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Spectral and X-ray Crystallographic Structure Determination of (E)-N'-[(Furan-2-yl)methylene)-benzohydrazide

KEYWORDS: benzene, benzamide, hydrogen bonds, ring motif

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ABSTRACT *The title compound, $C_{12}H_{10}N_2O_2$, represents an orthorhombic system, space group pbca with a = 9.4339 (10) Å, b = 9.6549 (9) Å, c = 23.418 (3) Å, V = 2133.0 (4) Å^3, Z = 8, F(000) = 896, Dx = 1.334 Mg m−3, R= 0.041 and wR= 0.136, T = 293 K. In the title compound, $C_{12}H_{10}N_2O_2$, the dihedral angle between the benzene and furan rings is 55.21(7)°. The benzamide fragment and furan ring are located on the opposite sides of the C=N bond, showing an E conformation. In the crystal, molecules are linked via intermolecular bifurcated (N,C)—H…O hydrogen bonds, generating an $R^1_2(6)$ ring motif, forming chains along the c axis. These chains are linked into a three-dimensional network by C—H…N and C—H…π interactions. The crystal structure of the title compound was characterized by X-ray studies and spectroscopic FTIR, ^{1}H and ^{13}C NMR techniques.*

INTRODUCTION

Schiff bases are a kind of versatile compounds, which possess excellent biological properties [1,2] and derived from an amino and carbonyl compound, are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively. In azomethine derivatives, the C=N linkage is essential for biological activity, several azomethines were reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities. Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical and biological activites [3]. Schiff bases and their complexes have a variety of applications in biological clinical and analytical fields. Recently there has been a considerable interest in the chemistry of hydrazine and hydrazone compounds because of their potential pharmacological applications [4]. These are also considered as popular ligands in co-ordination chemistry due to their ease of synthesis and their ability to be readily modified both electronically and sterically. We have synthesized a target compound, by the condensation of benzohydrazide with furfuraldehyde and its crystal structure has been determined and reported herein.

material and methods

General

Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded at 500 MHz respectively. Spectra were recorded in DMSO solution using residual solvent peak as the reference and coupling constants were measured in Hertz. Infrared spectrum was recorded on ShimadzuIR Affinity 1 spectrophotometer. For the crystal structure determination, the single-crystal of the compound $C_{12}H_{10}N_2O_2$ was used for data collection on a Bruker Kappa APEXII CCD diffractometer [5]. The MoKα radiation of wavelength, (λ = 0.71073 Å) and multi-scan technique for absorption were used for data collection. The lattice parameters were determined by the least-squares method on the basis of all reflections with $F^2>2\sigma$ (F^2).

Synthesis

The Benzohydrazide (3.4 g, 0.025 mol) was dissolved in 20 ml of ethanol and one pellet sodium hydroxide is added and stirred well for ½ h. After that time furfuraldehyde (2.4 ml, 0.025 mol) was added drop-wise and continuously stirred well in ice cold condition (-273K to 278K) for 2 h. The white precipitate obtained was filtered, dried and successively washed with petroleum ether and recrystallised from ethanol solution to obtain colourless blocks.

IR and NMR Spectra

IR (KBr, cm^{-1}): 3249(N-H), 3064 (C-H), 1642 (C=O), 1564 (C=C), 1544 (C=N), 1079 (C-O-C).

^{1}H NMR (500 MHz; DMSO, δ/ppm) : 6.64 (s, 1H, H$^{(3\ rd)}$ of furan), 6.94 (s, 1H, H H$^{(4\ th)}$ of furan), 7.53 (s, 1H, H$^{(5\ th)}$ of furan), 7.59 (d, 2H, Meta H of ph), 7.86 (s, 1H, para H of ph), 7.9 (s, 2H, ortho H of ph), 8.35 (s, 1H, C=N-), 11.7 (s, 1H, O=NH).

^{13}C NMR (500 MHz; DMSO, δ/ppm): 112,113 (furan ring), 138 (CH=), 128, 132, 133, 138 (ph ring), 149 (C_2 of furan ring), 163 (C=O).

X- ray Structure Determination

A suitable single crystal of dimensions 0.30X0.20X0.15 mm was selected for X- ray structure determination. The structures were solved by direct methods using SHELXS-97 and refined by a full-matrix least-squares procedure using the program SHELXL-97 [6]. The software used for Molecular graphics are ORTEP-3 for Windows [7] and PLATON [8]. The software used to prepare material for publication is WinGX publication routines [9].

