

## of 4'-Nitro-10-phenylphenothiazine

Misa V. Jovanovic and Edward R. Biehl\*

Department of Chemistry, Southern Methodist University,  
Dallas, Texas 75275

Patrice de Meester and Shirley S. C. Chu

School of Engineering and Applied Science, Southern Methodist University,  
Dallas, Texas 75275

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The crystal structure of 4'-nitro-10-phenylphenothiazine, **1**, has been determined by the single crystal x-ray diffraction studies and consists of two independent molecules in the asymmetric cell unit with a pseudo-center of symmetry. The crystal belongs to the monoclinic system with the space group  $P2_1/c$ . The central ring of the phenothiazine ring system is in a boat conformation and the 4'-nitro substituent is in a boat-axial conformation with respect to the central ring of phenothiazine. Compound **1** is the first reported 10-aryl phenothiazine in which the 10-phenyl ring is perpendicular to the plane bisecting the dihedral angle of the phenothiazine nucleus. This geometry allows for resonance interaction between the lone pair of electrons on N<sub>10</sub> and the 4'-nitro-10-phenyl ring which influences both the spectral properties and structure of the phenothiazine tricyclic ring. The correlation between the x-ray structure and <sup>13</sup>C nmr spectral properties of **1** is discussed. The uv/vis and esr studies of the radical cation of **1** indicate that the 10-aryl ring is twisted with respect to the phenothiazine ring.

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The discovery of the biological and pharmacological properties of phenothiazine has initiated extensive studies on many of its derivatives [1]. Compounds such as promazine and chlorpromazine have become firmly established in medical practice [2-4]. Furthermore, the incorporation of a pyridine "type" nitrogen into the tricyclic ring has enhanced further the psychotherapeutic properties of phenothiazines [5-8].

In our continuous search for biologically active heterocycles, we have prepared a series of substituted phenothiazines [9,10], heteroarylphenothiazines [11,12], and their pyridobenzothiazine analogs [11]. One of the most interesting aspects of these studies was the discovery that the 10-(2'-pyrazyl) ring in 10-(2'-pyrazyl)phenothiazine is perpendicular to the plane bisecting the dihedral angle of the phenothiazine nucleus [12]. The <sup>13</sup>C nmr revealed the existence of significant electronic interactions between the "electron-rich" phenothiazine and the  $\pi$ -deficient 10-(2'-pyrazyl) substituent [12]. We have extended those studies to other phenothiazine derivatives possessing  $\pi$ -deficient rings and now report the x-ray structure of 4'-nitro-10-phenylphenothiazine (**1**). In addition, the conformational requirements of **1** predicted by <sup>13</sup>C nmr analysis [12] are compared with the observed bond lengths and bond angles obtained by x-ray crystallography. The uv/vis spectroscopy was used to study the radical cation and dication of **1**.

## EXPERIMENTAL

The crystals of 4'-nitro-10-phenylphenothiazine, (**1**) are yellow prisms. A crystal of 0.80 × 0.40 × 0.30 mm in dimensions was used for the de-

termination of unit cell parameters and the intensity measurements. The unit cell parameters were obtained from a least-square analysis of 15 reflections with  $2\theta$  values measured on a Syntex P2, automatic diffractometer with graphite monochromatized CuK $\alpha$  radiation. The space group,  $P2_1$ , was deduced from the systematic absences ( $h0l$  absent with  $l = 2n + 1$  and  $0k0$  absent with  $k = 2n + 1$ ). The eight molecules in a unit cell, indicated that there are two crystallographically independent molecules in an asymmetric unit of the unit cell. The crystal data are summarized in Table I. The intensity data were collected with the  $\theta/2\theta$  scanning mode. A total of 5029 independent reflections were measured with  $2\theta$  values below  $130^\circ$ , of which 4031 reflections were considered as observed by the criterion  $I > \sigma(I)$ , where  $\sigma(I)$  was determined from coun-

Table I  
Crystal and Experimental Data I

Chemical formula	C <sub>18</sub> H <sub>12</sub> O <sub>2</sub> N <sub>2</sub> S
Formula weight	320.4
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 7.269(3)^\circ$ $b = 12.483(5)$ $c = 34.498(9)$ $\beta = 107.00(3)$ $V = 2994(2) \text{ \AA}^3$
Number of molecules per unit cell	8
Density (calculated)	1.419 g cm <sup>-3</sup>
X-radiation used for data collection	$\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$
Linear absorption coefficient	$\mu(\text{CuK}\alpha) = 19.04 \text{ cm}^{-1}$
Total number of reflections with $2\sigma < 130^\circ$	5029
Number of reflections with $I < 3 \sigma(I)$	4031
Maximum residue electron density	0.45 e $\text{\AA}^{-3}$
Disagreement index, R, for 4031 observed reflections	0.062
Weighted disagreement index, R <sub>w</sub> , for 4031 observed reflections	0.075
Crystal size	0.80 × 0.41 × 0.29 mm

