IRANIAN SOCIETY of CRYSTALLOGRAPHY and MINERALOGY

Vol.22, No. 4, Winter 1393/2015

Pages 109 to 114

IRANIAN JOURNAL of CRYSTALLOGRAPHY and MINERALOGY

Synthesis and crystal structure of a new thiosemicarbzone, acenaphthenequinone thiosemicarbazone mono methanol

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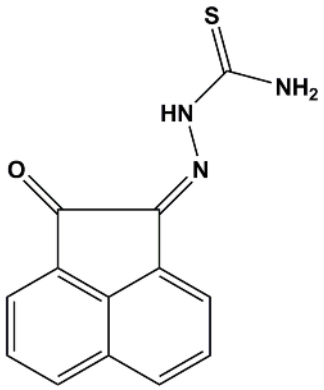
(Received: 27/9/2013, in revised form: 2/12/2013)

Abstract: A new thiosemicarbzone compound was prepared by the reaction of acenaphthenequinone and thiosemicarbazide (1:1 molar ratio) in absolute methanol at 70°C. The crystal structure of this compound, acenaphthenequinone thiosemicarbazone mono methanol, was determined by X-ray crystallography. The unit cell parameters are as follows: $\boldsymbol{a}$ = 7.0384(14) Å, $\boldsymbol{b}$ = 14.202(3) Å, $\boldsymbol{c}$ = 14.270(3) Å, $\boldsymbol{\beta}$ = 104.26(3)°. It crystallizes in a monoclinic system, with space group $P2_1/c$ and four molecules in the unit cell. The final $\boldsymbol{R}$ value is 0.0738 for 2422 independent reflection. Both inter and intramolecular hydrogen bonds exist in crystalline system.

Keywords: *Thiosemicarbazone, Crystal Structure, Acenaphthenequinone, Monoclinic*.

Introduction

Thiosemicarbazones have become a subject of intense research interest since the discovery of their considerable biological activities, e.g. anticarcinogenic, antibacterial, anti-HIV, anticancer, fungicides, antiviral, antifungal, antitumour, etc [1-7]. These compounds are an interesting group of multidentate ligands due to their mixed hard–soft donor character and versatile coordination behavior. These compounds containing thione (C=S) and thiole (C-S) groups occupy an important position among organic reagents as potential donor ligands for transition metal ions [8-12]. In the present work, we report the synthesis and crystal structure of a new aromatic thiosemicarbazone, which has one methanol molecule in its crystal system. The chemical structure of this compound has been shown in Scheme 1.



Scheme 1. The chemical structure of acenaphthenequinone thiosemicarbazone (**1**).

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Experimental

All reagents and solvents were purchased from chemical sources and used as received without further purifications. FT-IR spectrum in the 4000–400 cm^{-1} region was recorded from KBr pellet on a Shimadzu-8400S spectrophotometer.

Synthesis of acenaphthenequinone thiosemicarbazone mono methanol (1)

A solution of acenaphthenequinone (2.4mol, 0.045g) in 30 mL methanol was stirred 30 min at 70 °C. A solution of thiosemicarbazine (0.022g, 2.4mol) in 20 mL methanol was added drop wise to the above solution. The result mixture was heated at 70°C for 2h and then allowed to cool overnight to room temperature. Yellow crystals obtained at the bottom of the vessel during slow evaporation of the solvent. The resulting crystals were collected by filtration and dried at room temperature (mp 235-236°C). IR (KBr pellet, cm^{-1}): 3406 (NH), 3249-3144 (NH_2), 1689 (C=O), 1606 (C=N), 833 (C=S).

X-ray crystallography

The X-ray diffraction measurements were made on a STOE IPDSII diffractometer with graphite monochromated Mo-Ka radiation. A yellow block crystal of **1** with a dimension of 0.2 × 0.2 × 0.13 mm was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 2422 unique reflections. Data was collected at a temperature of 298(2) K to a maximum 2θ value of 24.98° and in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA software package [13]. The numerical absorption coefficient, μ, for Mo-Ka radiation is 0.239 mm^{-1}. A numerical absorption correction was applied using X-RED [14] and X-SHAPE [15] softwares. The data was corrected for Lorentz and Polarizing effects. The structure was solved by direct methods and subsequent difference Fourier maps and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [16]. All hydrogen atoms were located on a difference Fourier map and then refined isotropically. Atomic factors are from International Tables for X-ray Crystallography [17]. All refinements were performed using the X-STEP32 crystallographic software package [18]. Further details are summarized in Table 1.

