Structural Characterization of a New Schiff-Base Ligand, 1,4-Bis-(5-methyl-4-methylenamino-2,4-dihydro-[1,2,4]triazol-3-thion)-benzene [C₁₄H₁₄N₈S₂·2C₂H₆OS]

Masoumeh TABATABAEE,^{*†} Mitra GHASSEMZADEH,^{**} and Nazanin SOLEIMANI^{*}

^{*}Department of Chemistry, Islamic Azad University Yazd Branch, Yazd, Iran

^{**}Chemistry & Chemical Engineering Research Center of Iran, Tehran, Iran

The title compound, C₁₄H₁₄N₈S₂·2C₂H₆OS, crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 12.866(5), *b* = 8.126(3), *c* = 11.833(4) Å, β = 101.239(9)°, *Z* = 2, *D*_x = 1.409 g cm⁻³. In the solid states, N2-H2A...O1 and C4-H4A...S1 hydrogen bonds link 2 molecules of solvent (Me₂SO) to I.

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During the last few decades, there has been considerable interest in the chemistry of Schiff-base compounds.^{1,2} Schiff bases containing different donor atoms find use in metal coordination.^{3,4} In a sequence of studies, we investigated the synthesis and crystal structure of several Schiff bases: derived 4-amino-5-methyl-2*H*-1,2,4-triazole-3(4*H*)-thione (AMTT) and 4-amino-6-methyl-3-thio-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (AMTTO) and their Ag(I) and Cu(I) complexes.^{4,5} Here, we wish to report on the preparation and characterization of a new Schiff base, based on AMTT.

4-Amino-5-methyl-3-thioxo-2*H*-1,2,4-triazole was prepared according to the literature procedure.³ 1,4-Bis(5-methyl-4-methylenamino-2,4-dihydro[1,2,4]triazol-3-thion) benzene (Fig. 1) was prepared by the following method: A solution of (AMTT) (1.3 g, 10 mmol) in ethanol (20 mL) was treated with terephthalaldehyde (0.81 g, 6 mmol), and the resulting mixture was acidified with 3 drops of hydrochloric acid (37.5%). The reaction mixture was refluxed. The progress of the reaction was monitored by TLC. After completion of the reaction (12 h), the solid crude product was filtered and washed with cold ethanol (5 mL) and recrystallized from dimethyl sulfoxide and ethanol (1:10 ratio), (yield 82%).

Fig. 1 Chemical structure of 1,4-bis(5-methyl-4-methylenamino-2,4-dihydro[1,2,4]triazol-3-thion)benzene.

The crystal structure of 1,4-bis(5-methyl-4-methylenamino-2,4-dihydro[1,2,4]triazol-3-thion)benzene was solved by direct methods and refined by full-matrix least squares on *F*² using the program SHELXTL-V. 6.12.⁶ The H atoms were refined isotropically.

The details of the crystal data and refinement are given in Table 1. The title compound crystallizes in the monoclinic space group *P*2₁/*c*; the molecular structure of 1,4-bis(5-methyl-4-methylenamino-2,4-dihydro[1,2,4]triazol-3-thion)benzene is shown in Fig. 2. There is a center of inversion at the center of the benzene ring. Hydrogen-bonds, N2-H2A...O1, link 2 molecules of solvent (Me₂SO) to title compound. The

Table 1 Crystal and experimental data

Formula	C ₁₈ H ₂₆ N ₈ O ₂ S ₄
Formula weight	514.71
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system, Space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 12.866(5) Å <i>b</i> = 8.126(3) Å <i>c</i> = 11.833(4) Å β = 101.239(9)°
Volume	1213.4(8) Å ³
<i>Z</i> , Calculated density	2, 1.424 Mg/m ³
Absorption coefficient (Mo <i>K</i> _α)	0.424 mm ⁻¹
<i>F</i> (0 0 0)	540
Crystal size	0.24 × 0.16 × 0.04 mm ³
θ range for data collection	3.06 to 26.15°
index range	-15 ≤ <i>h</i> ≤ 15, -10 ≤ <i>k</i> ≤ 10, -14 ≤ <i>l</i> ≤ 14
Reflections collected	10787
Independent reflections	2311 [<i>R</i> _{int} = 0.0833]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2311/0/148
Goodness-of-fit on <i>F</i> ²	1.006
Final <i>R</i> indices [for 1688 reflections with <i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0833, <i>wR</i> 2 = 0.2056
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1115, <i>wR</i> 2 = 0.2225
Largest diff. peak and hole	0.831 and -0.564 e Å ⁻³

[†] To whom correspondence should be addressed.
E-mail: tabatabaee45m@yahoo.com

Fig. 2 ORTEP drawing of the molecule structure of 1,4-bis(5-methyl-4-methylenamino-2,4-dihydro[1,2,4]triazol-3-thion)benzene (thermal ellipsoids drawn at 50% probability).

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1,4-bis(5-methyl-4-methylenamino-2,4-dihydro-[1,2,4]triazol-3-thion) benzene. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$U(\text{eq})$
S(1)	2887(1)	451(2)	5148(1)	28(1)
N(1)	2214(4)	-4230(6)	5032(4)	22(1)
N(2)	2201(4)	-2642(6)	4621(4)	21(1)
N(3)	3082(4)	-2531(6)	6330(4)	17(1)
N(4)	3704(4)	-2215(6)	7408(4)	20(1)
C(1)	2716(5)	-1559(8)	5371(5)	23(1)
C(2)	2769(4)	-4123(7)	6076(5)	19(1)
C(3)	3015(5)	-5503(7)	6903(5)	23(1)
C(4)	3781(4)	-720(7)	7765(5)	18(1)
C(5)	4411(4)	-373(7)	8916(5)	18(1)
C(6)	4503(4)	1256(7)	9297(5)	20(1)
C(7)	4912(4)	-1638(7)	9618(5)	18(1)
S(2)	9847(1)	1258(2)	8245(1)	27(1)
O(1)	8998(4)	2336(7)	7542(4)	40(1)
C(8)	11008(5)	1483(9)	7637(5)	30(1)
C(9)	10295(5)	2390(9)	9523(5)	34(2)

hydrogen-bond parameters are $\text{N}(2)\cdots\text{H}(2\text{A}) = 0.88$, $\text{H}\cdots\text{O}(1) = 1.87$, $\text{N}(2)\cdots\text{O}(1) = 2.730(7)\text{\AA}$ and $\angle(\text{N}(2)\text{H}(2\text{A})\text{O}) = 164^\circ$. Bond lengths and angles are unexceptional. The basic six-membered ring skeleton is planar, while the dihedral angle between the best planes through the six-membered ring and the thiotriazol ring is 4.8° .

Supplementary Material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request (quote the deposition number 674743 for $\text{C}_{18}\text{H}_{26}\text{N}_8\text{O}_2\text{S}_4$).

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