ting statistics. The intensity data were reduced 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 weighted multiresolution tangent-refinement program, MULTAN 78 [13]. The E map showed the positions of all non-hydrogen atoms. The refinements were carried out by full-matrix least-squares method using the SHELX system of programs [14]. 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  $1/[\sigma^2(F) + kF^2]$ , where  $\sigma(F)$  was calculated from counting statistics and  $k = 4.722 \times 10^{-3}$ . The quantity  $\sum w(F_o - F_c)^2$  was minimized. The final R index,  $\sum |F_o| |F_c| / \sum |F_o|$ , was 0.062 and the weighted disagreement index,  $R_w$ , was 0.075 for 4031 observed reflections. The final difference Fourier synthesis showed two electron density residues of 0.45 and  $0.37 \text{ e } \text{Å}^{-3}$  in the vicinity of the sulfur atom, all other residues of electron density are less than  $0.25 \text{ e } \text{Å}^{-3}$ . The atomic scattering factors used

for sulfur, nitrogen, carbon, and hydrogen were those from International Tables for X-ray Crystallography [15]. The final atomic parameters are given in Table 2.

The cation radical and dication of **1** were generated in 80% aqueous sulfuric acid and the uv/vis spectra were obtained using a Perkin-Elmer Lambda 3 uv/vis Spectrophotometer.

## Results and Discussion.

The two crystallographically independent molecules in the asymmetric unit has a pseudo-center of symmetry at approximately (0.75, 0.16, 0.75). The Weissenberg photographic method and the B-matrix lattice symmetry calculation carried out by Dr. Alan Mighell of the National Bureau of Standards have confirmed that the crystal does belong to monoclinic system with the space group  $P2_1/c$ . The

Table 2

Fractional atomic coordinates and thermal parameters ( $\times 10^4$ ) 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 the thermal parameters with U values in  $\text{Å}^2$  is:

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

Molecule A	X	Y	Z	U11	U22	U33	U12	U13	U23
C(1)A	4884(3)	2327(2)	8655(1)	491(14)	509(14)	722(16)	108(11)	115(12)	107(11)
C(2)A	3789(4)	2848(2)	8862(1)	606(16)	547(16)	1034(24)	156(15)	304(16)	127(13)
C(3)A	4554(5)	3060(2)	9272(1)	835(21)	571(16)	1034(24)	44(16)	529(19)	121(15)
C(4)A	6386(4)	2754(2)	9474(1)	852(19)	566(16)	686(17)	-56(13)	371(15)	-1(14)
C(4a)A	7521(3)	2246(2)	9268(1)	580(14)	486(13)	527(13)	-21(10)	196(11)	-22(11)
S(5)A	9871(1)	1796(1)	9517(0)	560(4)	709(4)	521(3)	-68(3)	39(3)	-30(3)
C(5a)A	9643(3)	524(2)	9280(1)	387(11)	621(15)	485(12)	57(10)	110(9)	78(10)
C(6)A	10323(4)	-404(2)	9500(1)	516(14)	788(18)	534(14)	189(13)	170(11)	199(13)
C(7)A	9980(4)	-1378(2)	9313(1)	670(17)	686(18)	787(19)	313(15)	307(15)	279(14)
C(8)A	8925(4)	-1453(2)	8907(1)	657(16)	471(14)	820(19)	36(12)	262(14)	122(12)
C(9)A	8251(4)	-533(2)	8684(1)	534(13)	556(14)	582(14)	25(11)	154(11)	87(11)
C(9a)A	8631(3)	458(2)	8870(1)	387(11)	502(12)	481(12)	86(10)	133(9)	105(10)
N(10)A	7906(3)	1426(2)	8662(1)	544(11)	485(10)	446(10)	49(8)	131(8)	133(9)
C(10a)A	6753(3)	2035(2)	8855(1)	484(12)	408(11)	539(13)	33(9)	167(10)	30(10)
C(1'A)	8477(3)	1823(2)	8341(1)	385(10)	493(12)	380(11)	1(9)	10(8)	17(9)
C(2'A)	8055(3)	2884(2)	8208(1)	498(13)	496(13)	557(14)	3(10)	106(11)	52(11)
C(3'A)	8579(4)	3277(2)	7887(1)	525(13)	481(14)	593(14)	90(11)	55(11)	17(11)
C(4'A)	9556(3)	2620(2)	7687(1)	430(12)	621(14)	415(11)	49(10)	19(9)	-84(11)
C(5'A)	10047(3)	1588(2)	7819(1)	472(12)	593(14)	504(13)	-44(11)	120(10)	-12(11)
C(6'A)	9530(3)	1187(2)	8146(1)	503(13)	479(12)	469(12)	22(9)	81(10)	59(10)
N(4'A)	9991(3)	3011(2)	7330(1)	552(12)	797(15)	518(12)	70(12)	64(10)	-161(12)
O(1'A)	9556(4)	3938(2)	7223(1)	1055(17)	795(14)	739(13)	243(11)	230(12)	-113(13)
O(2'A)	10744(3)	2406(2)	7142(1)	932(16)	1042(18)	647(12)	43(12)	346(12)	-42(13)
H(1)A	434(4)	215(2)	839(1)	83(8)					
H(2)A	248(4)	307(2)	869(1)	68(7)					
H(3)A	371(4)	337(2)	944(1)	83(9)					
H(4)A	687(4)	289(3)	975(1)	96(10)					
H(6)A	1098(4)	-37(2)	978(1)	82(9)					
H(7)A	1041(4)	-199(2)	945(1)	73(7)					
H(8)A	863(4)	-214(3)	879(1)	95(9)					
H(9)A	749(4)	-61(2)	840(1)	63(7)					
H(2'A)	743(4)	339(3)	835(1)	89(9)					
H(3'A)	834(3)	403(2)	780(1)	49(6)					
H(5'A)	1071(4)	113(2)	769(1)	60(7)					
H(6'A)	988(3)	47(2)	823(1)	41(5)					

