

NEW DIFFRACTION DATA

Structure elucidation of 3-[1-(6-methoxy-2-naphtyl)ethyl]-6-(2,4-dichlorophenyl)-7H-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazine, C₂₃H₁₈Cl₂N₄OS from synchrotron X-ray powder diffraction

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The 3-[1-(6-methoxy-2-naphtyl)ethyl]-6-(2,4-dichlorophenyl)-7H-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazine, C₂₃H₁₈Cl₂N₄OS compound was synthesized, as a member of the family of novel potential anticancer agents. The structure of the title compound was characterized by IR, ¹H-NMR, mass spectroscopy, and elemental analysis, previously. In this study, the crystal structure of this compound has been determined from synchrotron X-ray powder diffraction data. The crystal structure was solved by simulated annealing and the final structure was achieved by Rietveld refinement method using soft restrains on all interatomic bond lengths and angles. This compound crystallizes in space group *P*21, *Z*=2, with the unit-cell parameters *a* = 15.55645(11) Å, *b* = 8.61693(6) Å, *c* = 8.56702(6) Å, β = 104.3270(4)°, and *V* = 1112.68(1) Å³. In the crystal structure, strong C–H⋯π and weak intermolecular hydrogen-bonding interactions link the molecules into a three-dimensional network. The molecules are in a head-to-head arrangement in the unit cell. © 2017 International Centre for Diffraction Data. [doi:10.1017/S0885715617001099]

Key words: 1,2,4-triazolo[3,4-b]-1,3,4 thiadiazine derivative, synchrotron X-ray powder diffraction, Rietveld refinement, crystal structure

I. INTRODUCTION

Because of severe side effects, selectivity problems and resistance development potential of drugs used in cancer chemotherapy, the discovery of new drugs in this area is still a major topic. In recent years, combined anticancer therapies or multi-acting drugs are clinically preferred over the traditional cytotoxic treatment, with the aim of avoiding resistance and toxic side effects. The arrangement of multi-acting targets can be carried out either by the combination of several drugs with different mechanisms or by the usage of a single chemical compound capable of regulating several targets of a disease with multiple factors. The emergence of this information has greatly increased the interest in the discovery of new compounds addressing multiple biological targets.

There are many studies reporting the anticancer and cancer chemopreventive effects of conventional non-steroidal analgesic anti-inflammatory drugs (NSAIDs) and selective COX-2 inhibitors (Amir and Agarwal, 2005; Guadagni *et al.*, 2007; Cuzick *et al.*, 2009; Gupta *et al.*, 2013). It is also well documented that 1,2,4-triazole is one of the important core fragments that is incorporated in many anticancer agents. In recent years, a number of condensed 1,2,4-triazole derivatives such as triazolothiadiazole, triazolopyridazine, triazolotriazine, and triazolothiadiazine have attracted attention because of their cytotoxic effects (Zhang *et al.*, 2005;

Lauffer *et al.*, 2007, 2010; Lesyk *et al.*, 2007; Albrecht *et al.*, 2008; Bhat *et al.*, 2009; Boezio *et al.*, 2009; Ibrahim, 2009; Khan *et al.*, 2014b). Developing new compounds by combining several active groups into a single molecule can enhance the efficiency of the compounds compared with single-target drugs because of modulate multiple cellular pathways. In the light of this knowledge, in an earlier study, novel condensed triazol derivatives with the structure of triazolothiadiazine having structural motifs of NSAIDs were synthesized and investigated for their bioactivity against epithelial cancer cells (Aytaç *et al.*, 2016). The results we obtained in that study showed that these novel hybrid compounds can be good candidates for the treatment of epithelial cancers particularly liver cancer. The title compound is one of the members of this series having cytotoxic activity.

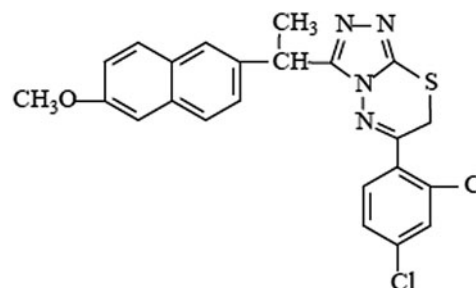


Figure 1. The structural formula of the title compound in the two-dimensional structure form.

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The authors present here the crystal structure of 3-[1-(6-methoxy-2-naphtyl)ethyl]-6-(2,4-dichlorophenyl)-7H-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazine (Figure 1) determined by synchrotron powder X-ray diffraction (XRD) analysis.

