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STRUCTURE OF ORGANIC COMPOUNDS

Crystal Structure of 4-[(Benzylidene-amino)]-2-(2-oxo-2-phenyl-ethyl)-5-thiophen-2-ylmethyl-2,4-dihydro-[1,2,4]triazol-3-one[1]

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Abstract—The molecular structure of the title compound $C_{22}H_{18}N_4O_2S$ was characterized by single crystal X-ray diffraction method. The compound crystallizes in the orthorhombic space group *Pbca* with $a = 10.1970$ (4) Å, $b = 26.8880$ (5) Å, $c = 15.2119$ (13) Å, $Z = 8$, $V = 4170.8$ (4) Å^3. In the title compound, benzyl rings and thiophene ring are bridged by 1,2,4-triazole ring system. The thiophene ring is disordered over two positions, which are approximately parallel and oppositely orientated. The major component refined to a site-occupancy factor of 0.731 (3). An intramolecular C—H···O hydrogen bond generates an S(6) ring motif. In the crystal, a C—H···O hydrogen bond links the molecules into a C(6) chain along the c axis. A weak C—H···π interaction also occurs.

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INTODUCTION

The chemistry and structure of heterocyclic compounds has been an interesting field of study for a long time. The synthesis of 1,2,4-triazoles and investigation of their chemical and biological behavior have gained more importance in recent decades for biological, medicinal and agricultural reasons [1]. 1,2,4-Triazole containing compounds have been shown to exhibit a variety of interesting biological actions, including antibacterial [2], anticonvulsant [3], antimicrobial [4,5], anticancer [6], antitubercular [7] and antifungal [8,9] activities. 1,2,4-triazole compounds containing Schiff base have attracted great and growing interest in chemistry and biology for many years due to their facile synthesis and wide applications [9].

Schiff bases (known as azomethines), i.e., compounds having a double C=N bond, are used as starting materials in the synthesis of important drugs, such as antibiotics and antiallergic, antiphlogistic, and antitumor substances [10–12]. On the industrial scale, they have a wide range of applications, such as dyes and pigments [13]. Schiff base complexes have been playing an important role in the development of coordination chemistry related to catalysis and enzymatic reactions [14–18], magnetism and molecular architectures [19–21].

EXPERIMENTAL

Synthesis. The title compound (Fig. 1), $C_{22}H_{18}N_4O_2S$, was synthesized by published method [22].

X-ray diffraction study. A yellow coloured prism-shaped crystal sample with dimensions of 0.16 × 0.33 × 0.63 mm was chosen for the crystallographic study. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated MoK_α radiation on a STOE IPDS II diffractometer. The systematic absences and intensity symmetries indicated the orthorhombic *Pbca* space group. A total of 22686 reflection (3667 unique) within the θ range of (2° < θ < 25°) were collected in the *w* scan mode and cell parameters were determined by using X-AREA software [23]. Absorption correction ($\mu = 0.18$ mm^{-1}) by integration method via X–RED32 software [23]. The structure was solved by direct methods using SHELXS97 [24]. The molecular graphics were done using ORTEP-3 [25]. All non-hydrogen atoms were refined anisotropically. The refinement was carried

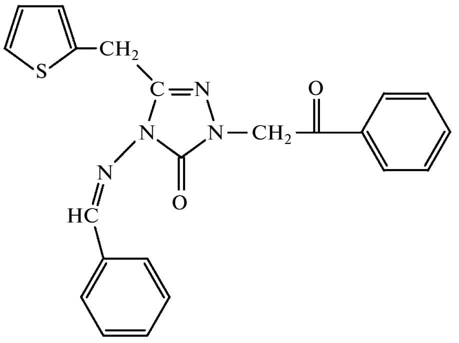

Fig. 1. Chemical diagram of 4-[(Benzylidene-amino)]-2-(2-oxo-2-phenyl-ethyl)-5-thiophen-2-ylmethyl-2,4-dihydro-[1,2,4]triazol-3-one.

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[1] The article is published in the original.

Table 1. Crystallographic characteristics and the X-ray data collection and structure-refinement parameters for $C_{22}H_{18}N_4O_2S$

System, sp. gr., Z	Orthorhombic, $Pbca$, 8
a, b, c, Å	10.1970(4), 26.8880(5), 15.2119(13)
α, β, γ, deg	90, 90, 90
V, Å^3	4170.8 (4)
D_x, g/cm^3	1.282
Radiation, λ, Å	MoK_α, 0.71073
μ, mm^{-1}	0.18
T, K	296
Sample size, mm	0.16 × 0.33 × 0.63
Diffractometer	STOE IPDS II
Scan mode	φ- and ω-scans
Absorption correction, $T_{\min}$, $T_{\max}$	0.9375, 0.9740
$\theta_{\max}$, deg	25
h, k, l ranges	$-12 \le h \le 12$, $-31 \le k \le 27$, $-18 \le l \le 18$
Number of reflections: measured/unique ($N1$), R_{int}/with $I > 2\sigma(I)$ ($N2$)	22686/3667, 0.053/1963
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	271
Reliability factors:	
$wR2$ relative to $N1$	0.090
$R1$ relative to $N2$	0.037
S	0.83
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e/Å^3	0.16/–0.30
Programs	X-AREA [23], X-RED32 [23], SHELXS97 [24], SHELXL97 [24], ORTEP-3 [25].