Table 2 (continued)

Molecule B Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
C(1)B	10062(4)	822(2)	6263(1)	700(17)	504(14)	869(20)	100(13)	262(15)	146(13)
C(2)B	11101(6)	243(3)	6052(1)	1018(26)	614(19)	1280(32)	188(19)	619(24)	182(17)
C(3)B	10282(7)	-12(3)	5656(2)	1192(32)	564(18)	1433(38)	2(20)	855(31)	97(19)
C(4)B	8433(6)	301(3)	5451(1)	1346(31)	603(18)	895(23)	-183(16)	703(23)	-292(20)
C(4a)B	7354(4)	884(2)	5659(1)	796(18)	518(14)	691(16)	-142(12)	368(14)	-216(13)
S(5)B	5016(1)	1351(1)	5418(0)	729(5)	959(6)	593(4)	-156(4)	105(3)	-338(4)
C(5a)B	5281(3)	2638(2)	5645(1)	402(12)	760(18)	577(14)	60(12)	91(10)	-57(12)
C(6)B	4573(4)	3549(3)	5420(1)	466(14)	1105(27)	693(18)	291(17)	87(13)	87(16)
C(7)B	4877(4)	4533(3)	5603(1)	619(18)	853(22)	974(23)	394(19)	283(16)	295(16)
C(8)B	5913(4)	4620(2)	6005(1)	711(18)	552(16)	1177(26)	110(16)	455(18)	168(14)
C(9)B	6650(4)	3717(2)	6229(1)	586(15)	533(14)	700(16)	-5(12)	199(12)	56(12)
C(9a)B	6307(3)	2723(2)	6053(1)	441(12)	559(14)	545(13)	48(11)	128(10)	39(10)
N(10)B	7084(3)	1758(2)	6263(1)	615(12)	476(11)	527(11)	2(9)	153(9)	94(9)
C(10a)B	8183(4)	1131(2)	6066(1)	676(15)	417(12)	658(15)	-21(11)	279(12)	-20(11)
C(1')B	6547(3)	1366(2)	6591(1)	480(12)	501(13)	436(12)	-27(9)	22(10)	-5(10)
C(2')B	6981(4)	301(2)	6721(1)	703(17)	513(14)	573(14)	-36(11)	168(13)	39(12)
C(3')B	6498(4)	-100(2)	7045(1)	577(15)	514(14)	607(15)	20(11)	74(12)	-25(11)
C(4')B	5543(3)	547(2)	7249(1)	409(12)	645(15)	437(12)	-17(10)	-2(9)	-92(11)
C(5')B	5048(3)	1582(2)	7125(1)	475(13)	654(16)	546(14)	-60(11)	105(11)	6(11)
C(6')B	5545(3)	1990(2)	6797(1)	518(13)	523(13)	558(14)	-5(11)	118(11)	54(11)
N(4')B	5094(3)	132(2)	7604(1)	516(12)	818(17)	535(12)	-17(12)	47(10)	-153(12)
O(1')B	5532(3)	-812(2)	7701(1)	942(15)	759(14)	722(13)	171(11)	161(11)	-92(12)
O(2')B	4334(3)	718(2)	7794(1)	871(16)	1101(19)	744(14)	60(13)	355(12)	-11(13)
H(1)B	1058(4)	98(2)	654(1)	77(8)					
H(2)B	1259(6)	-2(4)	622(1)	167(19)					
H(3)B	1120(4)	-34(3)	553(1)	100(11)					
H(4)B	778(4)	15(3)	515(1)	92(10)					
H(6)B	387(4)	341(2)	513(1)	82(9)					
H(7)B	435(4)	517(3)	543(1)	89(9)					
H(8)B	616(4)	526(2)	610(1)	84(9)					
H(9)B	745(4)	374(2)	650(1)	80(8)					
H(2')B	759(5)	-18(3)	658(1)	92(10)					
H(3')B	667(3)	-86(2)	711(1)	51(6)					
H(5')B	447(4)	200(2)	729(1)	77(8)					
H(6')B	528(4)	275(2)	672(1)	68(8)					

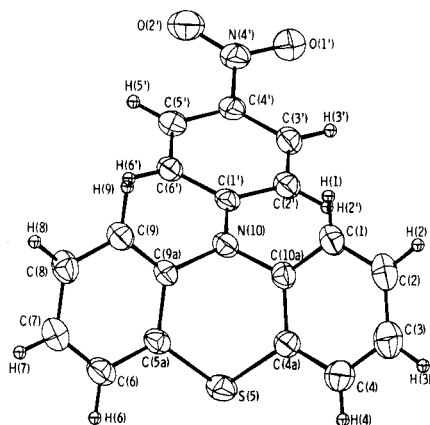


Figure 1. ORTEP drawing of molecule A, one of the two crystallographically independent molecules of I.

identification of the atoms and the configuration of the two crystallographically independent molecules, A and B, are shown in ORTEP [16] drawing in Figure 1. The bond lengths and bond angles, with their standard deviations, are shown in Figure 2, and they show good agreement between the two crystallographically independent molecules.