II. EXPERIMENTAL

A. Synthesis and crystallization

The synthesis of the title compound was carried out simply by refluxing equimolar amounts of 4-amino-3-[1-(6-methoxy-2-naphtyl)ethyl]-1,2,4-triazole-5-thione and 2,4-dichlorophenacyl chloride in ethanol. The required starting compound was obtained by the reaction of naproxen with thiocarbonylhydrazide by employing previously reported procedure (Aytaç *et al.*, 2016). The chemical composition of the compound was confirmed by spectral and elementary analysis, all results were given previously (Aytaç *et al.*, 2016).

B. XRD data collection

This compound has a tendency to crystallize as a very fine powder. No crystal of sufficient thickness and quality could be obtained to perform a single-crystal analysis, so the crystal structure determination was done by powder XRD.

First, a Bruker D8 Advance X-ray diffractometer with Mo-anode was used to collect the data. Strong peak overlap was observed in the powder pattern because of the instrumental broadening. The powder pattern was indexed successfully, but structure solution could not be obtained. The peak overlap

limits the reliability of intensity information. Then a high-resolution synchrotron measurement of the title compound was done at the beamline 11-BM at the Argonne National Laboratory using the mail-in program. This beamline has a unique multi-analyzer detection assembly, consisting of 12 independent Si (111) crystal analyzers and LaCl₃ scintillation detectors. The powder sample was contained in a 0.8 mm diameter kapton capillary and spun at 60 Hz during data collection. Powder XRD data were collected from 0.5 to 50° 2θ range with a step size of 0.001° at room temperature (295.0 K) with a wavelength of 0.459169 Å.

C. Indexing

The synchrotron powder XRD pattern of the title compound was indexed using the program TOPAS 4.2 (Coelho, 2009) giving the following unit cell with monoclinic metric symmetry *P*2₁; *a* = 15.557 Å, *b* = 8.616 Å, *c* = 8.566 Å, β = 104.3°, *V* = 1112.7 Å³ (Gof = 159.04). The synchrotron powder pattern was also indexed with the programs McMaille (Le Bail, 2004), DICVOL (Boultif and Louer, 1991), ITO (Visser, 1969), and NTREOR (Altomare *et al.*, 2000) in EXPO (Altomare *et al.*, 2013). The similar monoclinic cell was found with *a* = 15.560 Å, *b* = 8.617 Å, *c* = 8.569 Å, β = 104.3°, *V* = 1113.5 Å³ (*M*_N = 51.3, *F*_N = 576.0) by DICVOL; *a* = 15.559 Å, *b* = 8.617 Å, *c* = 8.567 Å, β = 104.3°, *V* = 1112.9 Å³ (FOM = 101.7) by ITO; *a* = 15.554 Å, *b* = 8.618 Å, *c* = 8.566 Å, β = 104.3°, *V* = 1112.6 Å³ (FOM = 391.76) by McMaille; and *a* = 15.556 Å, *b* = 8.616 Å, *c* = 8.568 Å, β = 104.3°, *V* = 1112.8 Å³ (*M*₂₀ = 176) by NTREOR.

TABLE I. X-ray powder pattern of the title compound [*P*2₁, *Z* = 2], *a* = 15.55617(10) Å, *b* = 8.61683(6) Å, *c* = 8.56690(5) Å, β = 104.32732(41)°, and *V* = 1112.633(13) Å³.

2θ _{obs} (°)	<i>d</i> _{obs} (Å)	<i>I</i> _{obs}	<i>h</i>	<i>k</i>	<i>L</i>	<i>M</i>	2θ _{cal} (°)	<i>d</i> _{cal} (Å)	Δ2θ (°)
1.7449	15.0777	413	1	0	0	2	1.7455	15.0723	-0.0006
3.1694	8.3019	388	0	0	1	2	3.1699	8.3005	-0.0005
3.2173	8.1783	117	-1	0	1	2	3.2183	8.1758	-0.0010
3.4910	7.5372	251	2	0	0	2	3.4915	7.5362	-0.0005
3.5168	7.4819	558	1	1	0	4	3.5174	7.4806	-0.0006
3.9794	6.6125	41	1	0	1	2	3.9796	6.6122	-0.0002
4.4366	5.9313	443	-1	1	1	4	4.4369	5.9310	-0.0003
4.6386	5.6732	199	2	1	0	4	4.6390	5.6727	-0.0004
5.1082	5.1520	652	-2	1	1	4	5.1084	5.1518	-0.0002
5.2658	4.9979	184	2	0	1	2	5.2658	4.9979	0.0000
5.4102	4.8646	27	-3	0	1	2	5.4105	4.8643	-0.0003
6.0644	4.3402	122	3	1	0	4	6.0643	4.3402	0.0001
6.1086	4.3088	179	0	2	0	2	6.1092	4.3084	-0.0006
6.1480	4.2812	35	-1	0	2	2	6.1474	4.2817	0.0006
6.2140	4.2358	430	-3	1	1	4	6.2138	4.2359	0.0002
6.3439	4.1492	205	0	0	2	2	6.3423	4.1502	0.0016
6.3538	4.1427	442	1	2	0	4	6.3541	4.1425	-0.0003
6.4387	4.0881	31	-2	0	2	2	6.4391	4.0879	-0.0004
6.8648	3.8347	1000	-1	1	2	4	6.8653	3.8344	-0.0005
6.8836	3.8242	61	0	2	1	4	6.8840	3.8240	-0.0004
6.9076	3.8109	78	-1	2	1	4	6.9064	3.8116	0.0012
6.9220	3.8030	267	-4	0	1	2	6.9209	3.8036	0.0011
6.9857	3.7684	41	4	0	0	2	6.9862	3.7681	-0.0005
7.0387	3.7401	156	2	2	0	4	7.0382	3.7403	0.0005
7.0406	3.7390	632	0	1	2	4	7.0404	3.7391	0.0002
7.1283	3.6931	165	-2	1	2	4	7.1278	3.6934	0.0005
7.1579	3.6779	62	-3	0	2	2	7.1583	3.6776	-0.0004

