Mengyuan Niu and Caixia Yuan*

Crystal structure of 4-[(5-chloro-2-hydroxybenzylidene)amino]-3-propyl-1*H*-1,2,4-triazole-5(4*H*)-thione, C₁₂H₁₃ClN₄OS

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.35 × 0.28 × 0.25 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.43 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7402, 4814, 0.043
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2550
$N(\text{param})_{\text{refined}}$:	347
Programs:	Bruker [1], SHELX [2, 3]

Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

0.5 mmol (0.079 g) 4-amino-5-propyl-1,2,4-triazole-3-thione was dissolved in 15 ml anhydrous ethanol. To the above solution, an anhydrous ethanol solution (10 ml) of 5-chlorosalicylaldehyde (0.5 mmol, 0.078 g) and 0.04 ml concentrated sulfuric acid was added dropwise, respectively. The mixture was stirred and refluxed at 80 °C for 4 h. The resulting mixture was cooled to room temperature and the pale yellow precipitate was collected by filtration. The precipitate was recrystallized from ethanol, and finally dried in vacuo. Yield 70%. **Elemental analysis** calculated for C₁₂H₁₃ClN₄OS: C 48.56, H 4.42, N 18.88%; found C 48.65, H 4.51, N 19.04%. **IR** (ν/cm^{-1}): 1605($\nu_{\text{C}=\text{N}}$ (imine)), 1584($\nu_{\text{C}=\text{N}}$ (triazole)), 1269($\nu_{\text{C}-\text{O}}$), 1170($\nu_{\text{C}=\text{S}}$). **UV-vis** in DMSO, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$): 259(18,740), 343(8400). **¹H-NMR** (DMSO-*d*₆) 13.77 (1H, NH-triazole), 10.76 (1H, N=CH), 10.31(1H, OH-Ar), 7.84–7.00 (3H, CH-Ar).

Experimental details

All non-H atoms were refined anisotropically using *SHELXTL* and using absorption corrected data. Hydrogen atoms attached to C and N atoms were placed geometrically

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Abstract

C₁₂H₁₃ClN₄OS, triclinic, $P\bar{1}$ (no. 2), $a = 7.875(4)$ Å, $b = 13.165(6)$ Å, $c = 13.295(6)$ Å, $\alpha = 97.199(8)^\circ$, $\beta = 93.065(9)^\circ$, $\gamma = 95.187(8)^\circ$, $V = 1359.0(11)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0638$, $\omega R_{\text{ref}}(F^2) = 0.2097$, $T = 296(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and

*Corresponding author: Caixia Yuan, Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Shanxi University, Taiyuan, Shanxi, 030006, People's Republic of China, E-mail: cxyuan@sxu.edu.cn.
<https://orcid.org/0000-0002-3681-4423>

