European Journal of Chemistry 5 (3) (2014) 394-396

European Journal of Chemistry

Journal homepage: www.eurjchem.com

Synthesis, characterization and crystal structure of *N*'-[(*E*)-furan-2-ylmethylidene]furan-2-carbohydrazide

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ARTICLE INFORMATION

DOI: 10.5155/eurjchem.5.3.394-396.1043

Received: 06 March 2014
Received in revised form: 07 March 2014
Accepted: 07 March 2014
Online: 30 September 2014

KEYWORDS

IR
NMR
Furfural
Crystal structure
Acylhydrazone
p-Chlorobenzhydrazide

ABSTRACT

A new compound, *N*'-[(*E*)-furan-2-ylmethylidene]furan-2-carbohydrazide was synthesized. Elemental analysis, IR spectrum, ^{1}H NMR and X-ray crystal structure studies were carried out to determine the compositions and molecular structure of the compound. It crystallizes in the orthorhombic space group P*bca* with unit cell parameters a = 11.3142(4) Å, b = 7.5526(2) Å and c = 22.9030(9) Å. The crystal structure studies reveal intermolecular N-H···O hydrogen bonding interactions in the solid state.

1. Introduction

Acyl hydrazones have stimulated lot of interest as anti-inflammatory agents, antimalarial agents and as antimicrobials due to their diverse pharmacological properties [1-7]. These compounds are undoubtedly versatile ligands for complexation to transition metals [8,9]. Availability of various substituents encourages synthesizing and characterizing new hydrazones. Structure of the compound is of great importance when structure-activity related studies (SAR) are undertaken. Due to the crystalline nature of majority of acyl hydrazones, their crystal structures are widely studied [10-12].

In this manuscript, we have discussed a simple procedure to synthesize the title compound and characterized it by elemental analysis, various spectroscopic methods and single crystal X-ray diffraction.

2. Experimental

2.1. Instrumentation

All chemicals used in our present study were of analytical grade and procured from Sigma-Aldrich and used without any further purification.

TLC was run on silica (60 F_{254} coated aluminum sheets) using ethyl acetate:petroleum ether (1:1, *v*:*v*) as mobile phase and visualized in UV light. IR spectrum was recorded using FT-IR Perkin Elmer spectrometer. ^{1}H NMR spectrum was obtained using Bruker NMR instrument 400MHz at room temperature. Elemental analysis was done using Elementar Vario EL III system.

Needle shaped, colorless single crystals of the title compound, suitable for X-ray analysis were obtained by slow evaporation at room temperature. X-ray intensity data were collected at 25 °C up to a $2\theta_{max}$ of 25 ° on a Bruker Kappa APEX2 detector with graphite monochromatic Mo-Kα radiation (0.71070 Å). The intensities were corrected for Lorentz, polarization and absorption effects. The structure was solved by direct methods and refined by full matrix least-squares method using SHELX-97 [13]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. The hydrogen atom bonded to nitrogen atom was located in a difference map and refined freely. The remaining hydrogen atoms were positioned geometrically (C-H=0.93 Å) and refined using a riding model, with U_{iso}(H)=1.2 U_{eq} (C). The refinement was continued until the maximum shift/e.s.d was zero. The crystal data and structure refinement details are given in Table 1.

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
http://dx.doi.org/10.5155/eurjchem.5.3.394-396.1043

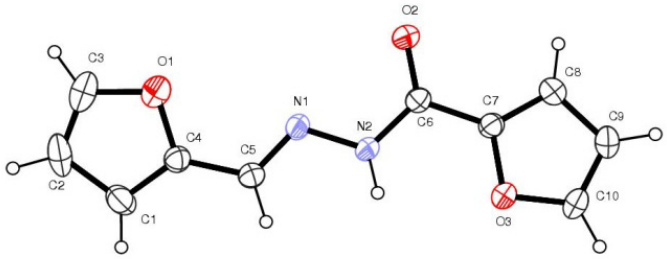
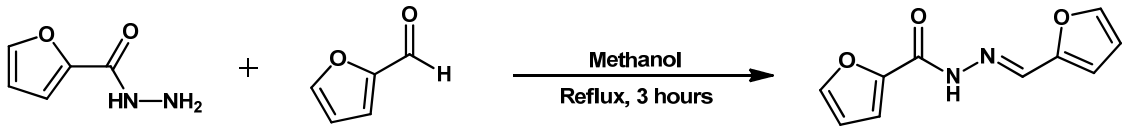


Figure 1. ORTEP view of the molecular structure with 50% probability ellipsoids.



