AUSTRALIAN JOURNAL OF BASIC AND APPLIED SCIENCES

ISSN:1991-8178 EISSN: 2309-8414
Journal home page: www.ajbasweb.com

Synthesis, Spectral Characterization and Crystal Structure of (*E*)-4-Hydroxy-N -(2-methoxybenzylidene) benzohydrazide

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ARTICLE INFO

Article history:
Received 12 December 2015
Accepted 22 January 2016
Available online 1 February 2016

Keywords:
2-methoxybenzaldehyde; 4-hydroxybenzoylhydrazine; Methanol; Hydrochloric acid.

ABSTRACT

A Schiff base, (*E*)-4-Hydroxy-N -(2-methoxybenzylidene) benzohydrazide, (E4HB) had been synthesized in good yield by the acid-catalyzed condensation reaction of 2-methoxybenzaldehyde and 4-hydroxybenzhydrazide in methanolic solution. The synthesized compound was elucidated by elemental analysis (CHN), FTIR, ^{1}H-NMR, ^{13}C-NMR and single crystal X-ray diffraction. E4HB crystallized in the orthorhombic crystal system with space group $Z = 8$, $V = 2656.74(10)$ Å^3 and unit cell parameters $a =$ 14.3951(3) Å, $b = 8.7449(2)$ Å, $c = 21.1047(4)$ Å . The crystal structure of the compound is stabilized by intermolecular N1—H1N1….O2, O1—H1O1…O2 and C13—H13A…O1 hydrogen bonds. A *π—π interaction* with centroid-centroid distance of 3.628 (6) A also occurs (*Cg*1 = C9— C14, *-x, -y, -z*).

INTRODUCTION

Hydrazones are organic compounds of formula $R_1C = N – NR_2$ where R_1 and R_2 represent H, aliphatic and aromatic group. The chemical properties of hydrazone derivatives have been intensively investigated in several research fields mainly due to their facile synthesis, tuneable electronic and steric properties, and good chelating ability (Pelizzi & Pelizzi, 1980). Schiff bases are nitrogen analogues of aldehydes and ketones, having a carbon-nitrogen double bond in place of the carbonyl group (Wade, 2005). The hydrazone unit offers a number of attractive features : a degree of rigidity, a conjugate π-system and a deprotonation (Beves*et al*., 2009). Hydrazone ligands have been thoroughly investigated due to their biological activity. The aryl hydrazones contain in their structure the (–CO–NH–N=C< group) that imparts on these chelating agents fungicidal.

Some derivatives of the title compound, (E4HB), were used for the determination of glucose (Lever, 1972). These compounds crystallize in the E conformation (Shan *et al.*, 2003; Fun *et al.*, 1996) and isomeric compounds have also been prepared (Ferguson *et al.*, 2005).

All parameters in (E4HB), are within normal ranges. The dihedral angle between C1—C6 and C9 C14 benzene ring is 66.56 (5) °.

In this paper, we report the synthesis, characterization and crystal structure of newly synthesized semicarbazone compound, namely as (*E*)-4-Hydroxy-N-(2-methoxybenzylidene) benzohydrazide, (E4HB).

1. Experimental:

In the preparation of E4AB, all the reagents were used as received. Elemental (CHN) analysis of the prepared of (*E*)-4-Hydroxy-N -(2-methoxybenzylidene) benzohydrazide, (E4HB) analysis were carried out using Perkin – Elmer Series II, 2400 elemental analysis. The infrared spectra (IR) was recorded by using KBr system on a Perkin - Elmer 2000 FT-IR spectroscopy unit within region of 400 – 4000 cm^{-1}. The 1H NMR

To Cite This Article: Hesham H.A. Rassem and Abdurahman H. Nour., Synthesis, Spectral Characterization and Crystal Structure of (E)-4-Hydroxy-N -(2-methoxybenzylidene) benzohydrazide. ***Aust. J. Basic & Appl. Sci.,*** *10(1): 513-516, 2016*

spectra and 13C NMR spectra were recorded using a Bruker 300 MHz spectrometer. in DMSO-*d6* using tetramethylsilane as an internal standard.