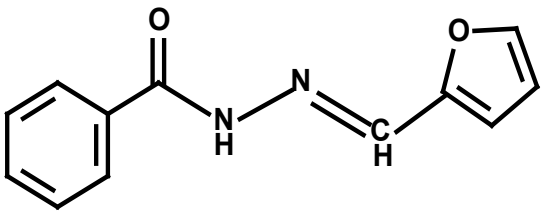
H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms: N—H=0.86 Å and C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C,N). Chemical structure of the title compound is shown in scheme 1**.** Molecular structure of the title compound showing the atomic numbering scheme is shown in Fig. 1. The crystallography details for the structures determination of the compound are displayed in

Volume : 3 | Issue : 12 | Dec 2013 | ISSN - 2249-555X

Table 1 and Hydrogen bond geometry are shown in Table 2 respectively.

RESULTS AND DISCUSSION

The chemical structure of the title compound as shown in scheme- 1.



Scheme 1. Chemical structure of the title compound.

Table 1. Crystal data and structure refinement parameters

Formula weight	214.22
Crystal shape, colour	block, colorless
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P b c a
Unit cell dimensions	a = 9.4339(10) Å b = 9.6549(9) Å c = 23.418(3) Å
Volume	2133.0(4) $Å^3$
Z	8
Density (calculated)	1.334 Mg/m^3
Absorption coefficient	0.09 mm^{-1}
F(000)	896
Crystal size	0.30x0.20x0.15 mm
Theta range for data collection	1.7° to 25.2°
Index ranges	-11 ≤ h ≤ 11 -6 ≤ k ≤ 11 -28 ≤ l ≤ 27
Reflection collected	10001
Completeness to theta	25.2°
Max. and min transmission	0.986 and 0.972
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1920/0/145
Goodness-of-fit on F^2	1.036
Final R indices [I >2sigma(I)]	R_1=0.0407 wR_2= 0.1359
R indices (all data)	R_1=0.0610 wR_2= 0.1096
Largest diff. peak and holes	0.20 e.$Å^{-3}$, and -0.26 e.$Å^{-3}$

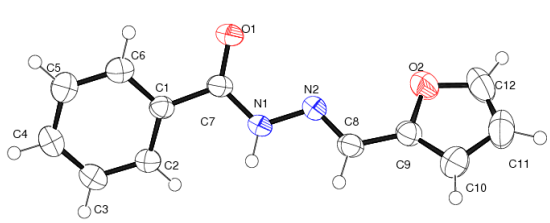


Fig. 1. The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

The title compound, $C_{12}H_{10}N_2O_2$, crystallized in an orthorhombic system, space group pbca with a = 9.4339 (10) Å, b = 9.6549 (9) Å, c = 23.418 (3) Å, V = 2133.0 (4) $Å^3$, Z = 8, F(000) = 896, *D*x = 1.334 Mg m−3, R= 0.041 and wR= 0.136, T = 293 K. The dihedral angle between the benzene ring (C1-C6) and the furan ring (C9—C12/O2) in the Schiff base molecule is 55.21(7)°, indicating that the two aromatic ring planes are not coplanar. This molecules adopts an E conformation with respect to the C8=N2 bond [N1—N2—C8—C9 = -179.7(15)°] and it exists in the amido form with a C7=O1 bond length of 1.2245(21) Å which is very close to the reported C=O bond length of similar structure [10-12]. The O1 and N2 atoms are in a Z conformation with respect to C7—N1 bond. Atom O1, C7, N1, N2 and C8 of the middle bridge lie nearly on the same plane with the torsion angle O1—C7—N1—N2 = -2.8(24)°. The mean plane through this middle bridge makes the dihedral angles of 24.26(8) and 31.86(10)° with benzene and furan rings, respectively.

Table 2. Hydrogen bonds geometry(Å, °)

D—H...A	D—H	H...A	D...A	D—H…A
N1—H1A···O1^{i}	0.86	2.11	2.9483 (19)	164
C2—H2···N2^{i}	0.93	2.58	3.372 (2)	143
C8—H8···O1^{i}	0.93	2.59	3.359 (2)	141
C12—H12···N2^{ii}	0.93	2.58	3.495 (3)	167
C10—H10…Cg (2)^{iii}	0.93	2.86	3.508 (2)	128

Symmetry codes:
(i) -*x*+1/2, *y*-1/2, *z*;

(ii) *x*+1/2, -*y*+1/2, -*z*;

(iii) 1+x, y, z.

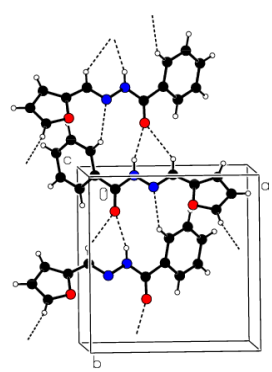


Fig. 2. Crystal packing of the title compound viewed down the c-axis showing $R_2^1(6)$ ring motif.

In the crystal packing as shown in Fig. 2, molecules are linked via intermolecular bifurcated N1—H1A…O1 and C8—H8…O1 acceptor bonds, generating an $R_2^1(6)$ ring motif [13], to form one-dimensional chains along the c-axis. These chains are linked into a three-dimensional network by C3—H3…N2 and C12—H12…N2 hydrogen bonds along b-axis as shown in Fig. 3 and Table 2.