Scheme 1

Table 1. Crystal data and structure refinement details of the title compound.

Empirical formula	$C_{10}H_8N_2O_3$
Formula weight	204.18
Crystal system	Orthorhombic
Space group	P*bca*
Unit cell dimensions	*a* = 11.3142(4) Å
	b = 7.5526(2) Å
	c = 22.9030(9) Å
Volume	1957.10(12) Å^3
Z	8
Calculated density	1.386 g/cm^3
F(000)	848
Crystal size	0.35 × 0.20 × 0.15 mm
Absorption coefficient	0.105 mm^{-1}
No. of observations (I > 2σ (I))	1646
Absorption correction	Psi-scan
Max. and min. transmission	0.964 and 0.984
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit indicator	1.049
Index ranges	-12 ≤*h*≤ 13
	-6 ≤*k*≤ 8
	-27 ≤*l*≤ 13
θ range for data collection	2.53 to 25.00 °
R (I > 2σ (I))	0.0411
R_w (I > 2σ (I))	0.1091
Largest diff. peak and hole	0.223 and -0.185 e.Å^{-3}
CCDC no.	953906

2.2. Synthesis

Synthesis procedure for the title compound is depicted in Scheme 1. Furfuraldehye (0.8 mL, 10 mmol) and furoic hydrazide (1.2 g, 10 mmol) were refluxed in methanol for three hours. TLC was checked for completion of the reaction. Upon evaporation of the solvent, product crystallized out. Single crystals suitable for X-ray diffraction were obtained by recrystallization from methanol solution.

N'-[(E)-furan-2-ylmethylidene]furan-2-carbohydrazide : Color: White. Yield: 78%. M.p.: 164-167 °C. FT-IR (KBr, ν, cm^{-1}): 3191 (m, NH), 1641 (s, C=O), 1618 (s, C=N), 1089 (s, C-O). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 11.77 (s, 1H, NH, D_2O exchangeable), 8.33 (s, 1H, CH=N), 7.92 (s, 1H, Ar-H), 7.83 (d, 1H, *J* = 1.6 MHz, Ar-H), 7.26 (s, 1H, Ar-H), 6.91 (d, 1H, *J* = 3.2 MHz, Ar-H), 6.69 (dd,1H, *J* = 1.6, 3.2 MHz, Ar-H), 6.62 (dd, 1H, *J* = 1.6, 3.2 MHz, Ar-H). Anal. calcd. for $C_{10}H_8N_2O_3$; C, 58.82; H, 3.95; N, 13.72. Found: C, 59.12; H, 4.10; N, 13.98%.

3. Results and discussion

The IR spectrum of the title compound showed two strong bands at 1652 and 1604 cm^{-1}, which hints the presence of amide C=O and C=N, respectively. A medium intensity band at 3278 and 3227 cm^{-1} confirm the presence of NH group. Strong band at 1100 cm^{-1} was assigned to C=O stretch. These characteristic IR bands of acyl hydrazones confirmed formation of the product. However ^{1}H NMR data of the compound further helped in elucidation of the structure.

The ^{1}H NMR spectrum of the compound exhibited resonance peak of NH group at 11.1 ppm, as a singlet and the assignment was confirmed by D_2O exchange. A singlet for azomethine proton (CH=N) appeared at 8.5 ppm, whereas peaks for furyl protons showed between 8-6 ppm. Chemical shifts, splitting patterns and coupling constants matched perfectly with the structure of the title compound.

The molecular structure of the title compound is given in Figure 1. The X-ray crystallographic study of the title compound showed that C5-N1 bond length (1.276(2) Å) conforms to the value for a double bond (Table 2). The bond length of 1.346(2) Å between N2 and C6 which is greater than the value for a double bond and less than that for a single bond indicates conjugation in the molecule. The bond lengths and angles are similar to those found in related compounds [14-17]. The *E*– configuration of the molecule is established by the torsion angle N2-N1-C5-C4 which assumes a value of 178.9(2)° (Table 2). The compound is found to exist in the *syn*-periplanar form. The two furyl rings are planar with a dihedral angle of 14.7° between them. Packing of molecules down *c*-axis in the unit cell is shown in Figure 2. The packing of molecules in the unit cell is through intermolecular N-H···O and C-H···O interactions (Table 3).

