# Crystal Structure of 10-(2'-Pyrazyl)phenothiazine and Spectroscopic Identification of Its Radical-Cations and Dications

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The crystal structure of 10-(2'-pyrazyl)phenothiazine has been determined by the single crystal x-ray diffraction technique. The crystal belongs to the orthorhombic system with a space group of Pbca. The unit cell parameters are a = 10.633(3), b = 7.525(2), and c = 32.984(6)Å, with eight molecules in a unit cell. The final disagreement index, R, is 0.057 for 1944 observed reflections. The central ring of the phenothiazine ring system is in a broad conformation and the 10-(2'-pyrazyl)substituent is attached to the phenothiazine central ring in a boat-axial conformation. This is the first reported phenothiazine whose 10-substituent is perpendicular to the plane bisecting the dihedral angle of the phenothiazine nucleus.

Ultraviolet absorption maxima of the title compound in various oxidizing and non-oxidizing medium is reported. These data indicate that the geometry of **3** changes when it is oxidized to its radical-cations and dications.

Recently, the synthesis of 10-heteroarylphenothiazines and pyridobenzothiazines has been reported [1]. These compounds are structural synthons of alkyl- and dialkyl-amino groups responsible for the antipsychotic activity of phenothiazine drugs [2]. One of the most striking features of these substances is the electronic interaction between the phenothiazine nucleus and the π-deficient 10-substituent. This interaction was revealed by ¹H and ¹³C nmr studies which also allowed us to deduce the geometric conformation of these heterocycles [1,3].

The crystal structures of 10-(2'-pyrazyl)phenothiazine, **3**, is reported in this paper. The conformation and configuration of the title compound supports the evidence deduced from spectroscopic data on the change in geometry of its and other derivatives upon oxidation to radical-cations and dications.

## EXPERIMENTAL

Single Crystal Data.

Single crystals of the title compound were grown from absolute ethanol in the form of clear prisms. The unit cell parameters and intensity data were measured on a Syntex P2₁ computer controlled diffractometer. The crystal data are summarized in Table 1. The intensity data were collected with graphite monochromatized CuKα radiation by θ ± 2θ scan technique. The scan rate is variable over the range of 2.93 − 14.65° min⁻¹ using 1.0° below Kα₁ to 1.0° above Kα₂ as the scan width. The background counts were measured at the beginning and the end of each scan for a total time equal to the scan time. A reflection was considered as observed if the intensity I, was greater than 3.0 times of its standard deviation, σ(I), and the standard deviation was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and Polarization factors, and no absorption corrections were applied.

Structure Determination.

The structure was determined by the application of direct methods and was refined using the SHELX 76 [4] system of programs. The refinement was carried out by the full-matrix least-squares method with anisotropic temperature factors for non-hydrogen atoms. Most of the hydrogen positions were located on a difference Fourier synthesis and the rest were calculated from the geometry of the molecule. Isotropic temperature factors were used for the hydrogen atoms and the positional parameters were varied with constraints on the C-H bond distances. The weighting scheme was w = 1/σ²(F), where σ(F) is the standard deviation of the structure amplitudes as derived from counting statistics. Reflections with I less than 3.0 σ(I) were excluded from the refinement. The final disagreement index, R = (Σ‖F$_o$| − |F$_c$‖)/Σ|F$_o$| was 0.057 for 1944 observed reflections. The weighted disagreement index, R$_w$, was 0.068. The atomic scattering factors used for sulfur, nitrogen, carbon, and hydrogen atoms were those from International Tables for X-ray Crystallography [5]. The final positional and thermal parameters are given in Table 2.
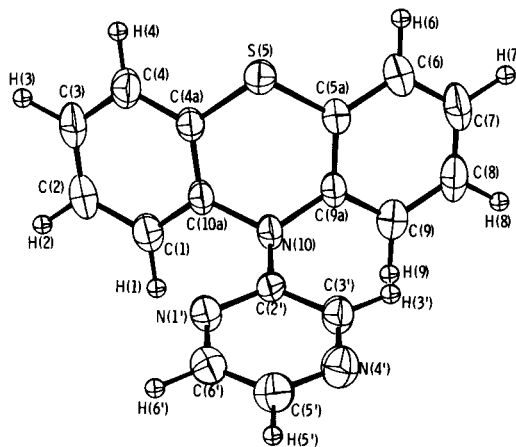