Continued

TABLE I. Continued

$2\theta_{\text{obs}}$ (°)	d_{obs} (Å)	I_{obs}	h	k	L	M	$2\theta_{\text{cal}}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
7.2922	3.6102	86	1	2	1	4	7.2931	3.6098	-0.0009
7.4209	3.5477	160	3	1	1	4	7.4215	3.5474	-0.0006
7.5653	3.4801	63	-4	1	1	4	7.5661	3.4797	-0.0008
7.6245	3.4531	74	1	1	2	4	7.6232	3.4536	0.0013
7.6264	3.4522	131	4	1	0	4	7.6259	3.4524	0.0005
7.7837	3.3825	226	-3	1	2	4	7.7840	3.3824	-0.0003
7.9643	3.3059	30	2	0	2	2	7.9640	3.3061	0.0003
8.0511	3.2704	94	3	2	0	4	8.0507	3.2705	0.0004
8.1637	3.2253	194	-3	2	1	4	8.1640	3.2252	-0.0003
8.1949	3.2131	38	-4	0	2	2	8.1939	3.2135	0.0010
8.5237	3.0894	26	-5	0	1	2	8.5239	3.0893	-0.0002
8.6702	3.0373	140	-1	2	2	4	8.6709	3.0370	-0.0007
8.7361	3.0144	82	5	0	0	2	8.7358	3.0145	0.0003
8.7435	3.0118	20	-4	1	2	4	8.7462	3.0109	-0.0027
8.8102	2.9891	115	0	2	2	4	8.8104	2.9890	-0.0002
8.8802	2.9656	44	-2	2	2	4	8.8805	2.9655	-0.0003
8.9002	2.9589	86	4	1	1	4	8.9009	2.9587	-0.0007
9.0566	2.9079	48	-5	1	1	4	9.0562	2.9080	0.0004
9.1172	2.8886	23	3	2	1	4	9.1182	2.8883	-0.0010
9.2425	2.8495	53	-1	0	3	2	9.2429	2.8494	-0.0004
9.3344	2.8216	44	1	3	0	4	9.3346	2.8215	-0.0002
9.6676	2.7245	27	-3	0	3	2	9.6650	2.7253	0.0026
9.7042	2.7143	18	0	3	1	4	9.7039	2.7144	0.0003
9.7364	2.7053	25	-1	1	3	4	9.7363	2.7054	0.0001
9.7857	2.6917	23	-2	1	3	4	9.7839	2.6922	0.0018
9.8140	2.6840	35	2	3	0	4	9.8141	2.6840	-0.0001
9.9267	2.6536	56	-5	1	2	4	9.9266	2.6536	0.0001
10.0422	2.6231	40	2	2	2	4	10.0433	2.6229	-0.0011
10.0462	2.6221	22	-2	3	1	4	10.0454	2.6223	0.0008
10.1377	2.5985	64	-3	1	3	4	10.1380	2.5984	-0.0003
10.1780	2.5882	19	-6	0	1	2	10.1770	2.5885	0.0010
10.4663	2.5171	26	5	1	1	4	10.4656	2.5173	0.0007
10.4920	2.5110	49	-5	2	1	4	10.4937	2.5106	-0.0017
10.5520	2.4968	20	1	1	3	4	10.5503	2.4971	0.0017
10.5674	2.4931	23	3	3	0	4	10.5656	2.4936	0.0018
10.5789	2.4904	35	2	3	1	4	10.5793	2.4903	-0.0004
10.6535	2.4730	18	-3	3	1	4	10.6524	2.4733	0.0011
10.7670	2.4470	22	-4	1	3	4	10.7687	2.4466	-0.0017
10.9773	2.4003	29	4	1	2	4	10.9784	2.4001	-0.0012
11.0318	2.3885	51	3	2	2	4	11.0315	2.3885	0.0003
11.1571	2.3617	50	0	3	2	4	11.1567	2.3618	0.0004
11.2123	2.3501	18	-2	3	2	4	11.2122	2.3502	0.0001
11.2548	2.3413	59	-5	2	2	4	11.2545	2.3414	0.0003
11.3187	2.3281	20	0	2	3	4	11.3188	2.3281	-0.0001
11.4972	2.2921	26	-4	3	1	4	11.4969	2.2922	0.0002
11.5345	2.2847	34	1	3	2	4	11.5347	2.2847	-0.0002
12.4179	2.1227	21	4	3	1	4	12.4195	2.1225	-0.0016
12.5304	2.1038	23	-5	3	1	4	12.5317	2.1035	-0.0013
12.6196	2.0889	59	7	1	0	4	12.6195	2.0890	0.0001
12.7291	2.0710	19	2	4	0	4	12.7279	2.0713	0.0012
12.8591	2.0502	27	-3	1	4	4	12.8573	2.0505	0.0018
13.3878	1.9696	41	-3	4	1	4	13.3871	1.9697	0.0007
13.4391	1.9621	20	3	2	3	4	13.4383	1.9622	0.0008
13.5488	1.9463	28	6	0	2	2	13.5490	1.9463	-0.0002
13.7186	1.9223	18	-6	3	1	4	13.7146	1.9229	0.0040
13.7378	1.9196	45	7	1	1	4	13.7377	1.9197	0.0001
13.8220	1.9080	38	-1	2	4	4	13.8217	1.9080	0.0003
13.9901	1.8852	20	4	3	2	4	13.9893	1.8853	0.0008
14.0708	1.8744	26	-4	4	1	4	14.0705	1.8745	0.0003
14.2089	1.8563	22	-6	3	2	4	14.2104	1.8561	-0.0015
14.3292	1.8408	18	2	1	4	4	14.3253	1.8413	0.0039
14.5071	1.8183	24	4	2	3	4	14.5061	1.8185	0.0010
15.4309	1.7101	23	-1	3	4	4	15.4324	1.7099	-0.0015
16.2519	1.6242	22	-3	5	1	4	16.2499	1.6244	0.0020