2.1. Synthesis of (E)-4-Hydroxy-N - (2-methoxybenzylidene) benzohydrazide, (E4HB):

A solution of 2-methoxybenzaldehyde (S) (0.136 gm, 1 mmol) in methanol (10 mL) was added dropwise to a methanol solution (10 mL) of 4-hydroxybenzhydrazide, HB (0.152 gm, 1 mmol) and the mixture was refluxed for 2 h. The resulting solution was condensed on a steam bath to 5 mL and cooled to room temperature. Yellow crystals suitable for X-ray diffraction were separated out, filtered off, and then washed with 5 mL of cooled methanol and dried in air (Figure 1). Yield: 90%. . Analysis Calculated for $C_{15}H_{14}N_2O_3$: C 66.66, H 4.22, N 10.36%; found: C 66.52, H 4.63, N 10.21%. Main IR bands (KBr, cm^{-1}): 3254 (m), 3018 (m), 1607 (s), 1594 (s), 1493 (sh), 1049 (w). ^{1}H-NMR 500 MHz, (DMSO-d6) Ha : δ 6.88 ppm (2H, d, $^3J_{HH}$ = 6 Hz,), Hc δ 7.02 ppm (1H, t, $^3J_{HH}$ = 4.4 Hz,), Hd δ 7.11 ppm (1H, d, $^3J_{HH}$ = 4.9 Hz,), Hg δ 7.40 ppm (1H, t, $^3J_{HH}$ = 4.2 Hz,), Hb δ 7.83 ppm (2H, d, $^3J_{HH}$ = 5.2 Hz,), He δ 7.87 ppm (1H, d, $^3J_{HH}$ = 4.2 Hz,), Hh δ 8.80 ppm (1H, s), Hm δ 10.14 ppm (1H, s), Hn δ 11.67 ppm (1H, s) and Ho δ 3.86 ppm (3H s). ^{13}C NMR : δ 55.6, 111.80, 114.9, 120.7, 122.6, 123.9, 125.5, 129.6, 131.3, 142.3, 157.7, 160.6 and 162.6 ppm.

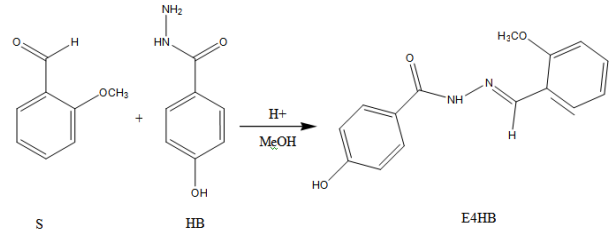

Fig. 1: Synthesis of 4-hydroxy-(2-methoxybenzylidene)benzohydrazide, E4HB.

2.2. Crystal Structure Determination:

Crystal data was collected *APEX2* (Bruker, 2009). The cell refinement and data reduction were performed using *SAINT* (Bruker, 2009) program(s) and the empirical absoption correction was performed using the SADABS program. The structurewas solved by direct methods and refined by least squares using SHELXTL software package (Sheldrick, 2008). The details of the crystal data and structure refinements are given in Table 1.

Table 1: Crystal data, data collection and refinement parameters of E4HB.

Compound	E4HB
Empirical formula	$C_{15}H_{14}N_2O_3$
Formula weight	270.28
Temperature (k)	100
Wavelength (Å)	0.71073
Crystal color	Yellow
Crystal shape	Block
Crystal size (mm)	0.49 x 0.28 x 0.09
Crystal system	orthorhombic
Space group	*Pbca*
Lattice constants	*a* 14.3951 (3) (Å), *b* 8.7449 (2) (Å) *c* 21.1047 (4) (Å), λ = 0.71073 (Å)
V (Å^3)	2656.74(10)
Z	8
D_{calc} (g cm^{-3})	1.351
μ (mm^{-1})	0.10
F (000)	1136
θ range	2.4-31.5
Limiting indices	$-21 \le h \le 21$; $-12 \le k \le 12$; $-30 \le l \le 31$
Reflections collected	4442
T_{min}/T_{max}	0.954/0.991
Refined parameter	190
R_{int}	0.036
Goodness of fit	1.03
w $R_2(F^2)$	0.114

RESULTS AND DISCUSSION

3.1. Description of the Crystal Structure:

The molecular view of E4HB (Figure 2) shows that E4HB contains two of each species in the asymmetric unit with similar geometries. All parameters in (I), are within normal ranges. The dihedral angle between C1—

C6 and C9 — C14 benzene ring is 66.56 (5) °. A π—π interaction with centroid-centroid distance of 3.628 (6) Å also occurs (*Cg*1 = C9— C14, *-x*, *-y*, *-z*). The selected bond lengths and angles are given in Table 2. In the crystal structure packing (Figure 3), adjacent the molecules are interconnected by N1—H1N1···O2^{i}, O1—H1O1···O2^{ii} and C13—H13A···O1^{iii} hydrogen bonds (Table 3).

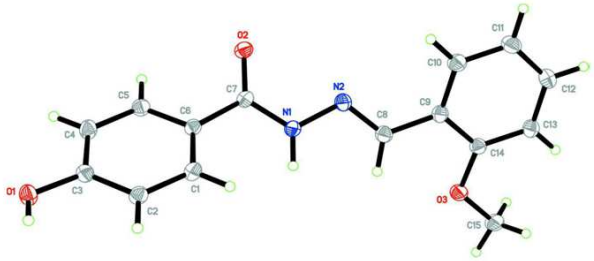

Fig. 2: The molecular structure, showing 50% probability displacement ellipsoids. Hydrogen atoms are shown as spheres of arbitrary radius.