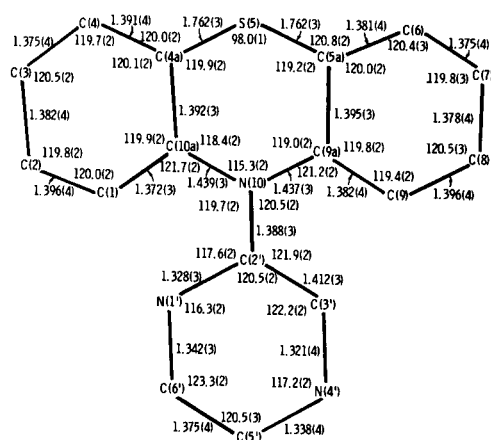Figure 1. ORTEP drawing of one molecule of the title compound.

Figure 2.   Bond lengths (Å) and bond angles (°) of the title compound with e.s.d. in parentheses.

### Results and Discussion.

### X-ray Analysis.

The identification of the atoms and the configuration of the molecule are shown in ORTEP drawing [6] in Figure 1. The bond lengths and bond angles, with their standard deviations, are shown in Figure 2. The C-S bond length of 1.762(3) Å and the C-S-C bond angle of 98.0(1)° are in good agreement with values from other phenothiazine derivatives [7,8,9]. The mean values of the two C-N bond lengths within the central ring of 1.438(3) Å is slightly longer than that in other phenothiazine derivatives and the C-N bond length of 1.388(3) Å, connecting the phenothiazine ring and the pyrazine ring, is significantly shorter with considerable double bond character. In addition, the C-N-C bond angle of 115.3(2)° within the central ring is also significantly smaller than the 120.4(3)° in 10-(p-bromophenyl)phenothiazine [9] and the 122.5(1)° in 10-(o-methoxyphenyl)phenothiazine [7]. These facts indicate that there is considerable electronic ineteraction between the phenothiazine and the pyrazine rings as shown in **3a**. This can be further demonstrated by the dihedral angles between the least-squares planes of the pyrazine ring and the central ring of the phenothiazine ring system as shown in Table 3 and Figure 3. The plane of the pyrazine ring is nearly perpendicular to the plane [S(5), N(10), C(2'), and C(5')] bisecting the phenothiazine molecule with a dihedral angle of 88.2(1)°. This is in contrast to the configuration of 10-(p-bromophenyl)phenothiazine [9] and 10-(o-methoxyphenyl)phenothiazine [7], in which the plane of phenyl ring is nearly parallel to the plane bisecting the phenothiazine ring as shown in **7**. The folding angle between the planes of the two benzo rings in the title compound is 132.2° as compared to 144.9° and 150.8° in the two crystallographically independent molecules of 10-(p-bromophenyl)phenothiazine and 157.5° in 10-(o-methoxy-