Table 1. Crystallographic and structure refinements data for **1**

Empirical formula	$C_{14}\ H_{13}\ N_3\ O_2\ S$
Formula weight	287.34
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal size (mm^3)	0.20 × 0.20 × 0.13
Crystal system	Monoclinic
Space group	$\boldsymbol{P}2_1/c$
Unit cell dimensions	
$\boldsymbol{a}$ = 7.0384(14) Å	
$\boldsymbol{b}$ = 14.202(3) Å	
$\boldsymbol{c}$ = 14.270(3) Å	
$\boldsymbol{\beta}$ = 104.26(3) °	
Volume ($Å^3$)	1382.5(5)
Z	4
Calculated density (Mg/m^3)	1.380
Absorption coefficient (mm^{-1})	0.239
F(000)	600
Theta range for data collection (°)	2.06 to 24.98
Reflections collected / unique	6694 / 2422 [$\boldsymbol{R}$(int) = 0.1453]
Max. and min. transmission	0.9696 and 0.9538
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2422 / 0 / 195
Goodness-of-fit on F^2	0.867
Final $\boldsymbol{R}$ indices [I>2sigma(I)]	$\boldsymbol{R}_1$ = 0.0738, w$\boldsymbol{R}_2$ = 0.1162
$\boldsymbol{R}$ indices (all data)	$\boldsymbol{R}_1$ = 0.1969, w$\boldsymbol{R}_2$ = 0.1426
Largest diff. peak and hole (e. $Å^{-3}$)	0.349 and -0.232 k k

Results and discussion

The title compound was prepared by reaction of equimolar amounts of acenaphthenequinone and thiosemicarbazide in absolute methanol at 70°C. It crystallizes in a monoclinic system, with space group $P2_1/c$ and four molecules in the unit cell. The perspective view of **1** obtained by the single-crystal X-ray diffraction is shown in Fig. 1 with numbering scheme. The final atomic coordinates and anisotropic displacement parameters for non-hydrogen atoms are listed in Table 2. Selected bond distances and angles are given in Table 3. There are inter and intramolecular hydrogen bonds in crystalline system. There is one methanol molecule in the crystal structure of **1** and connects two molecules of the title compound through intermolecular hydrogen bonds. The crystal packing and the hydrogen bonds are shown in Fig. 2. Hydrogen bond data are given in Table 4.

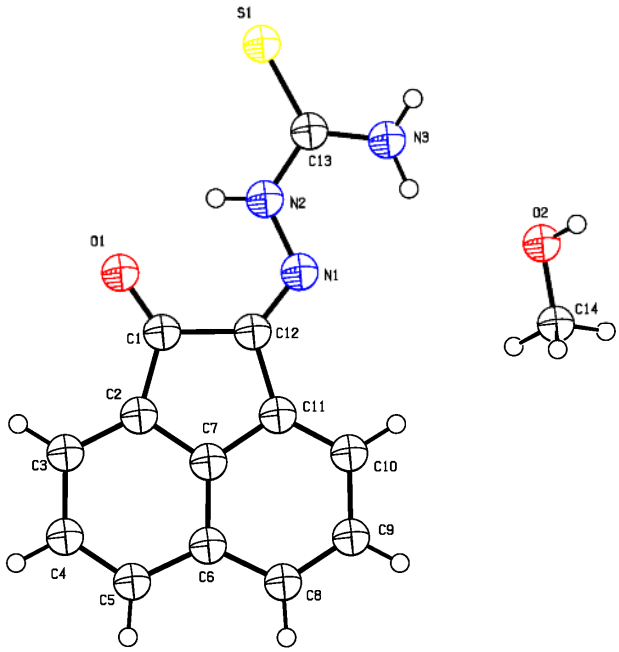

Fig. 1. ORTEP diagram of **1**. Thermal ellipsoids are at 50% probability level.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	4288(3)	8796(1)	4615(1)	67(1)
O(1)	4082(6)	6348(3)	6620(2)	51(1)
O(2)	2022(10)	6096(4)	1504(4)	112(2)
N(1)	2929(6)	6139(3)	4453(3)	40(1)
N(2)	3552(7)	7008(3)	4779(3)	42(1)
N(3)	3181(10)	7518(4)	3231(3)	56(2)
C(1)	3459(9)	5619(4)	6192(3)	40(1)
C(2)	3096(8)	4706(3)	6575(3)	38(1)
C(3)	3320(9)	4377(4)	7512(4)	51(2)
C(4)	2803(9)	3434(4)	7623(4)	56(2)
C(5)	2067(10)	2851(4)	6868(4)	58(2)
C(6)	1810(8)	3163(4)	5908(3)	39(1)
C(7)	2343(8)	4102(3)	5795(3)	36(1)
C(8)	1029(9)	2671(4)	5045(4)	54(2)
C(9)	823(9)	3100(4)	4166(4)	51(2)
C(10)	1417(8)	4039(4)	4083(3)	45(2)
C(11)	2187(8)	4543(4)	4899(3)	35(1)
C(12)	2866(8)	5517(4)	5097(3)	36(1)
C(13)	3635(9)	7725(4)	4156(4)	48(2)
C(14)	1195(16)	5199(6)	1431(6)	125(4)

Table 3. Selected bond distances (Å) and bond angles (◦) for **1**.

