# Crystal structure
# of 1-phenylamino-3-mercapto-6,7-tetramethylene-thieno[2,3-D] pyrimidine betaine, $C_{16}H_{15}N_3S_2$

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*Dedicated to the memory of Martin J. Buerger*

*Crystal structure | Thienopyrimidine derivatives*

**Abstract.** The crystal structure of the title compound has been determined. Crystal data: $C_{16}H_{15}N_3S_2$, monoclinic, $P2_1/c$, $a = 8.447(3)$, $b = 20.404(2)$, $c = 17.371(1)$ Å, $\beta = 97.82(1)°$, $V = 2966(1)$ $A^3$, $Z = 8$, $D_c = 1.404(3)$ g/cm$^3$, $M = 313.435$, $\mu = 31.579$/cm, $F(000) = 1312$, $\lambda = 1.5418$ Å, final $R = 0.063$ for 4540 independent reflections measured at room temperature.

The thienopyrimidine is planar and the cyclohexane ring fused to it has different conformations in the two independent molecules. The N atoms in the thienopyrimidine rings are bonded to $-NH_2$ groups and have positive charges. These are neutralized by negative charges localised in the $S-C-N-C$ part, as indicated by their short bond lengths with double bond character.

## Introduction

The title compound was synthesized by Prof. Madroñero and collaborators of the Instituto de Quimica Medica, CSIC, who provided the crystal for the X-ray analysis.

The crystal structure reported in this paper is carried out in order to elucidate the position of the substituents and determine their molecular geometry and the electronic interactions.
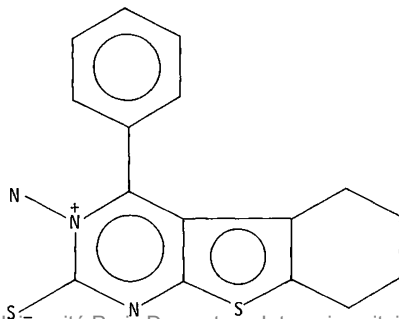
## Experimental

Preliminary cell dimensions and space group were obtained from Weissenberg and precession photographs. Accurate cell parameters were determined by least-squares methods from the setting angles of 50 reflections measured on a Philips PW1100 four-circle diffractometer with graphite monochromated $CuK\alpha$ radiation. Crystal data are given in the Abstract. There are two independent molecules in the asymmetric unit.

Intensities were measured from a crystal of $0.1 \times 0.2 \times 0.3$ mm on the same diffractometer and the same radiation for $2 < \theta < 65°$. The $\omega$-2 $\theta$ scan technique was used. Two reflections were measured as standard and remeasured after every 90 min; no decomposition was observed. Of the 5024 independent reflections measured, 4540 were considered as observed with $I > 2 \sigma(I)$, $\sigma$ being determined from counting statistics; Lorentz and polarization corrections were applied and also correction for absorption (Walker and Stuart, 1983). Scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography (1974)*.

The structure was solved by direct methods with MULTAN80 (Main et al., 1980), and DIRDIF (Beurskens et al., 1980).

The refinement was carried out by full-matrix least-squares methods minimizing $\Sigma[w(|F_o|-|F_c|)^2]$ with unit weights. After isotropic and anisotropic refinement, the resulting difference-density map revealed the positions of hydrogen atoms. Further refinement with isotropic and anisotropic temperature factors for the hydrogen and all the other atoms respectively, converged when the averaged $\Delta/\sigma < 0.07$. The final $R$ factors were $R = 0.063$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma(|F_o|^2)]^{\frac{1}{2}} = 0.081$ with $w$, an empirical weighting scheme, calculated such that $\langle w\Delta^2 F \rangle$ is independent of $\langle \sin\theta/\lambda \rangle$.

The computations were made with programs of the XRAY76 system (Stewart et al., 1976), PARST (Nardelli, 1983a), and PESOS (Martinez-Ripoll and Cano, 1975), on a VAX11/750 computer.