Table 1

Crystal and Experimental Data of 10-(2'-Pyrazyl)phenothiazine

| | |
|---|---|
| Chemical Formula | $C_{16}H_{11}N_3S$ |
| Formula Weight | 277.35 |
| Crystal System | Orthorhombic |
| Space Group | Pbca |
| Unit Cell Dimensions | a = 10.633(3) Å |
| | b = 7.525(2) |
| | C = 32.984(6) |
| | V = 2639.0(1.2) Å³ |
| Density (calculated) | 1.396 g cm⁻³ |
| Number of molecules per unit cell | 8 |
| X-radiation used for data collection | $\lambda(CuK_\alpha) = 1.5418$ Å |
| Linear absorption coefficient | $\mu(CuK_\alpha) = 19.85$ cm⁻¹ |
| Total number of reflections with $2\theta < 130°$ | 2227 |
| Number of reflections with $I > 3.0\sigma(I)$ | 1944 |
| Maximum residual electron density | 0.41e Å⁻³ |
| Disagreement index, R (1944 reflections) | 0.057 |
| Weighted disagreement index, $R_w$ | 0.068 |
| Crystal size | 0.35 × 0.60 × 0.31 mm |
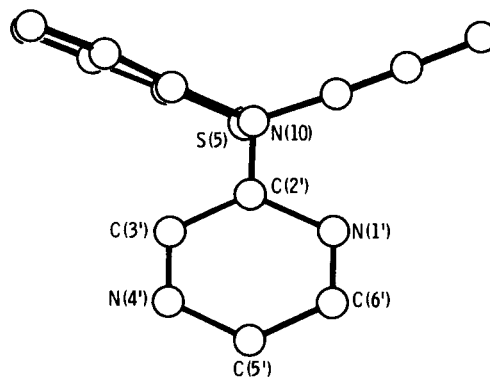


Figure 3.   Frontal view of the title compound showing the folding angle of the phenothiazine ring system. The plane of the pyrazine ring is nearly perpendicular to the plane [S(5), N(10), C(2'), and C(5')] bisecting the title compound.

phenyl)phenothiazine. The smaller folding angle in the



**3a**
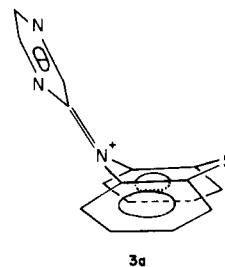
title compound is due apparently to the nonbonded interaction between the pyrazine ring and the phenothiazine ring system with the pyrazine ring extended to the convex side of the phenothiazeine. The closest nonbonded distance involving non-hydrogen atoms are 3.035(3) Å and

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:

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

| | X | Y | Z | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 5238(2) | 3037(3) | 6952(1) | 522(10) | 583(13) | 325(9) | 9(8) | −63(8) | −46(9) |
| C(2) | 4699(2) | 2278(3) | 7297(1) | 717(14) | 667(14) | 269(9) | 51(9) | −90(10) | −82(12) |
| C(3) | 4699(2) | 2005(3) | 7313(1) | 780(15) | 600(13) | 259(10) | 29(9) | 70(10) | −163(11) |
| C(4) | 2664(2) | 2462(3) | 6990(1) | 581(12) | 546(12) | 311(10) | −16(9) | 116(9) | −101(10) |
| C(4a) | 3199(2) | 3243(2) | 6649(1) | 424(10) | 382(10) | 259(9) | 11(7) | −28(7) | |
| S(5) | 2242(1) | 3859(1) | 6236(1) | 383(3) | 541(4) | 357(3) | 28(2) | 7(2) | 41(2) |
| C(5a) | 3279(2) | 3250(2) | 5843(1) | 429(10) | 403(10) | 265(9) | 44(7) | −13(7) | −9(8) |
| C(6) | 2830(2) | 2503(3) | 5489(1) | 639(14) | 557(12) | 313(11) | 54(9) | −109(9) | −104(11) |
| C(7) | 3646(3) | 2020(3) | 5185(1) | 893(17) | 605(14) | 274(10) | −38(9) | −42(10) | −150(13) |
| C(8) | 4923(2) | 2227(3) | 5239(1) | 864(16) | 629(14) | 279(10) | −52(9) | 154(11) | 5(13) |
| C(9) | 5396(2) | 2936(3) | 5599(1) | 561(11) | 592(13) | 333(9) | −19(8) | 90(8) | 2(9) |
| C(9a) | 4569(2) | 3496(2) | 5896(1) | 445(9) | 418(10) | 220(8) | −3(7) | 20(7) | −31(8) |
| N(10) | 5014(2) | 4274(2) | 6267(1) | 419(9) | 499(9) | 235(8) | 0(5) | 19(6) | −116(8) |
| C(10a) | 4491(2) | 3530(2) | 6632(1) | 447(10) | 403(9) | 215(8) | −20(7) | 14(7) | −66(8) |
| N(1') | 5636(2) | 6772(2) | 6629(1) | 450(12) | 499(9) | 312(8) | −4(7) | −24(7) | −62(7) |
| C(2') | 5492(2) | 5990(3) | 6271(1) | 265(9) | 478(11) | 292(10) | −1(6) | 16(6) | −12(8) |
| C(3') | 5831(2) | 6884(3) | 5911(1) | 491(11) | 545(12) | 326(10) | 29(8) | 77(9) | −80(9) |
| N(4') | 6257(2) | 8533(2) | 5912(1) | 588(11) | 530(10) | 466(11) | 59(8) | 109(8) | −92(9) |
| N(5') | 6363(2) | 9339(4) | 6272(1) | 518(13) | 500(12) | 575(16) | 16(9) | 38(9) | −89(11) |
| C(6') | 6062(2) | 8451(3) | 6623(1) | 521(12) | 515(11) | 416(11) | −50(9) | −44(9) | −59(10) |
| H(1) | 624(0) | 323(0) | 693(0) | 64(7) | | | | | |
| H(2) | 528(0) | 190(0) | 754(0) | 96(10) | | | | | |
| H(3) | 299(0) | 143(0) | 758(0) | 71(8) | | | | | |
| H(4) | 166(0) | 221(0) | 700(0) | 74(7) | | | | | |
| H(6) | (0) | 229(0) | 545(0) | 69(7) | | | | | |
| H(7) | 328(0) | 148(0) | 490(0) | 77(8) | | | | | |
| H(8) | 556(0) | 182(0) | 500(0) | 110(11) | | | | | |
| H(9) | 639(0) | 304(0) | 564(0) | 59(6) | | | | | |
| H(3') | 574(0) | 619(0) | 562(0) | 85(8) | | | | | |
| H(5') | 668(0) | 1069(0) | 628(0) | 67(8) | | | | | |
| H(6') | 617(0) | 913(0) | 690(0) | 65(7) | | | | | |