The central ring of the phenothiazine ring system is in a boat conformation as shown by the torsion angles around the central ring and by the puckering parameters [17] in Table 3. The least-squares planes of the benzo rings and the 10-phenyl ring, together with the deviations of the atoms from the planes of the two benzo rings are 120.8(1) and 124.4(1) $^\circ$  for molecules A and B, respectively. The conformation of the 10-phenyl ring is nearly perpendicular to the plane bisecting the folding angle of the phenothiazine ring as shown in Figure 3, and the dihedral angles in

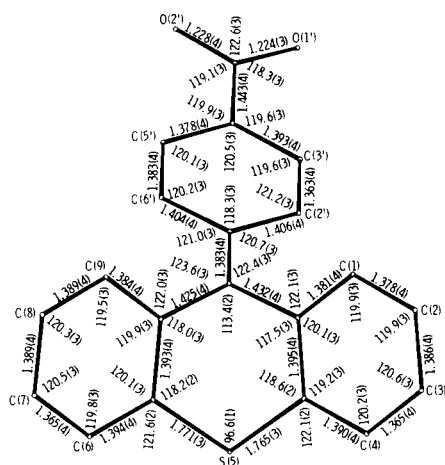


Figure 2(a).

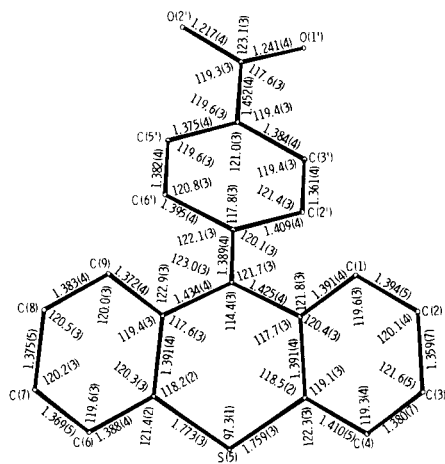


Figure 2(b).

Figure 2. Bond lengths (Å) and bond angles (°) of **1** with e.s.d.'s in parentheses. (a) and (b) refer to molecules A and B, respectively.

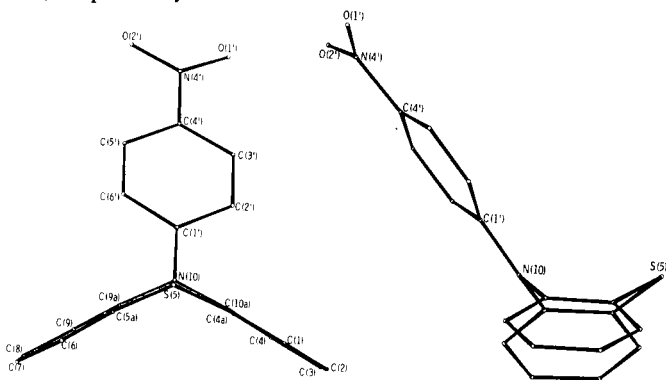


Figure 3(a).

Figure 3(b).

Figure 3. (a) Front view and (b) side view of **1** showing the conformation of the molecule.

Table 4. This is similar to that observed in 10-(2'-pyrazyl)-phenothiazine (**2**) in which the pyrazine ring is also perpendicular to the plane bisecting the phenothiazine ring [12]. The small magnitude of the folding angle in **1** is the consequence of the nonbonded interaction between the two ring systems due to the conformation of the 10-phenyl substituent. The folding angles are in the range of 145–155° in 10-arylphenothiazines when the plane of the 10-aryl ring is nearly parallel to the plane bisecting the phenothiazine ring [18–20].