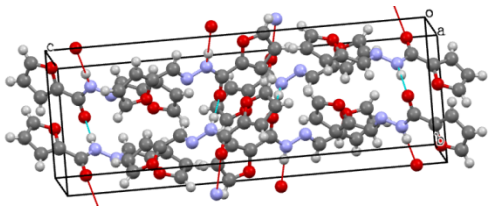


Figure 2. Packing of molecules in the unit cell.

Table 2. Selected geometric parameters for the title compound.

Bond lengths, Å					
C1-C4	1.341(3)	C4-C5	1.437(3)	C7-C8	1.339(3)
C1-C2	1.435(3)	C5-N1	1.276(2)	C7-O3	1.367(2)
C2-C3	1.306(4)	C6-O2	1.230(2)	C8-C9	1.409(3)
C3-O1	1.365(3)	C6-N2	1.346(2)	C9-C10	1.327(3)
C4-O1	1.358(2)	C6-C7	1.463(2)	C10-O3	1.357(2)
N1-N2	1.380(2)				
Bond angles, °					
C4-C1-C2	105.8(2)	O2-C6-N2	123.2(2)	C10-C9-C8	106.5(2)
C3-C2-C1	106.8(2)	O2-C6-C7	120.4(2)	C9-C10-O3	110.9(2)
C2-C3-O1	111.0(2)	N2-C6-C7	116.5(2)	C5-N1-N2	115.5(2)
C1-C4-O1	110.1(2)	C8-C7-O3	109.8(2)	C6-N2-N1	118.0(1)
C1-C4-C5	131.0(2)	C8-C7-C6	131.2(2)	C4-O1-C3	106.3(2)
O1-C4-C5	118.9(2)	O3-C7-C6	119.0(2)	C10-O3-C7	105.9(2)
Torsion angles, °					
C4-C1-C2-C3	1.6(3)	C8-C9-C10-O3	0.2(3)		
C1-C2-C3-O1	-0.9(3)	C4-C5-N1-N2	178.9(2)		
C2-C1-C4-O1	-1.7(2)	O2-C6-N2-N1	-1.6(2)		
C2-C1-C4-C5	178.3(2)	C7-C6-N2-N1	178.7(1)		
C1-C4-C5-N1	173.6(2)	C5-N1-N2-C6	177.5(2)		
O1-C4-C5-N1	-6.4(3)	C1-C4-O1-C3	1.2(3)		
O2-C6-C7-C8	-4.1(3)	C5-C4-O1-C3	-178.8(2)		
N2-C6-C7-C8	175.6(2)	C2-C3-O1-C4	-0.1(3)		
O2-C6-C7-O3	175.9(2)	C9-C10-O3-C7	-0.3(3)		
N2-C6-C7-O3	-4.4(2)	C8-C7-O3-C10	0.2(2)		
O3-C7-C8-C9	0.0(2)	C6-C7-O3-C10	-179.8(2)		
C6-C7-C8-C9	180.0(2)	C7-C8-C9-C10	-0.1(3)		

Table 3. Hydrogen bond geometry (Å, °) for the title compound (D-Donor; A-Acceptor; H- Hydrogen).

D-H···A	d (D-H)	d (H···A)	d (D···A)	∠DHA
N2-H2A···O2 ^{i}	0.860	2.119	2.949	161.99
C2-H2···O2 ^{ii}	0.930	2.468	3.384	168.54
C8-H8···O2 ^{iii}	0.930	2.430	3.360	178.87

Symmetry codes: (*i*) ½-*x*, ½+*y*, z; (*ii*) -½+*x*, *y*, ½-*z* ; (*iii*) 1-*x*, -*y*, -z.

4. Conclusion

This work describes the synthesis of an acyl hydrazone of furfuraldehyde by a convenient procedure which affords good yield. The IR and ^{1}H NMR analysis elucidate the structure of compound. Crystal structure of the compound was determined by single crystal X-ray diffraction at room temperature. Structure analysis of the compound indicated N-H···O hydrogen bonding in the solid state. The *E*-geometry of the C=N bond was also established by this study.

Acknowledgements

This work was supported by Centre for Research, Christ University, Bangalore, India (Project No: MRPDSC 1105). Authors are grateful to Indian Institute of Technology, Madras, India, for single crystal XRD data and IISC, Bangalore, India, for ^{1}H NMR results.

Supplementary material

CCDC-953906 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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