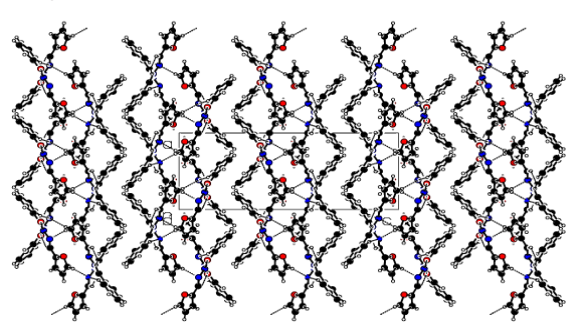


Fig. 3. Crystal packing of the title compound viewed down the b-axis showing the N—H…O, C—H…O and C—H…N interactions with dashed lines.

Volume : 3 | Issue : 12 | Dec 2013 | ISSN - 2249-555X

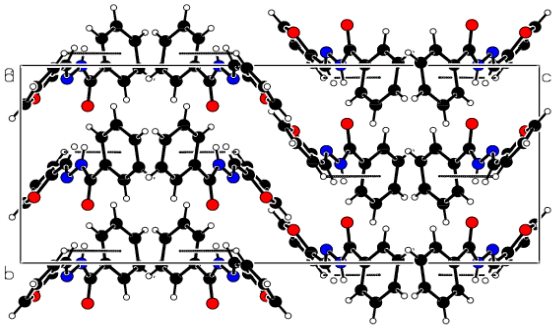


Fig. 4. The molecular interaction showing the weak C---H...π interactions and viewed along the a-axis. Cg is a centroid of C1-C6 ring.

The structure is further stabilized by C—H…π [3.508 (2) Å] hydrogen bonding interactions, as shown in Fig. 4.

CONCLUSIONS

The crystal structure of the title compound has been characterized by single crystal X-ray diffraction method and spectroscopic FTIR, ^{1}H and ^{13}C NMR techniques. The synthesized schiff base derivative may be used as a building block in medicinal and food industry.

SUPPLEMENTARY DATA

CCDC 935556 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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REFERENCE [1]Zhou, C., and Yang, T. (2009), "Crystal structure of 2-nitro-N'-(5-bromo-2-methoxybenzylidene)benzohydrazide, C15H12BrN3O4." Z. Kristallograhy, NCS, 224, 39-40. | [2] Hao, Y. –M. (2011), " Crystal structure of 2-chloro-N'-(2-hydroxy-3,5-dichlorobenzylidene)- benzohydrazide—methanol (1:1), C14H9Cl3N2O2 • CH3OH." Z. Kristallography, NCS, 226, 47-48. | [3]Mishra, A. P., and Soni, M. (2008), "Synthesis, Structural, and Biological Studies of Some Schiff Bases and Their Metal Complexes." Hindawi Publishing Corporation, Article ID 875410, 7 pages. | [4]Prakash, A., and Adhikari, D. (2011), " Application of Schiff bases and their metal complexes- a review." International journal of chemtech research. 3:1891-1896. | [5]Bruker, APEX2 and SAINT-plus, Bruker AXS Inc., Madison, 2004. | [6]Sheldrick, G. M. (1997), " SHELXS-97 and SHELXL-97." Program for Crystal structure solution and refinement, University of Gottingen. | [7]Farrugia, L. J. (1997), "ORTEP-3 for Windows- A version of ORTEP-III with a Graphical User Interrface (GUI)." Journal of Applied Ctytallography, IUCR, 30, 565. | [8] Spek , A. L. (2009), " Structure Validation in Chemical Crytallography." Acta Crystallography, IUCR, D 65:148-155. | [9] Farrugia, L. J. (1999), " WinGX Suite for small-Molecule Single-Crystal Crystallography." Journal of Applied Crystallography, IUCR, 32:837-838. | [10]Hua, N. H., and Shi, Y. L. (2009), " (E)-4-Methyl-N'-(3-nitrobenzylidene)-benzohydrazide." Acta Crystallography, IUCR, E68:o1613. | [11]Shan, S., Yan, L. H., Han, Q. G., Deng, F. L. and Jian, S. (2011), " (E)-N'-[1-(Thiophen-2-yl)ethylidene]-benzohydrazide." Acta Crystallography, IUCR, E67:o2498. | [12]Zhong, F. S., and Jia, M. L. (2012), "(E)-4-Amino-N'-(2-nitrobenzylidene)benzohydrazide." Acta Crystallography, IUCR, E68:o1726. | [13] Bernstein, J., Davis, R. E., Shimoni, L., and Chang, N. L.(1995), " Angew. Chem. Int. Ed. Engl." B34: 1555-1573.