3.178(4)Å for C(1)···N(1') and C(9)···C(3'), respectively. The distance of 3.305 Å between C(1) and N(1') indicates that there is no hydrogen bonding involved between the lone-pair electrons on the pyrazyl nitrogen and the H(1).

The central ring is in a boat conformation as shown from the torsion angles around the central ring and the puckering parameters [10] in Table 4, and from the side view of the molecule in Figure 4. The pyrazyl group in a boat-axial conformation. As in other phenothiazines, the sum of the three C-N-C bond angles is close to 360° indicating that the nitrogen atom has nearly sp² hybridization. The torsion angles about the N(10)-C(2') bond are also shown in Table 4 and in **3b**. The pyrazine ring is slightly
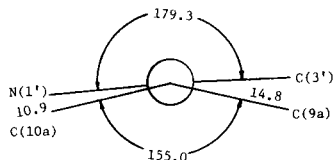


3b

tilted with the torsion angle of C(10a)-N(10)-C(2')-N(1') smaller than that of the C(9a)-N(10)-C(2')-C(3').

The packing of the molecules in a unit cell is determined by the van der Waals interaction as shown in Figure 5. There are no intermolecular contacts less than 3.5 Å between non-hydrogen atoms.

All structural information were calculated using a number of structure interpretation programs [11].

Spectroscopic Analysis.

Absorption maxima of 10-phenylphenothiazine, **1**, 10-phenylpyrido[3,2-b][1,4]benzothiazine, **2**, and 10-(2'-pyrazyl)phenothiazine, **3**, are given in Table 5. The uv spectra were recorded as dilute solution in hexane. The λ max values at lower wavelengths are due to the π-π* transitions and compare well with similar assignments for phenothiazine, **4** [2]. The λ max at higher wavelengths are much lower in intensity (forbidden transitions) and correspond to the n-π* electronic transitions. The small shoulder at 237 nm for **1** may well be part of the fine structure of the n-π* band envelope. Similar λ max appears at 247 nm for **3**.