The particular peak that has the strongest intensity in the entire pattern is assigned of 1000 and other lines are scaled relative to this value. The d -calc values are calculated values from refined lattice parameters. " I_{obs} " represents integrated intensity values and " M " represents multiplicity.

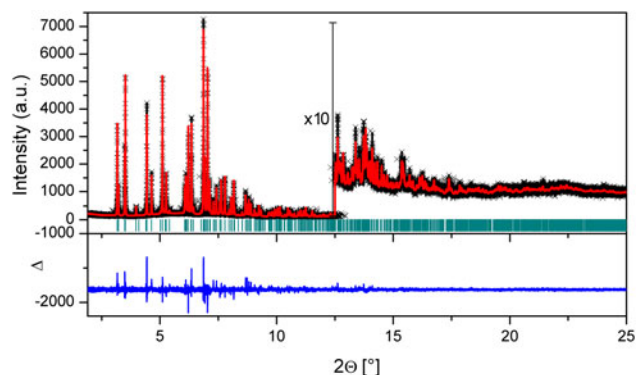


Figure 2. (Color online) Plot of the Rietveld refinement of the title compound. The red dots correspond to the measured powder diffraction pattern and the black line to the calculated one. The difference curve is shown in blue. Green vertical bars indicate Bragg reflections.

D. Structure solution

A rigid body of the molecule in the z -matrix notation was prepared using the Avogadro molecule drawing program (Hanwell *et al.*, 2012) including H atoms and optimized. The H atoms were removed because of their low scattering power and were not added up to the final refinement step. The unit-cell parameters obtained by TOPAS 4.2 and the z -matrix of the molecule were implemented in the DASH program (David *et al.*, 2006) to obtain starting structural model. The diffraction intensities were extracted with the Pawley method and then the simulated annealing was performed. During the simulated annealing calculations, the full pattern was used and the molecule conformation in the unit cell and torsion angles changed randomly. After nearly 10 million movements in the simulated annealing, the best solution (profile $\chi^2 = 5.1360$ and intensity $\chi^2 = 223.0303$) was gained.

E. Rietveld refinement

The structure solution found by DASH program was introduced in FullProf program (Rodríguez-Carvajal, 1993) to perform the Rietveld refinement. The refinement was performed using only the data from 1.2° to 25° 2θ range. The whole profile fitting was done using the LeBail method with

TABLE II. Crystal data and structure refinement parameters of the title compound.

