J Chem Crystallogr (2010) 40:927–932
DOI 10.1007/s10870-010-9765-z

ORIGINAL PAPER

Synthesis, Spectral and Structural Studies of a Novel Semicarbazone Synthesized from Quinoline-2-Carboxaldehyde and N^4-Phenyl-3-Semicarbazide

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Received: 21 October 2008 / Accepted: 7 May 2010 / Published online: 30 May 2010

Abstract A new semicarbazone, HL has been synthesized from quinoline-2-carboxaldehyde and N^4-phenyl-3-semicarbazide and structurally and spectrochemically characterized. ^{1}H NMR, ^{13}C NMR, IR and electronic spectra of the compound are studied. The existence of keto form in the solid state is supported by the crystal structure and IR data. The compound crystallizes into an orthorhombic space group $P2_12_12_1$. Intra and intermolecular hydrogen bonding interactions facilitates unit cell packing in the crystal lattice.

Keywords Crystal structure · IR spectra · Quinoline-2-carboxaldehyde · Semicarbazone

Introduction

Semicarbazones are compounds with versatile structural features and can coordinate to the metal either as a neutral or a deprotonated anion. The coordinating ability of semicarbazones is attributed to the extended delocalization of electron density over the NH–C(O)–NH–N= system, which is enhanced by the substitution at the N^4 position [1]. The biological applications of these compounds are due to their ability to form metal complexes [2]. It was reported that aryl semicarbazones were devoid of sedative hypnotic activity and exhibited anticonvulsant activity with less neurotoxicity [3]. Semicarbazones are also used as protected carbonyl compounds in synthesis [4]. Several semicarbazones and its metal complexes have been the subject of chemical and structural studies [5]. Semicarbazones have been known as anti-cancer and anti-viral agents for many years [6]. Semicarbazones exist in two tautomeric forms, keto (A) and enol (B) forms (Scheme 1). The keto form functions as bidentate neutral ligand and the enol form can deprotonate and act as anionic ligand. Here we report the structural and spectral perspectives of a new compound, quinoline-2-carboxaldehyde N^4-phenylsemicarbazone, HL (Figure 1).

Experimental

Synthesis of Quinoline-2-Carboxaldehyde-N^4-Phenylsemicarbazone (HL)

The synthesis of HL is given in Scheme 2. A methanolic solution of quinoline-2-carboxaldehyde (0.157 g, 1 mmol) was mixed with N^4-phenylsemicarbazide (0.151 g, 1 mmol) in methanol and 3 drops of glacial acetic acid. The reaction mixture was refluxed for 2 h. On slow evaporation, colorless crystalline compound formed was filtered, washed with ether and dried over P_4O_{10} in vacuo. Single crystals of HL suitable for X-ray analysis were obtained from its solution in 1:1 (v/v) mixture of methanol and DMF. Yield: $\sim$0.5 g. Elemental analysis, found (calculated): C 70.13 (70.33); H 4.99 (4.86); N 19.22 (19.30). IR (cm^{-1}): 3380 ν_a(N–H), 1702 ν(C=O), 1592 ν(C=N).

Materials and Physical Measurements

Commercial reagents, quinoline-2-carboxaldehyde (Aldrich) and N^4-phenylsemicarbazide (Aldrich) were used as received. Elemental analyses were carried out using a Vario EL III

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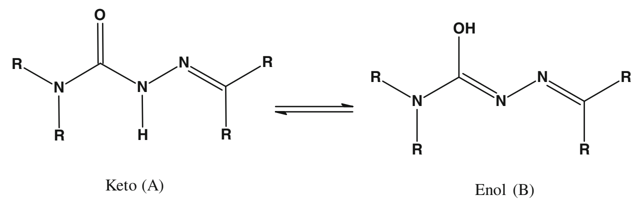


Scheme 1

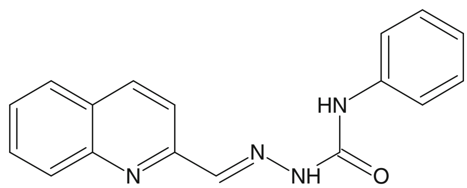


Fig. 1 Quinoline-2-carboxaldehyde-N^4-phenyl-3-semicarbazone, HL

CHNS analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a JASCO FT-IR-5300 spectrometer in 4000–400 cm^{-1} range using KBr pellets. Electronic spectra were recorded on a Cary 5000 Version 1.09 UV-VIS-NIR spectrophotometer using solution in DMF. The ^{1}H and ^{13}C NMR spectra were recorded using Bruker DRX 500 with $CDCl_3$ as solvent and TMS as standard at the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India.