Table 3

Least squares Planes and the Displacements (Å)
of Atoms From the Plane
Equation of planes: Ax + By + Cz = D, where x, y, z are in Å

| Plane | A | B | C | D |
|---|---|---|---|---|
| (a) | −0.125(1) | 0.907(2) | 0.402(1) | 10.60(3) |
| (b) | 0.057(1) | −0.912(1) | 0.406(1) | 5.78(2) |
| (c) | 0.9363(4) | −0.344(1) | 0.069(1) | 5.35(3) |
| (d) | −0.0365(8) | 0.009(1) | 0.9993(1) | 20.494(2) |

Displacements (Å) of atoms from the planes (* indicates atoms excluded
from the calculation of the least-squares planes).

| | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| C(1) | −0.009(4) | | | |
| C(2) | 0.002(4) | | | |
| C(3) | 0.007(4) | | | |
| C(4) | −0.009(4) | | | |
| C(4a) | 0.002(4) | | | |
| C(5a) | | 0.002(4) | | |
| C(6) | | 0.014(4) | | |
| C(7) | | −0.012(4) | | |
| C(8) | | −0.004(4) | | |
| C(9) | | 0.019(4) | | |
| C(9a) | | −0.018(4) | | |
| C(10a) | 0.003(3) | | | |
| S(5) | 0.002(4)* | 0.046(5)* | | 0.000(1) |
| N(10) | −0.042(4)* | −0.027(5)* | −0.045(4)* | −0.002(3) |
| N(1') | | | 0.009(3) | |
| C(2') | | | −0.013(3) | 0.004(3) |
| C(3') | | | 0.011(4) | |
| N(4') | | | 0.009(4) | |
| C(5') | | | −0.013(4) | −0.003(4) |
| C(6') | | | −0.003(4) | |

Dihedral angles between the least-squares planes

| | |
|---|---|
| Plane (a) and Plane (b) | 132.2(1)° |
| Plane (a) and Plane (d) | 65.5(1)° |
| Plane (b) and Plane (d) | 66.7(1)° |
| Plane (c) and Plane (d) | 88.2(1)° |

Table 4

Torsion Angles and Ring Puckering Parameters

Torsion angles around the central phenothiazine ring:

| | |
|---|---|
| C(4a)−S(5)−C(5a)−C(9a) | −36.2(2)° |
| S(5)−C(5a)−C(9a)−N(10) | −1.3(3) |
| C(5a)-C(9a)−N(10)−C(10a) | 47.6(3) |
| C(9a)−N(10)−C(10a)−C(4a) | −45.6(3) |
| N(10)−C(10a)−C(4a)−S(5) | −2.1(3) |
| C(10a)−C(4a)−S(5)−C(5a) | 38.1(2) |

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

| | |
|---|---|
| C(9a)−N(10)−C(2')−N(1') | 165.9(2)° |
| C(9a)−N(10)−C(2')−C(3') | −14.8(3) |
| C(10a)−N(10)−C(2')−N(1') | 10.9(3) |
| C(10a)−N(10)−C(2')−C(3') | −169.8(2) |

Puckering parameters:

| Central phenothiazine | Ideal boat conformation |
|---|---|
| $Q = 0.632$ Å | $q_2 = Q$ |
| $q_2 = 0.630$ | $Q_3 = 0$ |
| $q_3 = 0.046$ | |
| $\theta = 94.1°$ | $\theta = 90°$ |
| $\phi_2 = \mathbf{238.5°}$ | $\phi_2 = 240°$ |

Table 5 [a]

Major Absorption Maxima (nm) for Neutral Molecules

| Compound No. | n-π* | ε [b] | π-π* | ε [b] | Other Transitions ε [b] | |
|---|---|---|---|---|---|---|
| 1 | 256 | 118.8 | 314 | 80.2 | 237 [c] | — [d] |
| 2 | 251 | 65.8 | 325 | 8.0 | — | — |
| 3 | 247 | 56.7 | 334 | 10.2 | 276 | 18.9 |

[a] As dilute solutions in hexane (1 × 10⁻⁵ molar). [b] 1 × 10³. [c]
Non-bonding transitions. [d] Shoulder.