Table 4

Torsion Angles and Ring Puckering Parameters

Torsion angles (°) around the central phenothiazine ring.	Molecule A	Molecule B
N(10)—C(10a)—C(4a)—S(5)	2.3(4)	−0.4(4)
C(10a)—C(4a)—S(5)—C(5a)	−41.8(3)	40.1(3)
C(4a)—S(5)—C(5a)—C(9a)	39.2(3)	−39.9(3)
S(5)—C(5a)—C(9a)—N(10)	2.5(4)	0.0(4)
C(5a)—C(9a)—N(10)—C(10a)	−53.5(4)	51.2(4)
C(9a)—N(10)—C(10a)—C(4a)	50.7(4)	−51.1(4)
Torsion angles (°) around the N(10)—C(1') bond.	Molecule A	Molecule B
C(9a)—N(10)—C(1')—C(2')	−165.6(3)	164.4(3)
C(9a)—N(10)—C(1')—C(6')	12.9(4)	−14.4(4)
C(10a)—N(10)—C(1')—C(2')	4.6(4)	−4.1(4)
C(10a)—N(10)—C(1')—C(6')	−176.9(3)	177.1(3)
Torsion angles (°) around the C(4')—N(4') bond.	Molecule A	Molecule B
C(3')—C(4')—N(4')—O(1')	3.2(4)	−2.6(4)
C(3')—C(4')—N(4')—O(2')	−175.6(3)	176.6(3)
C(5')—C(4')—N(4')—O(1')	−179.1(3)	178.7(3)
C(5')—C(4')—N(4')—O(2')	2.1(4)	−2.1(4)

Puckering parameters of Central phenothiazine ring.

	Molecule A	Molecule B	Ideal boat conformation
Q	0.702 Å	0.687 Å	
q <sub>2</sub>	0.701	0.685	q <sub>2</sub> = Q
q <sub>3</sub>	−0.049	0.050	q <sub>3</sub> = 0
θ	94.0°	85.8°	θ = 90°
φ <sub>2</sub>	298.1°	119.9°	φ <sub>2</sub> = 300 or 120°

The packing of the molecule in the unit cell is shown in the stereoscopic drawing in Figure 4. There is no intermolecular distance less than the van der Waals separation.

The N<sub>10</sub>—C<sub>1'</sub> bond length of 1.389 Å compares favorably with the typical double-bond distance and shows that there is substantial overlap of the N<sub>10</sub> lone pair of electrons and the 4'-nitro-10-phenyl ring. The shortening of that bond results in the 10-aryl ring being lifted up and away above the butterfly angle in order to avoid *peri* interactions with H<sub>1[9]</sub> phenylene protons. In addition, the phenothiazine

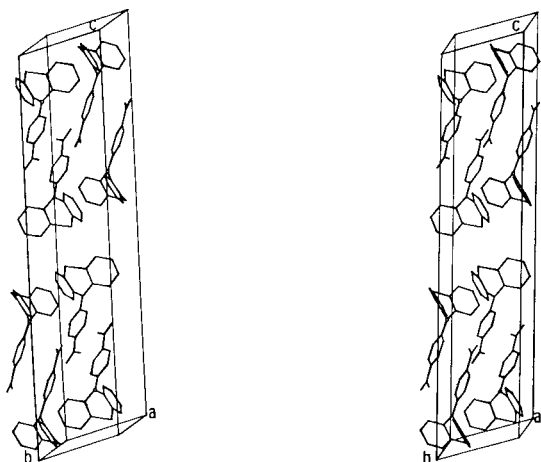
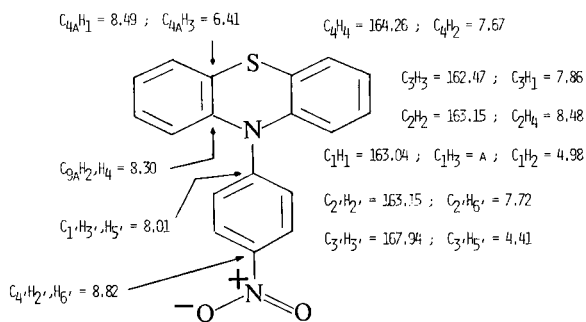


Figure 4. Stereoscopic drawing of molecular packing of **1**, excluding hydrogen atoms, in the unit cell.

ring is very puckered (dihedral angles of 120.8 and 124.4° for the two crystallographically independent molecules); this is the most puckering of a phenothiazine ring reported to date.

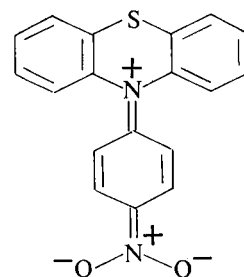
Although one must be careful in comparing directly x-ray structure of a compound with its structure in solution, the  $^{13}\text{C}$  coupling constants (in Hz) which are shown in structure **1b** are also consistent with the above argument. For example, the *ipso*  $^{13}\text{C}\text{H}$  couplings (in Hz) of **1** which are listed in **1b** are larger than for any other 10-arylphenothiazines which we have examined [18]. The increase in one-bond  $^{13}\text{C}\text{H}$  coupling is largest at  $\text{C}_1$  and  $\text{C}_4$  of **1** and are  $J(\text{C}_1\text{H}_1) = 163 \text{ Hz}$  and  $J(\text{C}_4\text{H}_4) = 164 \text{ Hz}$ , respectively. This compares with the typical average values of  $J(\text{C}_1\text{H}_1) = 158.5 \text{ Hz}$  and  $J(\text{C}_4\text{H}_4) = 160.5 \text{ Hz}$ , respectively, for other phenothiazines. The large  $J(\text{C}_3\text{H}_3)$  coupling of 168 Hz is not unusual since similar *ipso*  $^{13}\text{C}\text{H}$  coupling constants are observed for carbon atoms adjacent to the electronegative substituent [18,19].