Crystal data	
Chemical formula	$C_{23}H_{18}Cl_2N_4OS$
M_r	469.39
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	295
a, b, c (Å)	15.55645(11), 8.61693(6), 8.56702(6)
β (°)	104.3270(4)
V (Å ³)	1112.68(1)
Z	2
Radiation type	Synchrotron APS (11-BM), $\lambda = 0.459169$ Å
μ (mm ⁻¹)	0.13
Specimen shape, size (mm)	Cylinder, 10×0.8 mm
Data collection	
Diffractometer	Advanced Photon Source synchrotron
Specimen mounting	Kapton capillary
Data collection mode	Transmission
Scan method	Step
2θ values (°)	$2\theta_{\min} = 0.50$, $2\theta_{\max} = 25.00$, $2\theta_{\text{step}} = 0.000999$
Refinement	
R factors	$R_p = 0.055$, $R_{wp} = 0.069$, $R_{exp} = 0.070$, $R_{Bragg} = 0.046$
Goodness of fit	$\chi^2 = 0.9705$
No. of data points	24502
No. of parameters	145
No. of restraints	120

34 points chosen arbitrarily for defining the background by interpolation on the powder pattern. The X-ray powder pattern of the title compound is given in Table I. The particular peak that has the strongest intensity in the entire pattern is assigned of 1000 and other lines are scaled relative to this value. During the refinement, two asymmetry correction parameters with the pseudo-Voigt profile shape function (Thompson *et al.*, 1987) were used, which allow for angle-dependent asymmetry because of axial divergence (Finger *et al.*, 1994).

The refinement without the soft restrains of the bond lengths and angles failed as expected. To limit the number of free parameters, to gain chemically meaningful structure, and to achieve the convergence of the refinement, soft restraints for all bond lengths and angles were used during

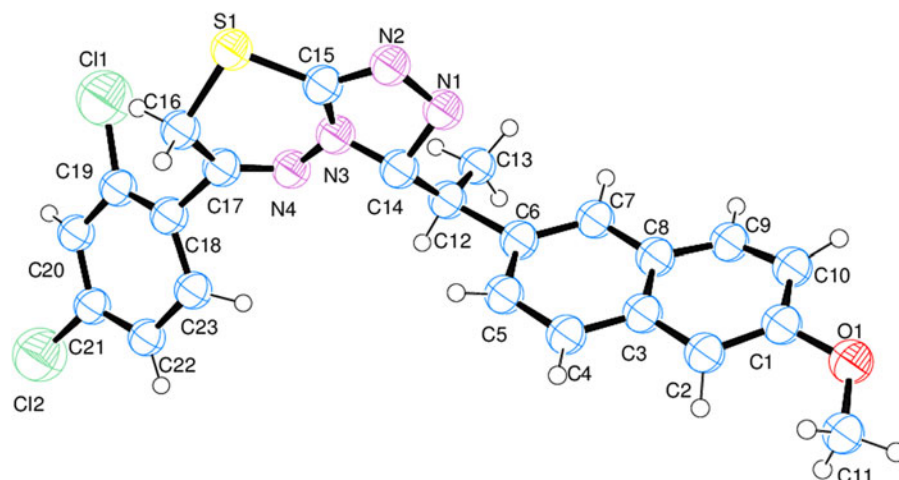


Figure 3. (Color online) Thermal ellipsoid plot of the molecule prepared by Ortep. The thermal ellipsoids are set to 50% probability.

TABLE III. Selected geometric parameters (Å, °) for the title compound.

C6–C12	1.568 (10)	C15–S1	1.723 (8)
C12–C14	1.478 (9)	S1–C16	1.819 (7)
C14–N1	1.347 (13)	C19–C11	1.696 (8)
C14–N3	1.349 (11)	C21–C12	1.721 (9)
N1–N2	1.356 (9)	N4–C17	1.304 (10)
N2–C15	1.297 (13)	C11–O1	1.454 (7)
N3–C15	1.354 (11)	C17–C16	1.497 (9)
N3–N4	1.325 (12)		
N1–C14–N3	106.8 (11)	C1–O1–C11	114.5 (7)
C14–N1–N2	109.6 (10)	C18–C17–N4	121.9 (11)
N1–N2–C15	105.6 (10)	C15–S1–C16	97.3 (4)
C14–N3–C15	105.9 (9)	N3–C15–S1	121.8 (7)
C13–C12–C14	116.9 (5)	S1–C16–C17	114.1 (4)
C6–C12–C13	107.5 (4)	N4–C17–C16	128.3 (8)
C12–C14–N1	127.3 (7)	N3–N4–C17	115.9 (8)
C7–C6–C12	125.7 (7)	C15–N3–N4	129.8 (8)
N2–C15–N3	111.8 (11)		
C19–C18–C17–N4	−108 (1)	C7–C6–C12–C14	−105.7 (9)
C6–C12–C14–N3	−151.2 (8)		

the refinement. Soft restraints were used and the atom positions were refined in two steps. At the first step, the sigma values, defining the weights of restraints, were set to 0.05° for the bond angles and 0.005 \AA for the bond lengths. At the second step, the sigma values were set to 0.1° and 0.01 \AA for the bond angles and bond lengths, respectively (Ivashkevich *et al.*, 2011).