Table 6 [a]

Major Absorption Maxima (nm) for Oxidized Molecules

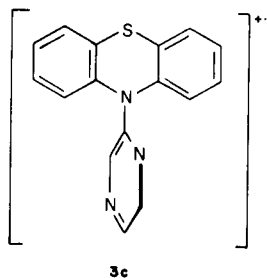| Compound No. | Solvent | n-π* | ε [b] | π-π* | ε [b] | A [c] | Other Transitions ε [b] | B | ε [b] |
|---|---|---|---|---|---|---|---|---|---|
| 3e | 20% HCl | 259 | 23.7 | 373 | 4.7 | 305 | weak | — | — |
| 1a | 38% HCl | 272 | 6.0 | 515 | weak | 314 | weak | 238 | 7.0 |
| 3e | 38% HCl | 259 | 44.0 | 376 | 8.6 | 305 | — [d] | — | — |
| 1a | 48% HBr [e] | — [e] | — [e] | 516 | 2.7 | 315 | weak | — | — |
| 3e | 48% HBr [e] | — [e] | — [e] | 374 | 21.3 | — [e] | — [e] | — | — |
| 1a | 86% H₃PO₄ | 272 | 6.8 | 514 | weak | 314 | weak | 238 | weak |
| 3e | 86% H₃PO₄ | 263 | 82.7 | 372 | 18.9 | 305 | weak | — | — |
| 3e | 40% H₂SO₄ | 261 | 92.8 | 374 | 19.3 | 306 | 1.2 | 239 | 20.4 |
| 1a | 96% H₂SO₄ | 274 | 169.0 | 514 | 28.1 | 314 | 6.3 | 239 | 47.5 |
| 1b | 96% H₂SO₄ | 291 | 65.5 | 468 | 19.8 | 314 | 6.3 | 239 | 47.5 |
| 3c | 96% H₂SO₄ | 259 | 137.9 | 511 | 9.0 | 305 | 3.9 | — | — |
| 3c-H | 96% H₂SO₄ | 257 | 87.8 | 409 | 23.4 | 305 | 7.3 | — | — |
| 1b | fuming H₂SO₄ [f] | 295 | 75.0 | 465 | — [d] | 311 | weak | 238 | 14.6 |
| 1c | fuming H₂SO₄ [f] | — | — | 480 | 77.6 | 311 | weak | 238 | 14.6 |
| 3d [g] | fuming H₂SO₄ [f] | 294 | 51.7 | 465 | — [d] | 305 | — [d] | — | — |

[a] Recorded as dilute solutions (1 × 10⁻⁵ molar). [b] 1 × 10³. [c] Absorptions assigned to non-bonding transitions. [d] Shoulder. [e] Solvent cut-off at 310 nm. [f] 65% oleum. [g] This species may exist as **3d-H** but there was no way to distinguish the two.

The second transition at 276 nm is very different from the one at 256 nm for 10-phenyl compound, **1**, and the literature assignment for pyrazine, **5**, in cyclohexane [12] at 258 nm. The lower energy $\pi$-$\pi^*$ transition (higher wavelengths) for **3** is considerable and is an indication of an increase in conjugation. This $\pi$ interaction between pyrazyl group and phenothiazine nucleus is consistent with the x-ray structure of **3**. Indeed, the delocalization of electrons onto the pyrazine ring as shown in **3a** could be responsible for the observed bathochromic shift.

Table 6 lists the $\lambda$ max for **1** and **3** in various mineral acids. In 96% sulfuric acid, ultraviolet spectrum of **1** has a very strong absorption at 274 nm and another in the visible spectrum at 514 nm which we attribute to 10-phenyl-phenothiazium radical-cation, **1a**, based on the similar assignments made for the radical-cation of 10-methylphenothiazine, **6a**, at 270 nm and 513 nm, respectively [13]. Similarly, bands at 291 nm and 468 nm are due to the dication of 10-phenyl derivative, **1b**, and it too is almost identical to dication band envelopes of 10-methyl compound, **6b**, at 290 nm and 464 nm [13]. Electronic transition at 239 nm and 314 nm for **1** cannot be assigned at present but may be due to transitions of non-bonded electrons.