The atomic parameters are listed in Table 1. Figure 1 displays a view of the molecules. Individual bond lengths and angles for the two independent molecules (I) and (II) are shown in Table 2[1].

## Discussion

The aromatic ring A is more planar in the molecule (II) than in molecule (I) [mean torsion angles in (I) and (II), 3.6(4) and 0.8(6)°], and atoms S1 and N3 are coplanar but C11 deviates somewhat from that plane. This

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[1] Additional material to this paper can be ordered referring to the no. CSD 52213, names of the authors and citation of the paper at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

**Table 1.** Atomic coordinates and isotropic thermal parameters $U_{eq} = 1/3\, U_{ij}a_i a_j a_i^* a_j^*$ [Å$^2$].

| Atom | | $x$ | $y$ | $z$ | $U_{eq}/U$ |
|------|------|------|------|------|------|
| S1 | I | 0.2801(1) | 0.0758(1) | 0.7970(1) | 0.0515(3) |
| S2 | I | −0.0758(2) | −0.1584(1) | 0.6630(1) | 0.0638(4) |
| N1 | I | 0.0303(3) | 0.0537(1) | 0.8706(2) | 0.0396(8) |
| N2 | I | 0.2004(3) | 0.1390(1) | 0.9213(2) | 0.0412(9) |
| N3 | I | 0.3422(5) | 0.1758(3) | 0.9186(2) | 0.0705(15) |
| C1 | I | 0.1623(4) | 0.0897(2) | 0.8654(2) | 0.0397(10) |
| C2 | I | 0.1186(3) | 0.1505(2) | 0.9820(2) | 0.0354(9) |
| C3 | I | −0.0215(3) | 0.1161(1) | 0.9845(2) | 0.0330(9) |
| C4 | I | −0.1393(3) | 0.1194(2) | 1.0372(2) | 0.0348(9) |
| C5 | I | −0.1440(4) | 0.1669(2) | 1.1032(2) | 0.0419(11) |
| C6 | I | −0.3068(4) | 0.1665(2) | 1.1322(2) | 0.0506(12) |
| C7 | I | −0.3629(4) | 0.0970(2) | 1.1415(2) | 0.0474(11) |
| C8 | I | −0.3933(4) | 0.0627(2) | 1.0630(2) | 0.0452(11) |
| C9 | I | −0.2544(4) | 0.0739(2) | 1.0192(2) | 0.0378(9) |
| C10 | I | −0.0559(3) | 0.0681(2) | 0.9263(2) | 0.0352(9) |
| C11 | I | 0.1897(3) | 0.1950(2) | 1.0449(2) | 0.0362(9) |
| C12 | I | 0.2011(4) | 0.2627(2) | 1.0362(2) | 0.0499(12) |
| C13 | I | 0.2681(5) | 0.2998(2) | 1.0983(3) | 0.0614(15) |