S(1)-C(13)	1.674(6)	N(2)-C(13)	1.362(6)
O(1)-C(1)	1.226(6)	N(3)-C(13)	1.314(7)
O(2)-(14)	1.394(9)	O(2)-H(2A)	0.8200
N(1)-C(12)	1.282(6)	N(2)-H(2)	0.82(7)
N(1)-N(2)	1.353(6)	N(3)-H(3A)	0.90(6)
N(2)-C(13)	1.362(6)	N(3)-H(3B)	0.83(5)
N(3)-C(13)	1.314(7)		
C(12)-N(1)-N(2)	116.6(4)	O(1)-C(1)-C(2)	129.8(4)
N(1)-N(2)-C(13)	121.4(4)	O(1)-C(1)-C(12)	124.4(5)
N(1)-N(2)-H(2)	117(6)	N(1)-C(12)-C(11)	125.3(4)
C(13)-N(2)-H(2)	122(6)	N(1)-C(12)-C(1)	128.4(5)
C(13)-N(3)-H(3A)	120(4)	N(3)-C(13)-N(2)	116.7(5)
C(13)-N(3)-H(3B)	116(4)	N(3)-C(13)-S(1)	124.9(4)
H(3A)-N(3)-H(3B)	122(5)	N(2)-C(13)-S(1)	118.4(4)

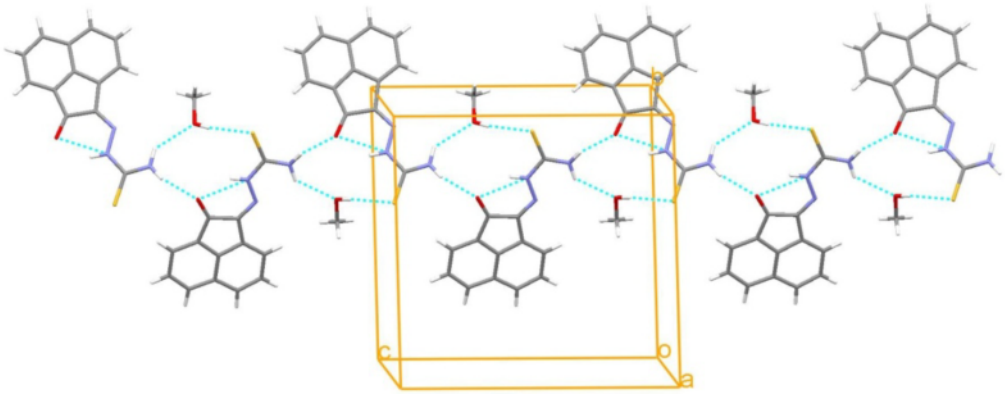

Fig. 2. Packing diagram of **1**. Hydrogen bonds are shown as dashed lines.

Table 4. Hydrogen bond geometries of compound **1** in the crystal packing (Å, °).

D-H···A	D-H	H···A	D···A	D-H···A
N(2)-H(2)...O(1)	0.82(7)	2.05(8)	2.728(5)	140(8)
O(2)-H(2A)...S(1)$^{\#1}$	0.82	2.64	3.457(5)	173.3
N(3)-H(3A)...O(2)	0.90(6)	2.42(6)	3.135(8)	136(5)
N(3)-H(3A)...N(1)	0.90(6)	2.30(6)	2.658(7)	103(4)
N(3)-H(3B)...O(1)$^{\#1}$	0.83(5)	2.19(6)	2.999(6)	164(5)

Symmetry code: #1 x,-y+3/2,z-1/2

Spectral characterization

The observed stretching vibrations at 3406, 3244 and 3144 cm^{-1} in the FT-IR spectrum of the title compound belong to NH and NH_2. The stretching vibration of C=S is appeared at 833 cm^{-1}. The strong absorption bands at 1062 and 1689 cm^{-1} can be attributed to C=N and C=O, respectively [7-12].

Crystal structure description

The title compound crystallizes in the monoclinic space group $P2_1/c$. The molecular structure of **1** with the atom numbering scheme has been shown in Fig. 1. The title compound is nearly a planar molecule, with a dihedral angle between the aromatic rings and the chain, 178.3(5)º. Bond

lengths and angles within the aromatic rings are in good agreement with those expected for sp^2 hybridization of aromatic carbon atoms. The bond distances of N1– C1(1.282Å) and N1–C13(1.362Å) are consistent with double and single bonds, respectively [8,9, 11]. There is one methanol molecule in the crystal structure of **1** and connects two molecules of the title compound through intermolecular hydrogen bonds. In other words, these intermolecular hydrogen bonds are N3-H(3B)···O1 (2.19 Å), O2-H(2A)···S1 (2.64 Å) and N3-H(3A)···O2 (2.42 Å). There is also one intramolecular hydrogen bond, N3-H(3A)···N1 (2.30 Å), in this compound, which leads to the formation of six-membered ring (Fig. 2 and Table 4).

Conclusion

In summary, a new thiosemicarbazone compound, acenaphthenequinone thiosemicarbazone mono methanol, was synthesized and characterized. Crystal structure of the title compound was determined by single-crystal X-ray diffraction. It crystallizes in a monoclinic system, with space group $P2_1/c$. There is one methanol molecule in the crystal structure of the title compound and connects two molecules of the title compound through intermolecular hydrogen bonds. There is also intramolecular hydrogen bond in crystalline system.

Supplementary data

Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to The Director, CCDC no. 956643, Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk or http:www.ccdc.cam.ac.uk.

Acknowledgement

We acknowledge the Iran University of Science and Technology for partial support of this work.

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