Compound **3**, however, has $\lambda$ max absorptions at 259 nm, 409 nm, and 511 nm. We assigned the first and the last absorptions to the radical-cation of **3c** on the basis of the similar absorption bands of the radical-cation of 10-methylphenothiazine **6a**. The absorption band at 409 nm was assigned to the protonated radical cation **3c-H** on the basis of the following observations. Repetitive scans of a solution of **3** in concentrated sulfuric acid revealed that, over a period of two months, the absorption bands of 511 nm and 259 nm slowly disappeared and that only the 409 nm band remained. The resulting solution gave a strong esr signal.

The weaker absorption at 305 nm is probably due to the nonbonding electrons. The observation that **3c** has a band in the visible region with the frequency almost identical to **1a** indicates that they are very similar. The apparent hypsochromic shift of the lower absorption of **3c** (259 nm) with respect to the same absorption of **1a** (274 nm) may be due to the decrease in conjugation. This could result from the change in geometry of **3c** as compared to **3** where the $\pi$ in-
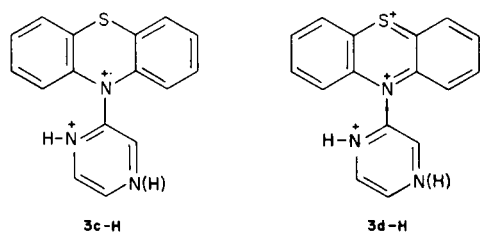
teractions are not possible. The 10-pyrazyl group assumes a twisted orientaiton and is contained in the plane bisecting the dihedral angle of phenothiazine and defined by S(5), N(10), C(2'), and C(5') atoms.

There is sufficient precedence from literature to warrant the above conclusion. For example, absorption maxima for radical-cations fo 10-alkylphenothiazines are in the range of 510-515 nm [12,13,14]. Interestingly, $\lambda$ max for 10-aryl compounds are also in that range [14]. The same is true for dications of alkylphenothiazines (457-460 nm) whose spectral properties are remarkably similar to those of 10-aryl derivatives [13,14]. These observations indicate that the aryl group is twisted with respect to the phenothiazine ring and therefore preventing the electronic interaction of N(10) with the 10-phenyl ring. Upon oxidation, the phenothiazine nucleus assumes a planar configuration in which unfavorable steric repulsions ixist between the aryl group and the 1,9-peri hydrogen atoms resulting in the perpendicular orientation of the 10-substituent of **1a** and **3c**. This is certainly the case with 2'-methoxy-10-phenylphenothiazine, **7**, whose $\lambda$ max for its radical-cation is at 509 nm [14]. Its $^1$H and $^{13}$C nmr data point to the same conclusion [3]. The x-ray data for **7** shows that in the solid state the 10-phenyl ring is perpendicular to the central ring of the phenothiazine nucleus [7] and this configuration might be expected to mimic the oxidized form, **7a**, since the ortho substituent prevents free-rotation around the N(10)-C(1') bond. This analogy is only speculative and points to the similarities which may exist between the solid state and molecular geometries in solution of these sterically hindered derivatives.



**7**
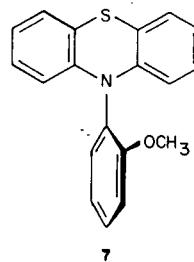
The above spectroscopic evidence strongly discounts electric delocalizaiton into the N-substituents and supports our statement that the geometric conformation of **3** changes as it forms its radical-cation, **3c**. Similar effects have been observed for 10-phenylacridines [15].

The formation of the dication **3d** of the weakly basic pyrazyl compound **3** was achieved in fuming sulfuric acid (65% oleum). The two major absorptions at 294 nm and 465 nm are similar to the analogous absorption bands of other 10-arylphenothiazines [13,14].



**3c**

Figure 5.   The molecular packing of the title compound in a unit cell viewed down the b-axis.