X-ray Crystallography

The crystallographic data and structure refinement parameters of compound HL are given in Table 1. A crystal with approximate dimensions 0.36 × 0.23 × 0.21 mm^3 was selected and was found to be orthorhombic with a space group $P2_12_12_1$. X-ray diffraction measurements were carried out on CRYSALIS CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. The program CRYSALIS RED was used for data reduction and cell refinement. The structure was solved by direct methods and refined by least-square on F_0^2 using SHELXL-97 [7]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except those attached to nitrogens were geometrically fixed at calculated positions. Those on nitrogen atoms were refined from Fourier maps. Refinement of F^2 was done against all reflections. All esds, expect the esd in the dihedral angle between two least square planes, are estimated using the full Covariance matrix. Flack x parameter is 0(2). As this value is 0, with small standard uncertainty, the absolute structure given by the structure refinement is likely correct [8]. The molecular graphics employed were DIAMOND version 3.1d [9] and PLATON [10]. The final refinement cycle was based on all 2488 independent reflections and 207 variables with R1 = 0.0628 and wR2 = 0.0834.

Table 1 Crystal data and structure refinement parameters of HL

CCDC no.	689742
Empirical formula	$C_{17}H_{14}N_4O$
Formula weight	290.32
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 6.4662(3) Å
	b = 10.3994(5) Å
	c = 21.0315(11) Å
	α = 90°
	β = 90°
	γ = 90°
Volume	1414.25(12) $Å^3$
Z	4
Density (calculated)	1.364 Mg/m^3
Absorption coefficient	0.089 mm^{-1}
F(000)	608
Crystal size	0.36 × 0.23 × 0.21 mm^3
θ range for data collection	3.30°–25.00°
Reflections collected	12679
Independent reflections	$-7 \leq h \leq 7$, $-12 \leq k \leq 12$, $-25 \leq l \leq 21$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2488/0/207
Goodness-of-fit on F^2	1.019
Final R indices [I > 2σ(I)]	R1 = 0.0427, wR2 = 0.0754
R indices (all data)	R1 = 0.0628, wR2 = 0.0834

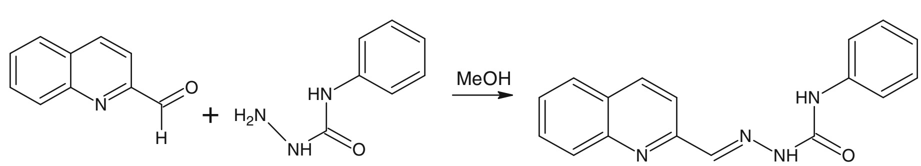
$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Results and Discussion

Crystal Structure

The molecular structure of HL along with the atom numbering scheme is given in Fig. 2 and selected bond lengths

Scheme 2



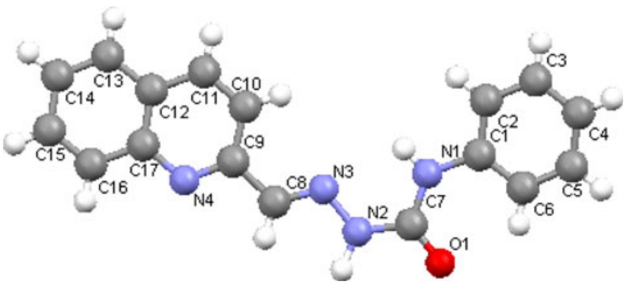


Fig. 2 Molecular structure of HL

Table 2 Selected bond lengths (Å) and bond angles (°) of HL

Bond lengths	Bond angles
C(1)–N(1) 1.422(3)	O(1)–C(7)–N(1) 125.4(2)
C(7)–O(1) 1.222(3)	O(1)–C(7)–N(2) 119.5(2)
C(7)–N(1) 1.353(3)	N(1)–C(7)–N(2) 115.0(2)
C(7)–N(2) 1.376(3)	N(3)–C(8)–C(9) 121.1(2)
C(8)–N(3) 1.282(3)	C(7)–N(2)–N(3) 121.2(2)
C(8)–C(9) 1.469(3)	C(8)–N(3)–N(2) 114.3(2)
N(2)–N(3) 1.378(3)	C(9)–N(4)–C(17) 118.1(2)

and angles are given in Table 2. The compound crystallizes into an orthorhombic space group $P2_12_12_1$. The molecule is almost planar and exists in the *E* configuration with respect to C8=N3 bond. A torsion angle value of 179.5(2)° corresponding to O(1)–C(7)–N(2)–N(3) moiety confirms the trans configuration of the O(1) atom with respect to hydrazine nitrogen atom N(3). The C(8)–N(3) bond distance [1.282(3) Å] is appreciably close to that of C=N double bond [1.28 Å], [11] confirming the azomethine bond formation. The existence of semicarbazone in the keto form in the solid state is evidenced by the C(7)–O(1) bond distance of 1.222(3) Å, which is very close to a formal C=O bond length [1.21 Å]. However, the N(3)–N(2) [1.379(3)] and N(2)–C(7) [1.376(3)] bond distances are intermediate between the ideal values of corresponding single [N–N; 1.45 and C–N; 1.47] and double bonds [N=N; 1.25 and C=N; 1.28], which is in support of an extended π delocalization along the semicarbazone chain [12, 13].