out using the full matrix least squares method on the positional and anisotropic temperature parameters of non-hydrogen atoms corresponding to 271 crystallographic parameters. All the H atoms were located geometrically and refined using a riding model fixing the bond lengths at 0.93 and 0.97 Å for CH and CH_2, respectively. The flip-type disorder means that in their alternative positions, the different types of atoms (in this case sulfur and carbon) occupy positions that are close to each other, which influences their U_{ij} values. The disordered atoms of the thiophene ring were refined using the following restraints: SIMU, DELU, FLAT and SADI [24]. Details of the data collection conditions and the parameters of the refinement process are given in Table 1.

Crystallographic data for the structural analysis have been deposited with Cambridge Crystallographic Data Centre, CCDC reference number 947829 Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB12 1EZ, UK. (Fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The molecular structure of the title compound is shown in Fig. 2. In the title compound, benzyl rings and thiophene ring are bridged by 1,2,4-triazole ring system in axial and equatorial positions, respectively. The minimum dihedral angle is shown between the benzyl (C12/C17) and 1,2,4-triazole (N1/C1) ring system, 20.05(1)°, while benzyl (C12/C17) and thiophene (C20/S1) rings are nearly perpendicular to the each other with the 87.90(1)° value. The torsion angles, (N1–C3–C4–C5) and (N3–N4–C11–C12) are 163.1(2)° and 178.4(2)°, shows that for the title compound, the side chain conformation induced by anti-conformations, respectively. Within the molecule of the title compound, a flip-disorder of the thiophene

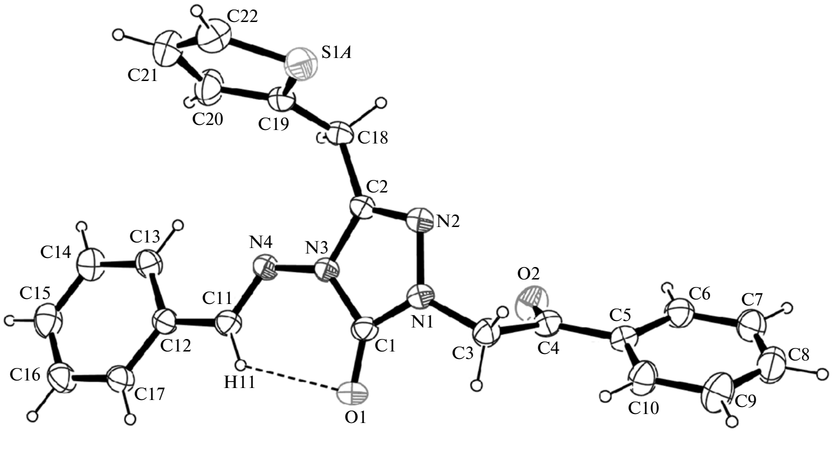

Fig. 2. An ORTEP-3 drawing of the title compound, with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as spheres of arbitrary radius. H bond is drawn as dashed lines.

Table 2. Selected molecular structure parameters (Å, deg)

Bond	Distance	Bond Angles		Torsion Angles	
O1—C1	1.217(3)	C1—N1—N2	113.0(2)	C2—N3—C1—O1	−176.5(3)
O2—C4	1.212(3)	C1—N1—C3	125.5(2)	N4—N3—C1—O1	−0.8(4)
N1—C1	1.356(3)	N2—N1—C3	119.2(2)	N3—N4—C11—C12	178.4(2)
N1—N2	1.390(3)	C2—N2—N1	104.7(2)	C2—C18—C19—C20*A*	−108.7(2)
N1—C3	1.434(3)	C2—N3—N4	120.6(2)	C2—C18—C19—C20*B*	71.6(3)
N2—C2	1.293(3)	C2—N3—C1	108.7(2)	C2—C18—C19—S1*B*	−110.1(3)
N3—C2	1.374(3)	N4—N3—C1	130.6(2)	C2—C18—C19—S1*A*	73.0(3)
N3—N4	1.384(3)	C11—N4—N3	118.1(2)	N4—N3—C2—C18	1.6(4)
N3—C1	1.395(3)	O1—C1—N1	129.0(2)	N4—C11—C12—C13	5.7(4)
N4—C11	1.274(3)	O1—C1—N3	128.7(3)	N4—C11—C12—C17	−173.2(3)
C19—C20*A*	1.387(7)	N1—C1—N3	102.3(2)		
C19—C20*B*	1.397(8)	N2—C2—N3	111.1(2)		
C19—S1*B*	1.659(4)	N2—C2—C18	124.5(2)		
C19—S1*A*	1.689(3)	N3—C2—C18	124.4(3)		
S1*A*—C22	1.643(4)	N1—C3—C4	111.5(2)		
C20*A*—C21	1.448(8)	O2—C4—C5	121.9(3)		
S1*B*—C21	1.626(5)	O2—C4—C3	119.7(3)		
C20*B*—C22	1.473(9)	C20*B*—C19—S1*B*	110.6(4)		
C21—C22	1.321(5)	C18—C19—S1*B*	119.9(2)		
		C20*A*—C19—S1*A*	110.2(3)		
		C18—C19—S1*A*	120.75(18)		
		S1*B*—C19—S1*A*	119.3(3)		
		C22—S1*A*—C19	91.53(17)		
		C21—S1*B*—C19	91.8(2)		
		C22—C21—S1*B*	119.6(2)		
		C21—C22—S1*A*	117.7(2)		