The absorption wavelength in the visible part of the spectrum of the dication, **3d**, also shows a small blue shift as compared to 468 nm for 10-phenyl derivative, **1b**. This, however, does not negate the poossibility that this shift may be due to the protonated from of **3d** in strong mineral acid soluitons. This is especially true for phenothiazines since they yield easily the triply charged ions upon ionization [2]. Compound **1** gave three absorption bands in fuming sulfuric acid, two of which were assigned to the dicattion of **1** (Table 6). The strong absorption at 480 nm could be attributed to the triply charged phenothiazine, **1c**. At this time, we can only speculate on the structure of this ionic species but structures **8a** and **8b** are reasonable representations of this highly oxidized form of **1**.
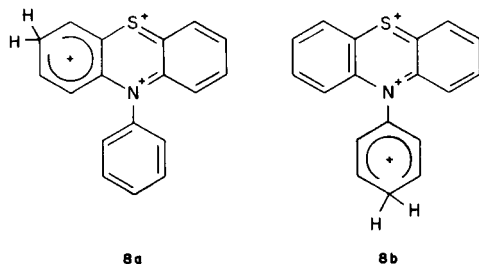


To elucidate the ease of protonation of **3**, the spectrum of the dilute solution of **3** in 40% aqueous sulfuric acid
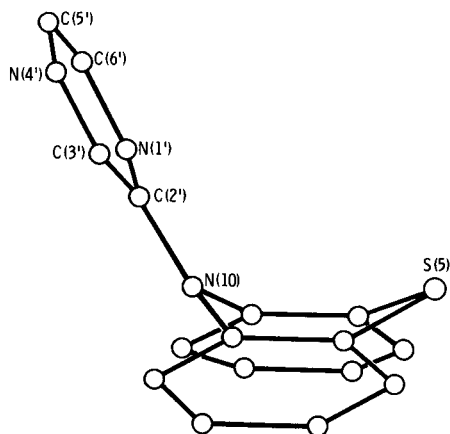
was obtained. Almost immediately, there is a very fast build-up of **3c** as indicated by the appearance of the absorption band at 517 nm. However, the pink color fades within 5 minutes and is replaced by a bright, solid yellow color. The absorption at 517 nm slowly disappears at the expense of the new band at 374 nm and after 30 minutes this transformation is complete. We assigned this second λ max to the protonated 10-(2'-pyrazyl) derivative, **3e**; protonation probably occurring at the more basic nitrogen, N(1').

Data in Table 6 support this conclusion. The uv spectra of **1** and **3** were obtained in non-oxidizing, oxygen-free acid media. In 20% hydrochloric acid, **1** produced no absorption bands whereas **3** yielded two strong absorptions at 259 nm and 376 nm and a weaker one at 305 nm (Table 6). Furthermore, these observations indicate that oxidation of **1** to **1a** and **1b** is more likely to occur than the protonation at N(10) or S(5) of **1**. As the concentration of hydrochloric acid was increased, small amounts of radical-cation **1b** were produced. The fact that HBr was a better oxidant than HCl in producing **1b** is due to the additional electron-exchange equilibria discussed elsewhere [16]. Some results were obtained in 86% phosphoric acid.





Figure 4.   Side view of the title compound showing the boat conformation of the central ring of the phenothiazine ring system.

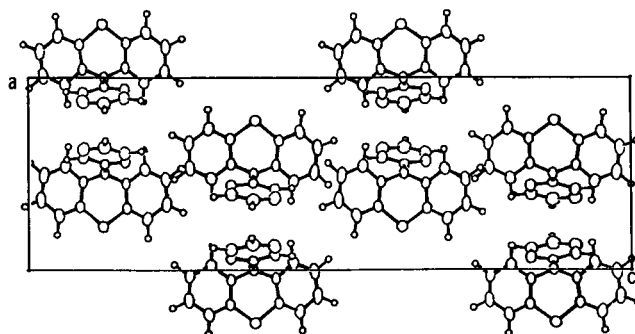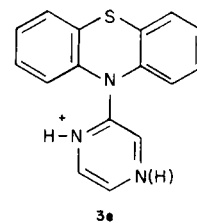## REFERENCES AND NOTES

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