| C14 | I | 0.3219(5) | 0.2715(2) | 1.1682(3) | 0.0608(15) |
| C15 | I | 0.3090(4) | 0.2051(2) | 1.1781(2) | 0.0527(12) |
| C16 | I | 0.2424(4) | 0.1669(2) | 1.1161(2) | 0.0411(10) |
| S1 | II | −0.0758(2) | −0.1584(1) | 0.6630(1) | 0.0638(4) |
| S2 | II | −0.2717(2) | −0.0134(1) | 0.4124(1) | 0.0826(5) |
| N1 | II | −0.1716(5) | −0.0825(2) | 0.5414(2) | 0.0645(13) |
| N2 | II | −0.1472(3) | −0.0304(1) | 0.6634(2) | 0.0413(8) |
| N3 | II | −0.1207(4) | −0.0371(2) | 0.7448(2) | 0.0512(11) |
| C1 | II | −0.1347(5) | −0.0873(2) | 0.6187(2) | 0.0503(12) |
| C2 | II | −0.1931(4) | 0.0292(2) | 0.6328(2) | 0.0371(9) |
| C3 | II | −0.2331(4) | 0.0336(2) | 0.5527(2) | 0.0423(10) |
| C4 | II | −0.2911(4) | 0.0876(2) | 0.5024(2) | 0.0446(11) |
| C5 | II | −0.3214(6) | 0.1566(2) | 0.5255(2) | 0.0581(14) |
| C6 | II | −0.3391(10) | 0.2036(3) | 0.4557(3) | 0.1035(27) |
| C7 | II | −0.4317(9) | 0.1767(3) | 0.3870(3) | 0.0859(22) |
| C8 | II | −0.3780(7) | 0.1115(2) | 0.3592(3) | 0.0717(17) |
| C9 | II | −0.3175(5) | 0.0687(2) | 0.4279(2) | 0.0576(13) |
| C10 | II | −0.2186(5) | −0.0245(2) | 0.5116(2) | 0.0551(13) |
| C11 | II | −0.1919(3) | 0.0858(2) | 0.6861(2) | 0.0353(9) |
| C12 | II | −0.3094(4) | 0.0941(2) | 0.7339(2) | 0.0452(11) |
| C13 | II | −0.3036(4) | 0.1484(2) | 0.7822(2) | 0.0532(12) |
| C14 | II | −0.1820(5) | 0.1938(2) | 0.7834(2) | 0.0532(12) |
| C15 | II | −0.0652(5) | 0.1852(2) | 0.7361(2) | 0.0507(12) |
| C16 | II | −0.0694(4) | 0.1317(2) | 0.6882(2) | 0.0427(10) |
| H31 | I | 0.388(7) | 0.164(3) | 0.879(3) | 0.063(17) |
| H32 | I | 0.300(10) | 0.218(4) | 0.901(5) | 0.131(36) |
| H51 | I | −0.111(5) | 0.210(5) | 1.086(2) | 0.032(11) |
| H52 | I | −0.058(5) | 0.154(2) | 1.148(2) | 0.028(10) |
| H61 | I | −0.298(5) | 0.192(2) | 1.184(2) | 0.027(10) |
| H62 | I | −0.385(5) | 0.191(2) | 1.095(2) | 0.034(11) |
| H71 | I | −0.458(5) | 0.096(2) | 1.168(2) | 0.030(10) |

