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Structural study of 6-methyl-4-(thiophen-2yl-methylene-amino)-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one

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ABSTRACT

The title compound was synthesized from the reaction of 4-amino-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)- one (TAMTTO) with thiophene-2-carbaldehyde. The crystal structure was determined by single-crystal X-ray diffraction. This compound is monoclinic C2/c with the following unit-cell parameters: a = 23.135(6)Å, b = 6.1108(13)Å, c = 16.378(4)Å, β = 106.805(3)°, Z = 8 and V = 2216.53 Å^3. The final R value was 0.0266 for 2246 measured reflections. The triazine and thiophene ring exhibit 60.02º deviation. The inter- and intramolecular interactions give rise to a 3D-network.

KEYWORDS

Triazin;
Crystal structure;
3D-network.

INTRODUCTION

The 1,2,4-triazine and its derivatives have been numerous investigated, due to their applications as starting materials for many products. 4-amino-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-ones (TAMTTO) derivatives have been widely studied and have great potential biological activity[1]. Schiff bases based on triazine have received considerable attention since, because of their pharmacological properties; they have numerous applications, for example as antibacterial and anticancer agents[2].

In our ongoing interest in the synthesis of triazine compounds[3-6], we reported the synthesis and crystal structure study of TAMTTO Schiff base.

EXPERIMENTAL

Synthesis and structure of the titled compound

The compound **(1)** was prepared according to following method. 4-amino-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5 (2H)-one (0.16 g, 1 mmol) in absolute ethanol (15 ml) was added to an equimolar quantity of thiophene-2-carbaldehyde (0.11 g, 1 mmol) and 1 ml sulfuric acid in the same solvent (25 ml). The mixture was refluxed for 1h. Yellow precipitate was formed after cooling and then filtered, washed with cold ethanol and dried in vacuo over silicagel (yield 93%). Yellow single crystals of compound, suitable for X-ray analysis, were obtained by slow evaporation of an ethanol solution after a day.

X-ray crystallography

Crystals of TAMTTO were grown from ethanol. The crystal data and the parameters for data collection, structure determination, and refinement are summarized in TABLE 1. The absorption was performed empirically from an equivalent by means of the SADABs program[7]. Diffraction data were collected on a Rigaku/MSC Mercury CCD diffractometer and calculations

were performed using the SHELXL97 program[8]. The structures were solved by direct methods followed by full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and all hydrogen atoms isotropic. Reflection data with $|I| > 2.0\sigma(I)$ were used. The molecular structure and crystal packing diagram of this complex are shown in Figures 1 and 2, respectively.

TABLE 1 : Crystal and experimental data

Formula	$C_9H_8N_4OS_2$
Formula weight	252.31
Space group	C2/c
Crystal system	monoclinic
Z	8
a	23.135(6) Å
b	6.1108(13) Å
c	16.378(4) Å
β	106.805(3)°
V	2216.5(9)Å^3
Temperature	113(2) K
D_x	1.512 Mg/m^3
Absorption coefficient	0.46 mm^{-1}
F(000)	1040
Crystal dimensions	0.20×0.20×0.20 mm^3
R	0.0266
Rw	0.067
range for data collection	3.5 to 27.5°
Goodness-of-fit	1.046
$(\Delta/\rho)_{max}$	0.002
$(\Delta\rho)_{max}$	0.37 eÅ^{-3}
$(\Delta\rho)_{min}$	–0.22 eÅ^{-3}
No. of reflections collected	2246
No. of parameters 151	151
Measurement	Bruker APEX-II CCD area detector
Program system	APEX2 and SAINT
Structural determination	direct method
Refinement	full-matrix least-square of F^2

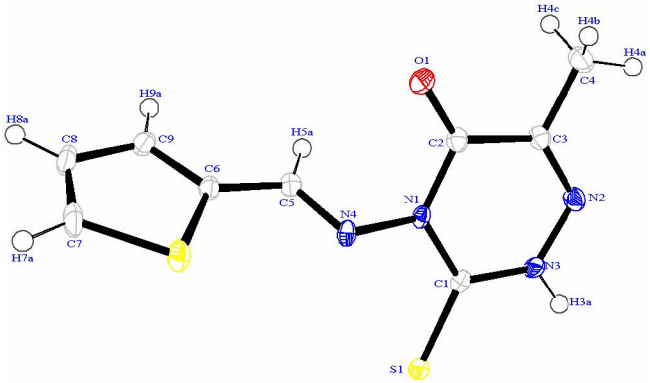


Figure 1 : Molecular structure of (TAMTTO) showing the atom numbering scheme and displacement ellipsoids drawn at the 50% probability level.

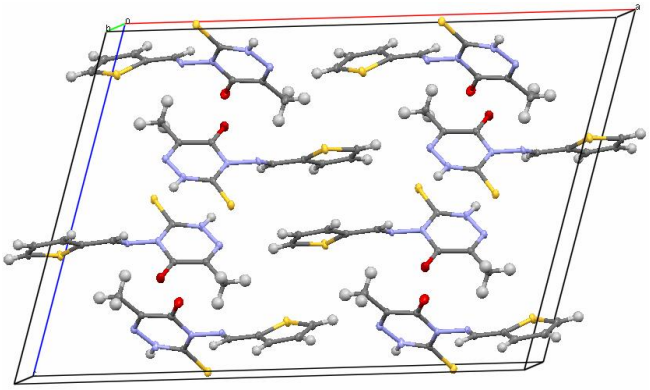


Figure 2 : Unit-cell packing diagram of (TAMTTO).