At the beginning of the refinement of atomic positions, the coordinates of the Cl atoms were refined. Then the coordinates of the S and O atoms were refined, respectively. While refining one type of atom position, the other positions of atoms were kept fixed. The atoms of each ring were refined together followed by one ring after another.

The displacement parameters were constrained for each atom type and refined isotropically from the heavy atoms to the light atoms individually. All non-H atoms were located in their calculated positions and a reasonable solution was obtained with $R_p = 0.06$, $R_{wp} = 0.076$, and $\chi^2 = 1.16$ confidence values.

TABLE IV. Hydrogen-bond geometry (Å, °) for the title compound.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C5–H5...N2 ⁱ	0.95	2.51	3.422 (11)	160
C9–H9...N4 ⁱⁱ	0.95	2.61	3.480 (12)	152
C11–H113...S1 ⁱⁱⁱ	0.95	2.89	3.697 (3)	143
C16–H161...C11	0.95	2.53	3.266 (5)	134

Symmetry codes: (i) $-x, y + 1/2, -z$; (ii) $-x, y - 1/2, -z + 1$; (iii) $x - 1, y, z - 1$.

Finally, the hydrogen atoms were placed geometrically with their calculated positions [$C-H = 0.96 \text{ \AA}$ and $B_{iso}(H) = 1.5 B_{iso}(C)$] using Crystals program (Cooper *et al.*, 2010). The sigma values of the hydrogen atoms were set to 0.05° and 0.00001 \AA for the bond angles and bond lengths, respectively, and were fixed at their calculated atomic positions. At each step, profile and unit-cell parameters were also refined, simultaneously. After the final Rietveld refinement, a good agreement between calculated and experimental powder diffraction patterns was achieved with the confidence values of $R_p = 0.055$, $R_{wp} = 0.069$, and $\chi^2 = 0.9705$ (Figure 2).

III. DISCUSSION

Crystal data, data collection, and structure refinement details are summarized in Table II. A thermal ellipsoid plot of the molecule was prepared using Ortep-3 (Farrugia, 2012) with the atomic numbering (Figure 3). The probability of the ellipsoid was set to 50%. The selected bond lengths, bond angles, and torsion angles of the title compound are listed in Table III. For calculating molecular interactions and molecular geometry calculations, Platon (Spek, 2003), Mercury (Macrae *et al.*, 2006), and OLEX2 (Dolomanov *et al.*, 2009) programs were used.

In the title compound, all of the bond lengths and angles in the phenyl rings are in the normal range. In the 1,2,4-triazole ring, the $C=N$ bond lengths are $1.347(13) \text{ \AA}$ and $1.354(11) \text{ \AA}$, which are longer than that found in the 1,2,4-triazole ring-containing structures (Abdel-Aziz *et al.*, 2011; Aytac *et al.*, 2009; Fun *et al.*, 2012; Kaynak *et al.*, 2010;

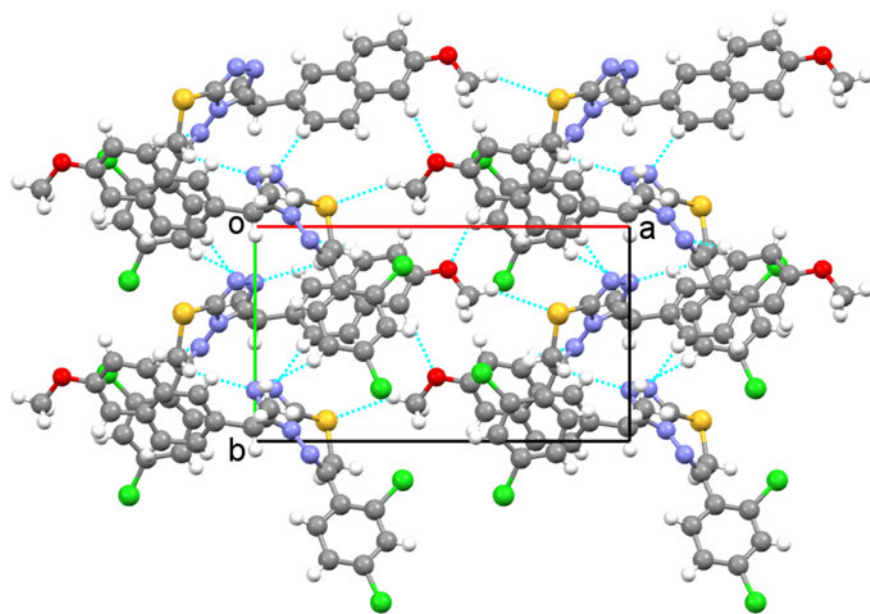


Figure 4. (Color online) Intermolecular hydrogen bonding interactions.

