflections. The final difference Fourier synthesis showed a maximum residue of electron density of 0.46 e Å^{-3} in the vicinity of the sulfur atom. The atomic scattering factors were used for sulfur, nitrogen, carbon, and hydrogen were those from International Tables for X-ray Crystallography [19]. The final atomic parameters are given in Table 2.

NMR Spectra.

All spectra were recorded as dilute solutions (1.2-1.5 M) in deuteriochloroform using a WP200-SY Bruker multilinear spectrometer at a frequency of 50.327 MHz. Spectral widths of 200 ppm were employed using 1-4 s acquisition times with 16K data points. Smaller spectral widths (1500-2000 Hz) were used to evaluate coupling constants. Typically, interpulse delays were 4s with pulse width of 8 μs corresponding to 30° flip angles.

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