**Table 1.** (Continuation)

| Atom | | $x$ | $y$ | $z$ | $U_{eq}/U$ |
|------|------|------|------|------|------|
| H72 | I | −0.275(5) | 0.072(2) | 1.177(2) | 0.028(11) |
| H81 | I | −0.497(6) | 0.080(2) | 1.027(3) | 0.038(13) |
| H82 | I | −0.399(5) | 0.016(2) | 1.071(2) | 0.031(12) |
| H12 | I | 0.180(6) | 0.283(2) | 0.984(3) | 0.046(13) |
| H13 | I | 0.292(6) | 0.343(3) | 1.093(3) | 0.054(16) |
| H14 | I | 0.358(6) | 0.297(2) | 1.213(3) | 0.041(13) |
| H15 | I | 0.344(5) | 0.184(2) | 1.229(3) | 0.033(12) |
| H16 | I | 0.232(4) | 0.122(2) | 1.123(2) | 0.018(9) |
| H31 | II | −0.074(6) | −0.077(3) | 0.745(3) | 0.045(14) |
| H32 | II | −0.069(6) | −0.004(3) | 0.765(3) | 0.038(14) |
| H51 | II | −0.399(6) | 0.156(2) | 0.557(3) | 0.045(14) |
| H52 | II | −0.241(9) | 0.172(3) | 0.564(4) | 0.074(23) |
| H61 | II | −0.289(12) | 0.187(5) | 0.395(6) | 0.132(36) |
| H62 | II | −0.396(7) | 0.250(3) | 0.473(3) | 0.072(18) |
| H71 | II | −0.454(7) | 0.207(3) | 0.340(3) | 0.062(17) |
| H72 | II | −0.530(15) | 0.170(6) | 0.439(6) | 0.146(48) |
| H81 | II | −0.458(7) | 0.090(3) | 0.327(3) | 0.052(15) |
| H82 | II | −0.297(7) | 0.111(3) | 0.318(4) | 0.078(19) |
| H12 | II | −0.396(5) | 0.060(2) | 0.733(2) | 0.024(11) |
| H13 | II | −0.390(4) | 0.152(2) | 0.818(2) | 0.020(9) |
| H14 | II | −0.176(6) | 0.233(2) | 0.820(3) | 0.042(12) |
| H15 | II | 0.018(5) | 0.218(2) | 0.737(2) | 0.028(11) |
| H16 | II | 0.009(5) | 0.124(2) | 0.659(2) | 0.016(9) |
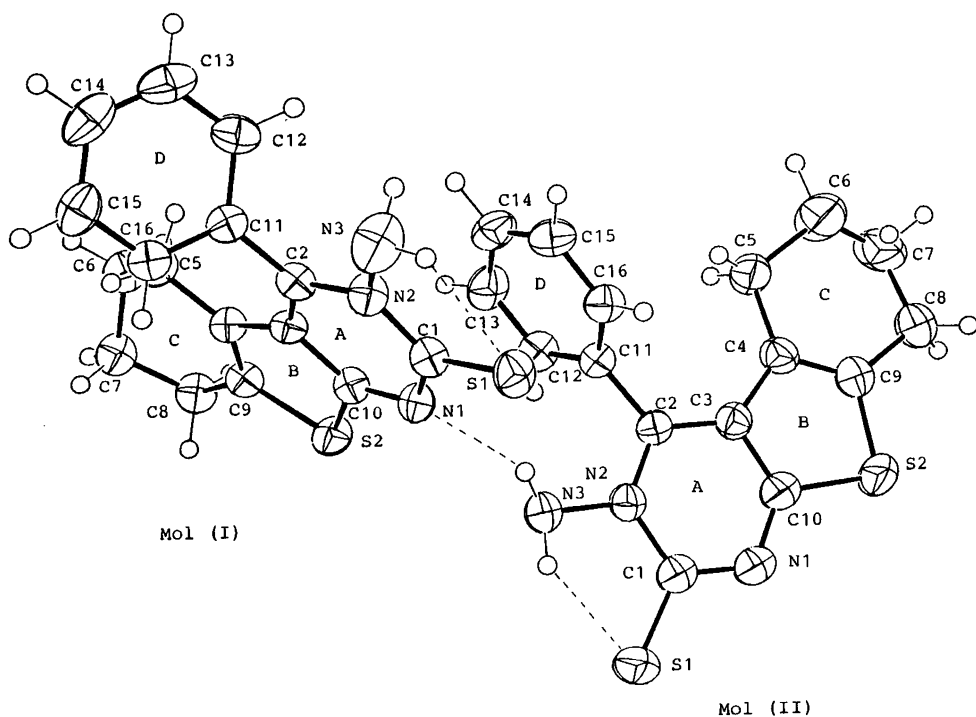