Mengyuan Niu, Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Shanxi University, Taiyuan, Shanxi, 030006, People's Republic of China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cl1	0.8845 (2)	0.16795 (13)	1.08850 (13)	0.0844 (5)
Cl2	1.0143 (2)	−0.07998 (12)	0.19328 (12)	0.0787 (5)
S1	0.99495 (19)	0.40727 (10)	0.63980 (10)	0.0623 (4)
S2	0.63581 (18)	0.37232 (10)	0.41167 (10)	0.0600 (4)
O1	0.6987 (5)	0.5739 (3)	1.0208 (3)	0.0729 (11)
H1	0.7213	0.5868	0.9639	0.109*
O2	0.6861 (5)	−0.0232 (3)	0.5760 (3)	0.0628 (9)
H2	0.6465	0.0325	0.5850	0.094*
N1	0.8059 (5)	0.5360 (3)	0.8368 (3)	0.0474 (9)
N2	0.8375 (5)	0.5659 (3)	0.7435 (3)	0.0463 (9)
N3	0.9093 (5)	0.5901 (3)	0.5979 (3)	0.0584 (11)
H3A	0.9489	0.5818	0.5387	0.070*
N4	0.8375 (6)	0.6765 (3)	0.6337 (3)	0.0591 (11)
N5	0.6543 (5)	0.1655 (3)	0.5417 (3)	0.0459 (9)
N6	0.5949 (5)	0.2588 (3)	0.5729 (3)	0.0467 (9)
N7	0.5072 (6)	0.4054 (3)	0.5943 (3)	0.0606 (11)
H7A	0.4802	0.4654	0.5843	0.073*
N8	0.4785 (5)	0.3659 (3)	0.6825 (3)	0.0572 (11)
C1	0.8178 (6)	0.4196 (4)	0.9577 (4)	0.0493 (12)
C2	0.7461 (6)	0.4806 (4)	1.0340 (4)	0.0545 (13)
C3	0.7221 (7)	0.4453 (5)	1.1263 (4)	0.0649 (15)
H3	0.6750	0.4865	1.1775	0.078*
C4	0.7667 (7)	0.3506 (5)	1.1432 (4)	0.0641 (15)
H4	0.7509	0.3276	1.2058	0.077*
C5	0.8341 (6)	0.2903 (4)	1.0680 (4)	0.0588 (13)
C6	0.8619 (6)	0.3232 (4)	0.9767 (4)	0.0533 (12)
H6	0.9104	0.2813	0.9268	0.064*
C7	0.8499 (6)	0.4510 (4)	0.8594 (4)	0.0492 (11)
H7	0.9033	0.4085	0.8124	0.059*
C8	0.9137 (6)	0.5199 (4)	0.6605 (4)	0.0504 (12)
C9	0.7946 (6)	0.6599 (4)	0.7228 (4)	0.0502 (12)
C10	0.7059 (6)	0.7302 (3)	0.7926 (4)	0.0526 (12)
H10A	0.7718	0.7454	0.8573	0.063*
H10B	0.5952	0.6967	0.8043	0.063*
C11	0.6815 (7)	0.8297 (4)	0.7501 (4)	0.0636 (14)
H11A	0.7927	0.8641	0.7406	0.076*
H11B	0.6199	0.8140	0.6840	0.076*
C12	0.5856 (9)	0.9016 (5)	0.8176 (5)	0.097 (2)
H12A	0.4769	0.8673	0.8293	0.145*
H12B	0.5682	0.9614	0.7854	0.145*
H12C	0.6504	0.9219	0.8813	0.145*
C13	0.7791 (6)	0.0478 (3)	0.4283 (4)	0.0468 (11)
C14	0.7605 (6)	−0.0321 (4)	0.4877 (4)	0.0483 (11)
C15	0.8203 (6)	−0.1254 (4)	0.4552 (4)	0.0590 (13)
H15	0.8074	−0.1791	0.4943	0.071*
C16	0.8985 (6)	−0.1390 (4)	0.3654 (4)	0.0592 (14)
H16	0.9393	−0.2018	0.3442	0.071*
C17	0.9168 (6)	−0.0609 (4)	0.3072 (4)	0.0568 (13)
C18	0.8584 (6)	0.0315 (4)	0.3375 (4)	0.0539 (12)
H18	0.8716	0.0842	0.2971	0.065*
C19	0.7224 (6)	0.1484 (4)	0.4588 (4)	0.0491 (12)
H19	0.7364	0.1999	0.4171	0.059*
C20	0.5801 (6)	0.3448 (3)	0.5245 (4)	0.0510 (12)
C21	0.5320 (6)	0.2756 (4)	0.6669 (4)	0.0485 (11)
C22	0.5277 (7)	0.2002 (4)	0.7403 (4)	0.0551 (13)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H22A	0.6437	0.1869	0.7590	0.066*
H22B	0.4668	0.1359	0.7084	0.066*
C23	0.4418 (7)	0.2377 (4)	0.8353 (4)	0.0615 (14)
H23A	0.5029	0.3019	0.8672	0.074*
H23B	0.3261	0.2512	0.8164	0.074*
C24	0.4362 (8)	0.1611 (5)	0.9107 (4)	0.0798 (17)
H24A	0.3768	0.0971	0.8794	0.120*
H24B	0.3777	0.1872	0.9685	0.120*
H24C	0.5506	0.1501	0.9323	0.120*

and refined using a riding model approximation, with C–H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Hydrogen atoms attached to O atoms were located from difference Fourier maps and refined using their global U_{iso} value.

Comment

Compounds containing the triazole heterocyclic structure have drawn attention owing to their application in the broad range of areas including materials, biomaterials, metallopharmaceuticals, supramolecular chemistry, chemical sensing and catalysis etc. [4, 5]. Moreover, triazoles are also key synthons for the syntheses of the polydentate chelate reagents. The incorporation of the 1,2,4-triazole unit into Schiff base rings is of considerable current interest [6]. Recently, such compounds have been employed as models for biological systems because of their unique properties [7–9]. In coordination chemistry substituted Schiff bases bearing additional donor groups represent the most important class of heteropolydentate ligands capable of forming mono-, bi-, and polynuclear complexes [10].

The title compound C₁₂H₁₃ClN₄OS, is a Schiff base obtained by condensation between 5-chlorosalicylaldehyde and 3-propyl-1*H*-1,2,4-triazole-5(4*H*)-thione. In the two crystallographically independent molecules (see the figure), the dihedral angles between the triazole and the phenyl moiety in each molecule are 7.33 and 3.08°, exhibiting the coplanar features. This twist similar to that of the reported compound 4-[(5-bromo-2-hydroxybenzylidene)amino]-3-propyl-1*H*-1,2,4-triazole-5(4*H*)-thione [11], while it is different from that of the reported 4-[(5-chloro-2-hydroxybenzylidene)amino]-3-ethyl-1*H*-1,2,4-triazole-5(4*H*)-thione in which the dihedral angles between the triazol rings relative to the phenyl ring planes are 54.6 and 56.0° [12]. The structure shows that the alkyl chain length at

the triazole ring can influence on the distortion degree of the Schiff base compounds. In the crystal structure, the bond length of the N1=C7, N4=C9, N2=C8, N3=C8 are 1.268 (6) Å, 1.288 (6) Å, 1.383 (6) Å and 1.321 (6) Å, respectively, indicating significant double bond character [12, 13]. The bond length of the C=S (1.659 (5) Å) in the compound is close to the C=S double bond (1.646 Å) [14], which indicates that the compound exists in the thione form. In addition, the crystal structure is stabilized by intermolecular N–H⋯S hydrogen bonds and intramolecular O–H⋯N hydrogen bonds. Moreover, the intermolecular hydrogen bonds link the molecules into a two-dimensional network.

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