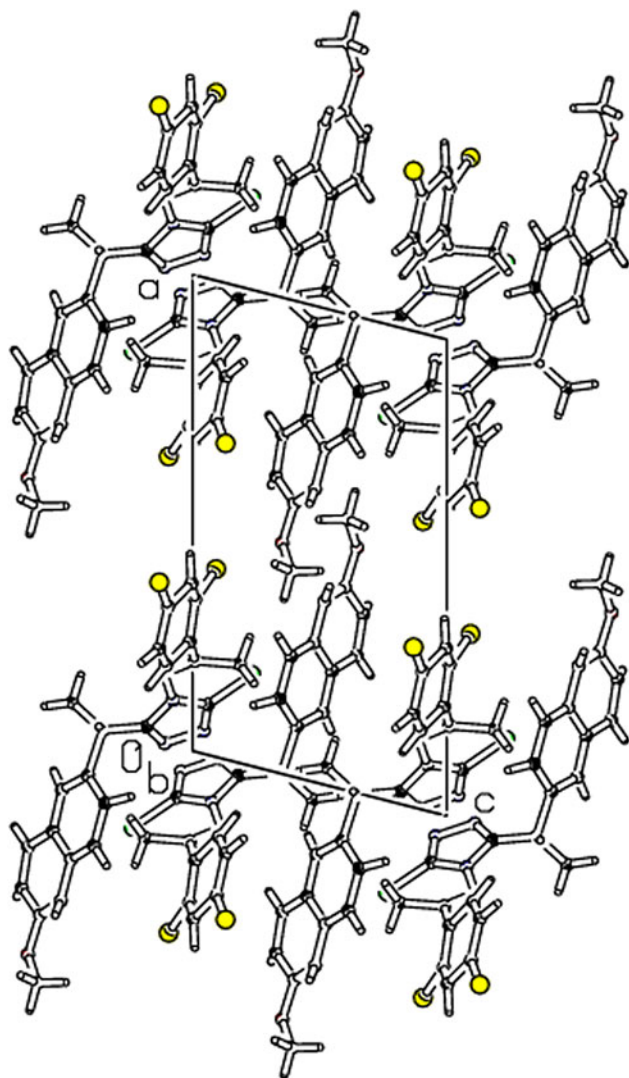


Figure 5. (Color online) Crystal packing of the title compound projected onto *ac* plane.

Khan *et al.*, 2014a). The N–N bond length is 1.356(9) Å, which is shorter than the 1,2,4-triazole ring-containing structures cited previously. In the 1,3,4 thiadiazine ring, the bond lengths are compatible with the 1,2,4-triazole ring and the 1,3,4 thiadiazine ring-containing structures (Aytaç *et al.*, 2009; Kaynak *et al.*, 2010; Abdel-Aziz *et al.*, 2011; Fun *et al.*, 2012), except the N–N bond length with 1.325(12) Å. The 1,3,4-thiadiazine ring is not planar and the r.m.s. deviation from planarity is 0.173 Å. S1 atom is displaced from the mean plane C15/N3/N4/C17/C16 by 0.61 Å. The 1,2,4-triazolo ring is planar with r.m.s. deviation 0.027 Å. The phenyl rings are approximately planar with r.m.s. deviation 0.037 Å (C3–C8), 0.068 Å (C18–C23), and 0.056 Å (C1/C2/C3/C8/C9/C10). Atom C12 is almost in the same plane with the C18–C23 ring, but the C11 atom is placed 0.203 Å below this plane. Structural results show that the C1/C2/C3/C8/C9/C10 ring adopts the envelope conformation having spherical polar set values of $Q = 0.138(9)$ Å, $\theta = 63(4)^\circ$, and $\varphi = 60(4)^\circ$.

The dihedral angle between the 1,2,4-triazolo and 1,3,4-thiadiazine rings is 11.1(5)° and between the 1,2,4-triazolo [3,4-*b*]-1,3,4-thiadiazine ring and the 2,4-dichlorophenyl ring is 50.74°. The 1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazine ring is almost perpendicular to 3-[1-(6-methoxy-2-naphyl)ethyl] ring with an angle of 86.72°.