ring containing S1 is observed. There are two positions of the thiophene ring, rotated by *ca* 180° about the single C18—C19 bond. These two orientations are not equivalent; the site-occupation factors refined to 0.731(3) and 0.269(3).

The some selected bond lengths, bond angles and torsion angles are given in Table 2. In the title molecule, the bond lengths and angles are within normal ranges and they are comparable with those related structure [26–28]. Title compound containing the triazole ring display the characteristic features of 1,2,4-triazole derivatives. The interatomic distances within the five-membered triazole cycle are not equal. The C2—N2 is double bond and shorter than the conjugated C2—N3, C1—N1 and C1—N3 bonds. The C—N bond distances in the triazole ring are comparable with those found in related structures [29, 30]. The length of the azomethine C11 = N4 double bond is 1.274(3) Å, which is slightly shorter than standard 1.28 Å, but it is consistent with related structures [31, 32]. The imino group is syn-periplanar with the triazole ring as can be shown by the C1—N3—N4—C11 torsion angle of 17.4(4)°.

Table 3. Hydrogen-bond geometry (Å, deg)

D—H···*A*^{a}	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O1	0.93	2.28	2.934(3)	127
C3—H3*B*···O1^{i}	0.97	2.40	3.235(4)	143
C8—H8···Cg1^{ii}	0.93	2.78	3.702	173

^{a} Symmetry code: (i) $x - 1/2, y, -z + 1/2$, (ii) $1/2 - x, 1/2 + y, z$.

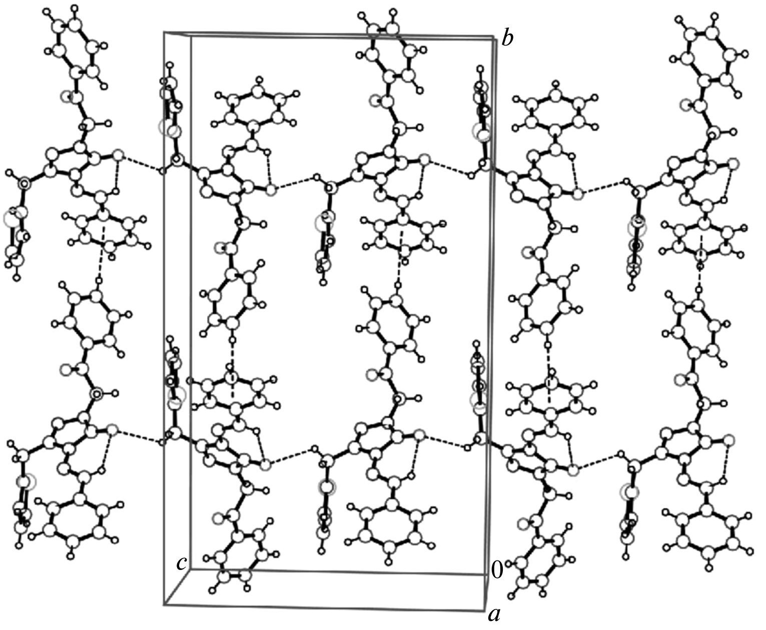

Fig. 3. Packing diagram of the title compound.

The crystal structure is stabilized by C–H···O type intra and intermolecular hydrogen bonds. An intramolecular hydrogen bond C11–H11···O1, forming rings with the graph set S(6) [33] (Fig. 2). In the crystal structure, C3–H3B···O1 (symmetry code: $x - 1/2$, y, $-z + 1/2$) hydrogen bond links the molecules into a C(6) [33] chain along the c axis. The crystal structure is further stabilized by an intermolecular C–H···π stacking interaction (C8–H8···*Cg*1 with symmetry code: $1/2 - x$, $1/2 + y$, z; the *Cg*1 ring is consistent with C12–C17). The details of the hydrogen bonds are summarized in Table 2. A packing diagram of the title compound is shown in Fig. 3.

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