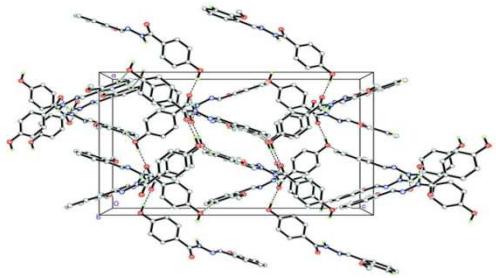

Fig. 3: The crystal packing of E4HB. Dashed lines indicate hydrogen bonds. H atoms not involved in the hydrogen bond interactions have been omitted for clarity.

Table 2: Selected bond lengths (Å) and bond angles (°).

Bond	Length(Å)	Bond	Angle(^{0})
O1—C3	1.3565(12)	C3—O1—H1O1	111.1(12)
O1—H1O1	0.87(2)	C14—O3—C15	117.06(8)
O2—C7	1.2510(13)	C7—N1—N2	119.07(9)
O3—C14	1.3650(13)	C7—N1—H1N1	122.3(9)
O3—C15	1.4287(14)	N2—N1—H1N1	118.5(9)
N1—C7	1.3432(14)	C8—N2—N1	113.78(9)
N1—N2	1.3905(12)	C2—C1—C6	120.38(10)
N1—N1H1	0.917(16)	C1—C2—C3	119.79(10)
N2—C8	1.2848(14)	O1—C3—C4	117.28(10)
C1—C2	1.3904(14)	O1—C3—C2	122.73(10)
C1—C6	1.3974(15)	C4—C3—C2	119.99(10)
C2—C3	1.3973(15)	C5—C4—C3	119.82(10)
C3—C4	1.3969(15)	C4—C5—C6	120.81(10)
C4—C5	1.3806(15)	C1—C6—C5	119.18(9)
C5—C6	1.3978(14)	C1—C6—C7	122.68(9)
C6—C7	1.4782(14)	C5—C6—C7	117.92(9)
C8—C9	1.4609(14)	O2—C7—N1	122.63(9)
C9—C10	1.3956(15)	O2—C7—C6	120.24(9)
C9—C14	1.4068(16)	N1—C7—C6	117.09(9)
C10—C11	1.3885(15)	N2—C8—C9	121.12(10)
C11—C12	1.3880(17)	C10—C9—C14	119.05(10)
C12—C13	1.3856(16)	C10—C9—C8	121.89(10)
C13—C14	1.3953(14)	C14—C9—C8	119.03(10)
		C11—C10—C9	121.01(11)
		C12—C11—C10	119.17(10)
		C13—C12—C11	121.11(10)
		C12—C13—C14	119.72(11)
		O3—C14—C13	123.85(10)
		O3—C14—C9	116.20(9)
		C13—C14—C9	119.93(10)

Table 3: Geometries of intermolecular hydrogen bonds in E4HB.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/Å
N1-H1*N*1···O2^{i}	0.916(16)	2.009(16)	2.9202(12)	172.8(15)
O1-H1*O*1···O2^{ii}	0.87(2)	1.80(2)	2.6528(11)	164.2(17)
C13-H13*A*···O1^{iii}	0.95	2.52	3.4669(15)	171

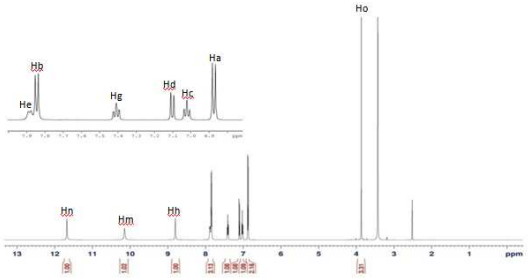

Fig. 4: The 1H NMR spectrum of E4HB in DMSO-*d6*.

3.2. FT-IR Spectrum:

In the FT-IR spectrum of E4HB, the results showed that the O-H group at 3254 cm^{-1}. The C=N stretching vibrations of an azomethine group is attributed to an absorption at 1594 cm^{-1} (Stamatoiu *et al*., 2008). The characteristic of C=O stretching frequency is observed at 1607 cm^{-1} .A strong bond at 1493 cm^{-1} can be assigned to the C=C stretching (Yeap *et al*., 2003).

3.3. ^{1}H-NMR Spectroscopy:

^{1}H-NMR spectrum of E4HB is shown in Figure 4. A singlet at δ 8.80, 10.14, 11.67 and 3.86 ppm are assigned to Hh, Hm, Hn and Ho, respectively. Meanwhile the doublet at δ 6.88, 7.11, 7.83 and 7.87 ppm are attributed to Ha, Hd, Hb and He, respectively. Hc and Hg are observed as triplets at δ 7.02 and 7.40 ppm. The N-H proton in E4HB (Hn) is observed at 11.67 ppm. The ^{1}H NMR spectrum also displayed the O-H protons of the phenolic groups and azomethine protons (H-C=N).

Conclusions:

(*E*)-4-Hydroxy-N -(2-methoxybenzylidene) benzohydrazide, E4HB had been synthesized in good yield. Results obtained from the elemental, spectral (FTIR, NMR) and X-ray crystallography had confirmed the proposed structure of the title compound.

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