**1b**

A = UNDESCRIBABLE DUE TO OVERLAPING OF SIGNALS

The three-bond allylic  $^{13}\text{C}\text{H}$  coupling is even more sensitive to changes in bond order. Therefore, it is important to mention that the allylic coupling of the substituted carbon atom ( $\text{C}_4$ ) in compound **1** is only 8.82 Hz (*meta* hydrogens =  $\text{H}_2$  and  $\text{H}_6$ ) [18]. This compares to the similar  $^{13}\text{C}$  coupling of 11 Hz for all other 4'-substituted 10-arylphenothiazines and may be an indication of the partial "quinoidal" nature of **1** (as shown in **1c**).



**1c**

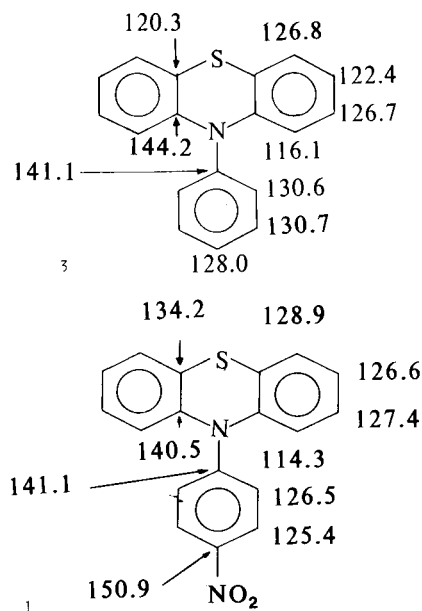


FIGURE 5(A).

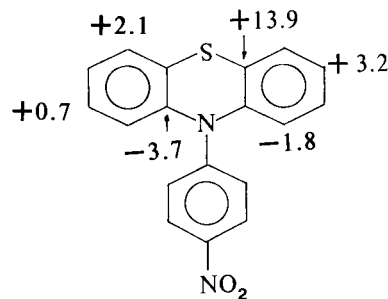
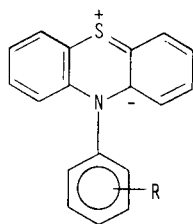


FIGURE 5(B).

Figure 5

Lastly, the  $^{13}\text{C}$  carbon chemical shifts have been reported and, except for compound **1**, the deviations of phenothiazine ring carbon chemical shifts of these derivatives are within  $\pm 1$  ppm of the analogous carbon resonances of 10-phenylphenothiazine (**3**). However, several of the phenothiazine ring carbon resonances in the 4'-nitro compound, **1**, are significantly different from the corresponding ones in **3**. Figure 5 lists the difference in chemical shift in ppm between **1** and **3** for each phenothiazine ring carbon atom. A positive value indicates that the carbon atom in **1** is deshielded with respect to the corresponding one in **3** whereas a negative value shows that the carbon atom is shielded with respect to the corresponding one in **3**. Interestingly, the resonance of the carbon atom most deshielded by the incorporation of the 4'-nitro group is not  $\text{C}_{9a}$ , the one next to  $\text{N}_{10}$ , but  $\text{C}_{4a}$ , the one adjacent to sulfur,  $\text{C}_{4a(sa)}$  (+13.9 ppm); in fact, the former is shielded (-3.9 ppm) in compound **1** as compared to that in compound **3**. We had explained the changes in chemical shifts of these two carbon resonances in terms of resonance structure **1d** in which the positively charged 10-nitrogen

**1d**

R = ELECTRONEGATIVE GROUP

atom inductively stabilizes the negative charge placed on  $\text{C}_{9a}$  by sulfur resonance interaction with the benzene moiety of the phenothiazine ring [18]. However this explanation cannot be correct since x-ray data show that the sulfur-carbon distance is approximately the same in both **1** and **3**. Further, the butterfly structure of the central ring

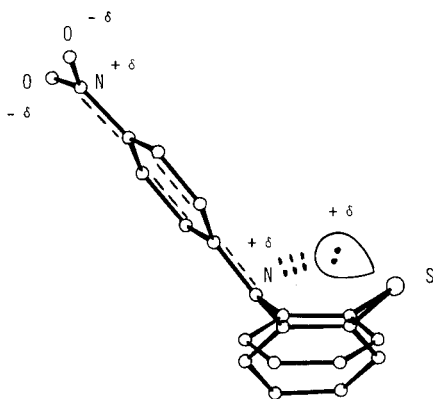


Figure 6

prevents efficient overlap of the non-bonding orbital of sulfur with the  $\pi$ -system. The puckering about sulfur is the largest reported for a phenothiazine derivative which suggests that the partially charged  $\text{N}_{10}$  atom polarizes the sulfur *via* a field effect as shown in Figure 6. The transfer of positive charge from nitrogen sulfur coupled with the increased puckering about sulfur accounts most likely for the differences in chemical shifts of  $\text{C}_{1a}$  and  $\text{C}_{4a}$  in **1** and **3**.