**Fig. 1.** A view and numbering scheme of the two independent molecules.

**Table 2**

| Bond distances (A) | Mol I | Mol II |
|---|---|---|
| S1 – C1 | 1.675(4) | 1.685(4) |
| S2 – C9 | 1.750(4) | 1.748(5) |
| S2 – C10 | 1.736(3) | 1.735(4) |
| N1 – C1 | 1.349(4) | 1.340(5) |
| N1 – C10 | 1.321(5) | 1.331(6) |
| N2 – N3 | 1.420(6) | 1.408(5) |
| N2 – C1 | 1.405(5) | 1.409(5) |
| N2 – C2 | 1.357(5) | 1.362(5) |
| C2 – C3 | 1.382(4) | 1.389(5) |
| C2 – C11 | 1.483(5) | 1.479(6) |
| C3 – C4 | 1.442(5) | 1.450(5) |
| C3 – C10 | 1.409(5) | 1.398(6) |
| C4 – C5 | 1.506(5) | 1.496(6) |
| C4 – C9 | 1.350(5) | 1.340(5) |
| C5 – C6 | 1.528(5) | 1.537(7) |
| C6 – C7 | 1.511(6) | 1.443(8) |
| C7 – C8 | 1.523(5) | 1.506(8) |
| C8 – C9 | 1.500(5) | 1.511(6) |
| C11 – C12 | 1.394(6) | 1.388(5) |
| C11 – C16 | 1.381(5) | 1.392(5) |
| C12 – C13 | 1.375(6) | 1.387(6) |
| C13 – C14 | 1.365(7) | 1.381(6) |
| C14 – C15 | 1.372(6) | 1.378(6) |
| C15 – C16 | 1.385(6) | 1.370(6) |

| Bond angles (°) | Mol I | Mol II |
|---|---|---|
| C9 – S2 – C10 | 90.8(2) | 90.3(2) |
| C1 – N1 – C10 | 118.1(3) | 118.1(4) |
| C1 – N2 – C2 | 124.6(3) | 124.0(3) |
| N3 – N2 – C2 | 117.1(3) | 118.5(3) |
| N3 – N2 – C1 | 118.1(3) | 117.4(3) |
| N1 – C1 – N2 | 117.2(3) | 117.9(3) |
| S1 – C1 – N2 | 120.6(3) | 119.8(3) |
| S1 – C1 – N1 | 122.1(3) | 122.3(3) |
| N2 – C2 – C11 | 118.7(3) | 118.4(3) |
| N2 – C2 – C3 | 117.7(3) | 117.8(4) |
| C3 – C2 – C11 | 123.4(3) | 123.8(3) |
| C2 – C3 – C10 | 115.1(3) | 115.5(3) |
| C2 – C3 – C4 | 131.6(3) | 132.0(4) |
| C4 – C3 – C10 | 113.3(3) | 112.5(3) |
| C3 – C4 – C9 | 111.0(3) | 111.2(4) |
| C3 – C4 – C5 | 127.2(3) | 127.6(3) |
| C5 – C4 – C9 | 121.8(3) | 121.2(4) |
| C4 – C5 – C6 | 111.5(3) | 112.3(3) |
| C5 – C6 – C7 | 110.5(3) | 113.5(5) |
| C6 – C7 – C8 | 110.7(3) | 116.6(5) |
| C7 – C8 – C9 | 109.6(3) | 110.0(4) |
| C4 – C9 – C8 | 125.1(3) | 126.2(4) |
| S2 – C9 – C8 | 120.7(3) | 119.4(3) |
| S2 – C9 – C4 | 114.2(3) | 114.4(3) |

**Table 2.** (Continuation)

| Bond angles (°) | Mol I | Mol II |
|---|---|---|
| N1 − C10 − C3 | 126.9(3) | 126.7(3) |
| S2 − C10 − C3 | 110.7(2) | 111.6(3) |
| S2 − C10 − N1 | 122.4(3) | 121.7(3) |
| C2 − C11 − C16 | 117.0(4) | 118.9(3) |
| C2 − C11 − C12 | 123.6(3) | 121.7(3) |
| C12 − C11 − C16 | 119.3(4) | 119.4(3) |
| C11 − C12 − C13 | 119.2(4) | 119.4(3) |
| C12 − C13 − C14 | 121.1(4) | 120.7(3) |
| C13 − C14 − C15 | 120.4(4) | 119.8(4) |
| C14 − C15 − C16 | 119.3(4) | 120.1(4) |
| C11 − C16 − C15 | 120.7(4) | 120.6(3) |