RESULTS AND DISCUSSION

The triazine ring bond distances and angles are different. The triazine ring is planar, with a maximum deviation from the least-squares plane of 0.013 Å for C2. In this compound the three substituent groups are pla-

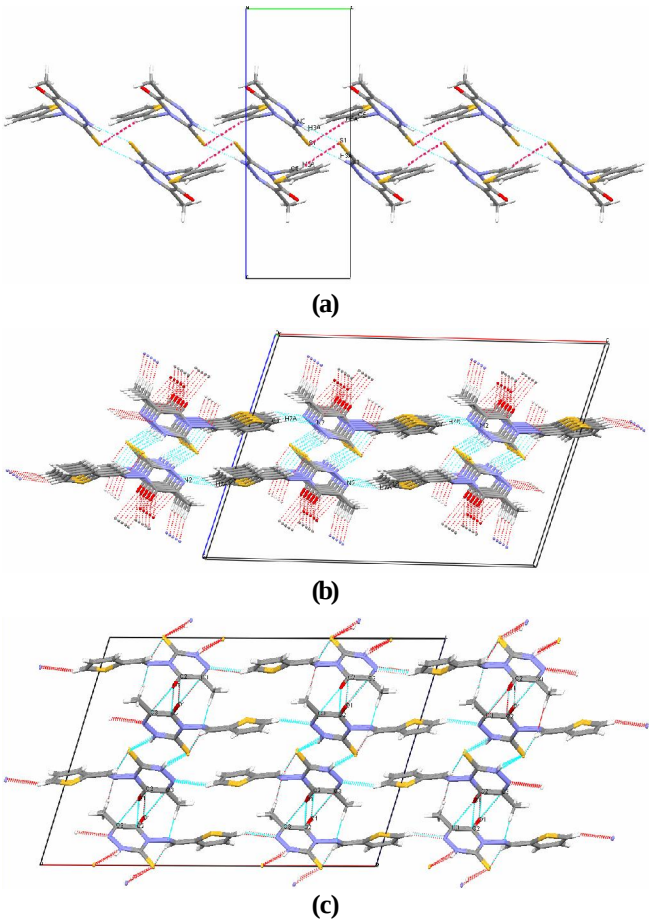
TABLE 2 : Selected bond distance (Å), bond angels (°)

S1-C1	1.6759(16)	N3-C1-N1	115.07(13)
C1-N3	1.3465(19)	N3-C1-S1	121.60(12)
C1-N1	1.3738(19)	N1-C1-S1	123.30(11)
N1-C2	1.411(2)	C1-N1-C2	123.19(12)
N1-N4	1.4209(16)	C1-N1-N4	115.78(12)
C2-O1	1.2107(19)	C2-N1-N4	119.34(11)
C2-C3	1.477(2)	O1-C2-N1	122.29(13)
C3-N2	1.289(2)	O1-C2-C3	123.79(14)
C3-C4	1.490(2)	N1-C2-C3	113.92(13)
N2-N3	1.3611(18)	N2-C3-C2	123.14(14)
N4-C5	1.282(2)	N2-C3-C4	119.46(13)
C5-C6	1.4437(19)	C2-C3-C4	117.40(14)
C6-C9	1.375(2)	C3-N2-N3	117.14(12)
C6-S2	1.7270(16)	C1-N3-N2	127.48(13)
S2-C7	1.7153(16)	C5-N4-N1	113.59(12)
C7-C8	1.361(3)	N4-C5-C6	120.06(14)
C8-C9	1.418(2)	C9-C6-C5	125.85(14)
		C9-C6-S2	111.71(11)
		C5-C6-S2	122.45(12)
		C7-S2-C6	91.07(8)
		C8-C7-S2	112.63(12)
		C7-C8-C9	112.35(14)
		C6-C9-C8	112.25(15)

nar with maximum deviations from the mean plane of triazine ring for atom S1 (0.042 Å). The N2=C3 and N4=C5 bond length of 1.289(2) Å and 1.282(2) Å agreement to the value for a double bond, respectively. The distance value 1.210(2) Å and 1.677(2) Å show that C2=O1 and C1=S1 have double bond characterization, respectively.

TABLE 2 shows the selected bond distances bond angels of Schiff base.

In the crystal structure, two molecules are linked each other by intermolecular N3-H3A···S1 hydrogen interactions to form dimer. These dimers are jointed with C5-H5A···S1 hydrogen bonds to creation one dimension chain along *a* axes (Figure 3a). The N2···H7A-C7 interactions result in attachment of one-dimensional chains to each other in *ac* plane and subsequently in formation of two-dimensional layer (Figure 3b). Finally, intermolecular interactions of C2···O1 and C3···O1 will complete the three-dimension network of crystal (Figure 3c).



(a)

(b)

(c)

Figure 3 : 1D (a), 2D(b) and 3D(c) grown of (TAMTTO) in lattice.

ACKNOWLEDGEMENTS

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SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 742945. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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