The structure of the radical cation and dication of **1** was studied by esr and uv/vis spectroscopy. A 60-80% aqueous solution of sulfuric acid was required to oxidize **1** to its respective cation radical dication. This sulfuric acid concentration is much higher than that generally needed to generate radical cation ions from 10-substituted phenothiazine compounds. However, because of the resonance interactions between the 4'-nitro group and the lone-pair of electrons on  $\text{N}_{10}$ , oxidation of **1** and **2** to their radical cations

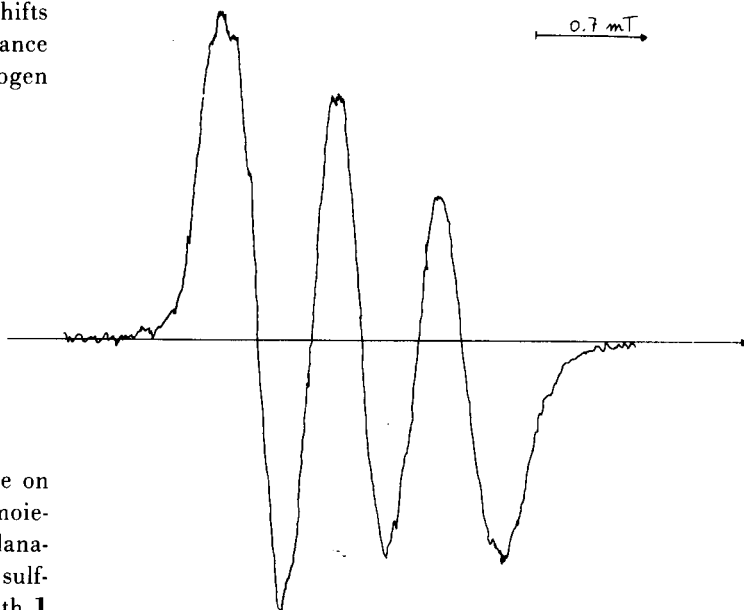


Figure 7. The esr signal of  $1 \times 10^{-3}M$  solution of 4'-nitro-10-phenylphenothiazinium cation radical, **6**, in 96% aqueous sulfuric acid.

would be expected to be much more difficult than that for other phenothiazines. We have shown by uv/vis and esr spectroscopy that there is a high twist angle between the pyrazyl ring and the phenothiazine ring in 10-(2'-pyrazyl)-phenothiazinium radical cation, **4** [12]. For example, the absorption maxima of **4** was in the same range (510-515 nm) as that of cation radicals of 10-alkyl- and 10-arylphenothiazines [20,21]. This infers the absence of conjugation between the pyrazyl group and phenothiazine ring and that the pyrazyl group assumes a twisted orientation with

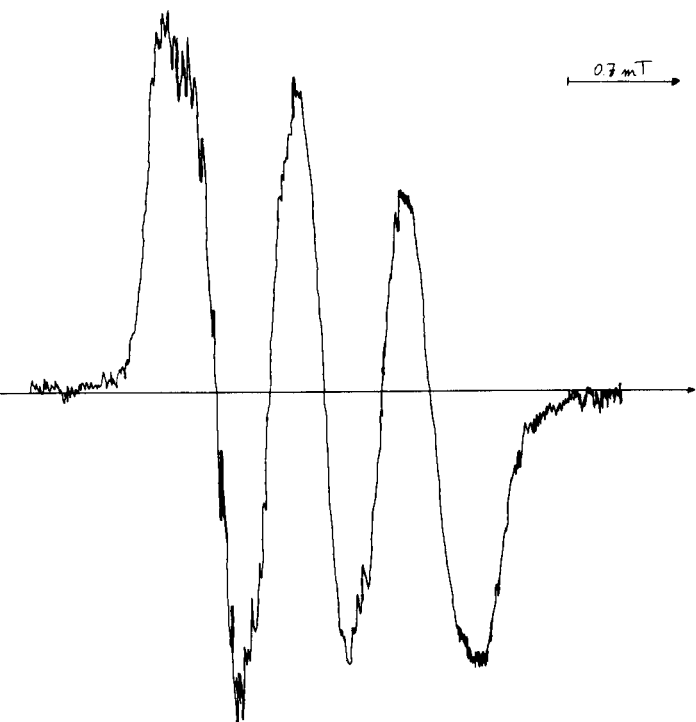


Figure 8. The esr signal of  $1 \times 10^{-3}M$  solution of 10-phenylphenothiazinium cation radical, **9**, in 96% aqueous sulfuric acid.

respect to the plane bisecting the dihedral angle of the phenothiazine ring [12]. The band envelopes for 2'-nitro-10-phenylphenothiazinium radical cation, **5**, appear in the same uv/vis portion of the spectrum as do the  $n-\pi^*$  and  $\pi-\pi^*$  electronic transitions of 4'-nitro-10-phenylphenothiazinium radical cation **6** ( $\lambda_{\max} = 273, 514 \text{ nm}$  and  $\lambda_{\max} = 272, 517 \text{ nm}$  for **6** and **5**, respectively). The absorption bands for the dications show comparable similarities; 4'-nitro-10-phenylphenothiazine dication, **7**,  $\lambda_{\max} = 288, 471 \text{ nm}$  and 2'-nitro-10-phenothiazine dication, **8**,  $\lambda_{\max} = 288, 468 \text{ nm}$ . This confirms that the positive charge in **6** and **7** is phenothiazine ring centered.