| Torsion angles (°) | Mol I | Mol II |
|---|---|---|
| C2 − N2 − C1 − S1 | −175.0(3) | 179.7(3) |
| N1 − C1 − N2 − N3 | 177.7(3) | 175.0(4) |
| N1 − C1 − N2 − C2 | 3.5(5) | −0.6(6) |
| S1 − C1 − N2 − N3 | −0.9(5) | −5.7(5) |
| C5 − C4 − C9 − C8 | −2.9(6) | 0.2(6) |
| C3 − C4 − C9 − S2 | −1.0(4) | −1.3(4) |
| C4 − C3 − C10 − S2 | −1.4(4) | 1.0(4) |
| C2 − C3 − C10 − N1 | −179.6(3) | 0.3(6) |
| C5 − C4 − C9 − S2 | 177.5(3) | 178.9(3) |
| C4 − C3 − C10 − N1 | −179.6(3) | −178.6(4) |
| C3 − C4 − C9 − C8 | 178.6(3) | −180.0(4) |
| C2 − C3 − C10 − S2 | 177.5(3) | 179.9(3) |
| C9 − C4 − C5 − C6 | −12.7(5) | −15.4(6) |
| C4 − C5 − C6 − C7 | 45.7(4) | 41.4(7) |
| C5 − C6 − C7 − C8 | −65.3(4) | −54.4(7) |
| C6 − C7 − C8 − C9 | 47.6(4) | 36.7(7) |

deviation is smaller in (II) [−0.286(4) Å] than in (I) [0.083(3) Å], in good agreement with the greater planarity of that ring.

The rings B show mean torsion angles of 1.1(3) and 1.1(4)° in molecules (I) and (II) and atoms C5 and C8 are coplanar with the five-membered rings.

The dihedral angle formed by the least-squares planes of rings A and B are 0.8(1) and 1.6(1)° for (I) and (II). Consequently, the two fused rings, that form the thienopyrimidine, are planar as verified by the torsion angles, Table 2.

A interesting feature is that the two rings C have different conformation in the two independent molecules. The torsion angles suggest a half-chair conformation in (I) and a twist deformed conformation in (II). The asymmetry parameters for such rings are: (I): $C_2^{4-9} = 0.009(2)$; (II): $C_2^{4-9} = 0.023(2)$, $C_2^5 = 0.141(1)$ (Nardelli, 1983 b).

Finally the rings D are planar with mean torsion angles of 0.8(6) and 0.6(6)° in molecules (I) and (II). The torsion angles around the C2 − C11 bond are 111.0(1) and 105.3(1)° respectively for (I) and (II).

Bond lengths and angles are almost identical in the two independent molecules, as shown in Table 2.

In the thiophen ring, bond lengths and angles are analogous to the other thiophene fused system found in the literature (Sutherland and Rawas, 1985; Butcher and Hamor, 1985; Mossini et al., 1979).

Of special interest in the molecule is the geometry in ring A and around atoms N3 and S1 because ring A is aromatic and N2 is bonded to N3, there is a positive charge on N2. This charge is neutralized by a negative charge localised on the S1 − C1 − N1 − C10 part which shows bond lengths with values near that a double bond length, especially the S1 − C1 bond.

On the other hand, there is an intramolecular hydrogen bond N3 − H...S1, with mean dimensions in the two independent molecules of: N3 − H31 = 0.89(6), H31...S1 = 2.29(5), N3...S1 = 2.918(5) Å, angle N3 − H31...S1 = 128°.

The crystal packing mainly results from an intermolecular H bond, N3 − H...N1 between molecules (I) and (II) with dimensions: N3 − H32 = 0.85(6), H32...N1 = 2.24(5), N3...N1 = 3.013(5) Å, angle N3 − H32...N1 = 150(5)°.

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