The crystal structure of the title compound is stabilized by inter- and intra-molecular hydrogen bonds. The hydrogen-bonding geometry is given in Table IV and is shown in Figure 4. As can be seen from the packing diagram in Figure 5, the molecules are in a head-to-head arrangement. In the crystal structure, there are also strong C–H... π and weak intermolecular hydrogen-bonding interactions which link the molecules into a three-dimensional network. The C–H... π interactions are C16–H162...Cg(C3–C8) and C22–H221...Cg(1,2,4-triazole). The distance of H162 to the centroid of the C3–C8 ring is 2.54 Å (symmetry code: $-x, 1/2 + y, -z$) and the centroid angle is 140° (Figure 6). The distance of H221 to the centroid of the 1,2,4-triazole ring is 2.94 Å (symmetry code: $x, 1 + y, z$) and the centroid angle is 118° (Figure 7).

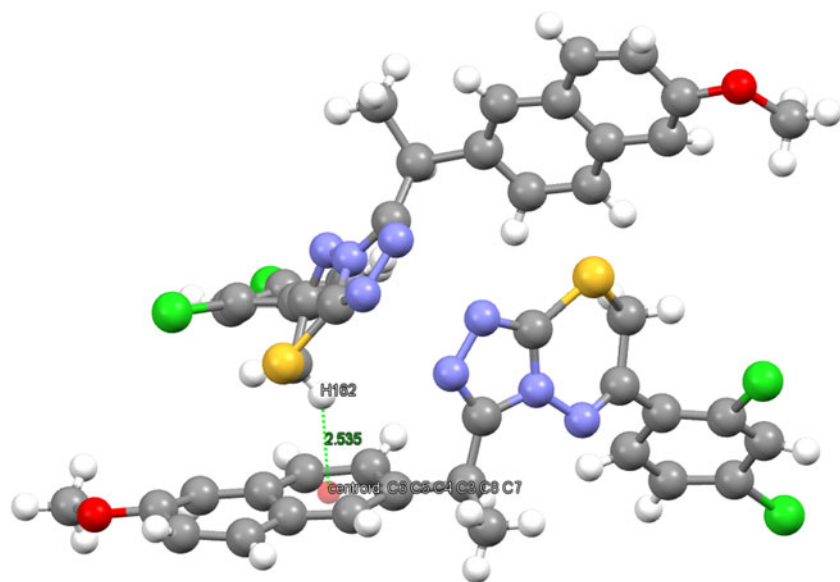


Figure 6. (Color online) C(16)–H(162)...Cg(C3–C8) interaction.

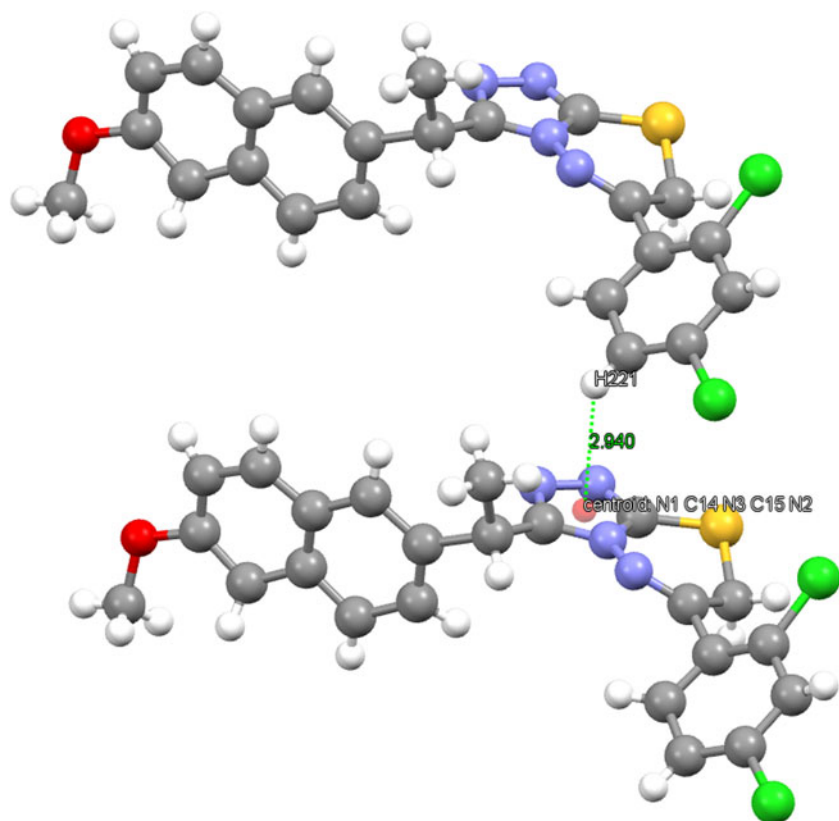


Figure 7. (Color online) C(22)–H(221)···Cg (1,2,4-triazole) interaction.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at <https://doi.org/10.1017/S0885715617001099>.

NOTE

This study has been performed from the PhD thesis of Gülsüm Gündoğdu.

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