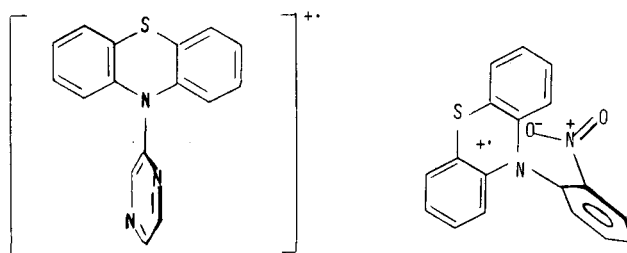


Table 3

Least-squares planes and the displacements ( $\text{\AA}$ ) of atoms from the plane  
Equation of planes:  $Ax + By + Cz = D$ , where  $x, y, z$  are in fractional coordinates

Molecule A					Molecule B				
Plane	A	B	C	D	Plane	A	B	C	D
(a)A	-3.01(1)	-11.043(9)	11.27(5)	5.71(4)	(a)B	-3.21(1)	-10.69(1)	13.26(6)	4.20(3)
(b)A	-7.024(3)	-0.83(2)	17.96(4)	9.84(4)	(b)B	-7.001(3)	-1.04(2)	18.15(4)	6.27(3)
(c)A	5.187(7)	3.99(2)	13.36(5)	16.29(3)	(c)B	-5.274(7)	3.92(2)	12.88(5)	12.47(3)
(d)A	-4.23(1)	10.15(2)	5.29(2)	2.68(2)	(d)B	-4.32(1)	10.04(2)	5.63(2)	2.24(1)

Displacements ( $\text{\AA}$ ) of atoms from the plane (\* indicates atoms excluded from the calculation of the least-squares planes)

	(a)A	(b)A	(c)A	(d)A	(a)B	(b)B	(c)B	(d)B
C(1)	0.009(4)				-0.005(4)			
C(2)	-0.004(4)				0.001(5)			
C(3)	-0.006(4)				0.011(8)			
C(4)	0.009(4)				-0.002(5)			
C(4a)	-0.004(4)				-0.003(4)			
C(5a)		0.008(4)				-0.002(4)		
C(6)		0.003(4)				-0.009(5)		
C(7)		-0.011(4)				0.008(5)		
C(8)		0.007(4)				0.003(4)		
C(9)		0.004(4)				-0.012(4)		
C(9a)		-0.012(4)				0.012(4)		
C(10a)	-0.005(4)				0.006(4)			
S(5)	0.067(5)*	0.168(5)*		0.000(2)	-0.072(5)*	-0.094(5)*		0.000(2)
N(10)	0.103(6)*	0.044(6)*	-0.045(5)*	0.003(5)	-0.050(6)*	-0.051(6)*	0.027(5)*	-0.009(5)
C(1')			-0.019(4)	-0.005(4)			0.013(4)	0.014(4)
C(2')			0.008(4)				-0.008(4)	
C(3')			0.008(4)				-0.003(4)	
C(4')			-0.015(4)	0.002(5)			0.010(4)	-0.005(5)
C(5')			0.004(4)				-0.005(4)	
C(6')			0.013(4)				-0.006(4)	
N(4')			-0.110(6)*				0.068(6)*	
O(1')			-0.108(6)*				0.054(6)*	
O(2')			-0.212(6)*				0.141(6)*	

Table 3 (continued)

Planes	Dihedral Angle (°)	
	Molecule A	Molecule B
(a) and (b)	120.8(1)	124.4(1)
(a) and (c)	116.4(1)	115.2(1)
(a) and (d)	118.7(2)	115.2(2)
(b) and (c)	123.8(1)	124.6(1)
(b) and (d)	123.6(2)	120.2(1)
(c) and (d)	80.5(1)	79.3(1)

The esr studies are supportive of this interpretation. Figure 7 is the esr spectra of **6** taken in aqueous sulfuric acid (see experimental section for details). The electron density is localized mainly at the N<sub>10</sub>, the large triplet due to the nitrogen coupling. That the unpaired electron is phenothiazine centered indicates that the radical is not exclusively redistributed onto the 10-substituent. Thus, oxidation of **1** causes the tricyclic phenothiazine ring to achieve a more planar configuration which forces the 10-aryl group to twist in order to minimize the steric repulsion which would exist between the substituent and neighboring atoms (H<sub>1</sub> and H<sub>9</sub>).

Gilbert and co-workers have demonstrated that the amount of twist can be measured and is directly proportional to the decrease in the *para* H coupling of the 10-aryl groups [22]. Their calculated coupling constants for the 70° angle between the 10-phenyl group and phenothiazine ring agreed with the observed value. Therefore, the amount redistribution of electron spin density onto the 10-aryl group is small. Figure 8 shows the esr spectrum of 10-phenylphenothiazinium cation radical, **9**, which is superimposable upon that of **6**. Further esr studies are in progress.

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