Figure 3 shows the packing diagram of HL. The assemblage of molecules in the respective manner in the unit cell is resulted by the π–π, C–H···π and hydrogen bonding interactions. The centroid Cg(1) is involved in π–π interaction with Cg(2) of the neighbouring molecule at a distance of 4.5426 Å and a C–H···π interaction, C(14)–H(14) → Cg(3) at a distance of 2.67 Å contribute stability to the unit cell packing. The unit cell comprises of four molecules. The crystal structure is stabilized by intra and intermolecular hydrogen-bonding and the molecules are arranged in opposite manner. Two prominent intramolecular hydrogen-bonding interactions, viz. N(1)–H(1)···N(3) and C(6)–H(6)···O(1) led to the formation of one-five-membered ring and one-six-membered ring comprising of atoms N(3), N(2), C(7), N(1), H(1)N and O(1), C(7), N(1), C(1), C(6), H(6)C respectively [14, 15]. An intermolecular hydrogen-bonding, N(2)–H(2)···N(4) at a N(2)–N(4) distance of 3.028(3) Å also supports the present conformation of the semicarbazones (Table 3; Fig. 4).

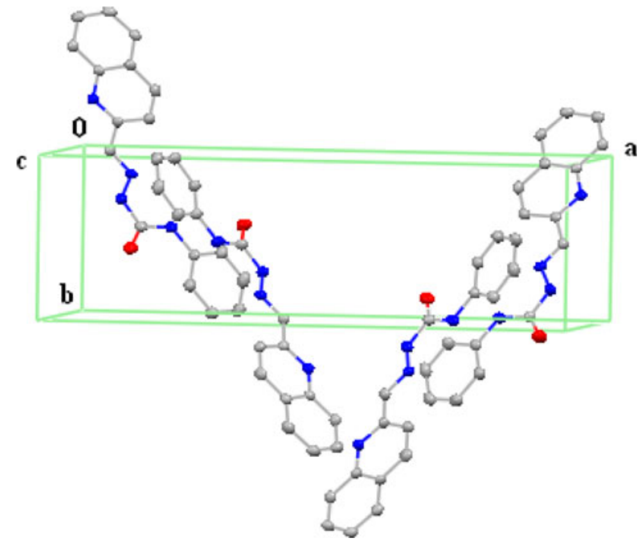


Fig. 3 Molecular packing diagram of HL, the unit cell is viewed down the c axis

Table 3 Interaction parameters of the compound HL

Cg(I)···Cg(J)	Cg–Cg (Å)		α°	β°
$\pi\cdots\pi$ interactions[A]				
Cg(1)···Cg(2)[a]	4.5426		14.60	51.04
Cg(2)···Cg(1)[b]	4.5426		14.60	37.25
XH(I)···Cg(J)	H···Cg (Å)		X–H···Cg (°)	X···Cg (Å)
CH···π interactions[B]				
C(14)–H(14)···Cg(3)[c]	2.67		146	3.498
D–H···A	D···H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
Hydrogen-bonding[C]				
N(1)–H(1)···N(3)	0.860(3)	2.280(3)	2.662(3)	107(2)
C(6)–H(6)···O(1)	0.950	2.230	2.848(3)	122
N(2)–H(2)···N(4)[d]	1.04(3)	1.99(3)	3.028(3)	173(2)

[A] Equivalent position code: a = 1 + *x*, *y*, *z*; b = −1 + *x*, *y*, *z*. Cg(1) = N(4), C(9), C(10), C(11), C(12), C(17); Cg(2) = C(1), C(2), C(3), C(4), C(5), C(6). α = Dihedral angle between planes 1 and 2(°). β = Angle Cg(1) –> Cg(2) or Cg(1) –> Me vector and normal to plane 1 (°)

[B] Equivalent position code: c = 1/2 + *x*, 1/2−*y*, 1 − *z*. Cg(3) = C(12), C(13), C(14), C(15), C(16), C(17)

[C] D = donor, A = acceptor, Equivalent position code: d = −1/2 + *x*, −1/2−*y*, 1 − *z*

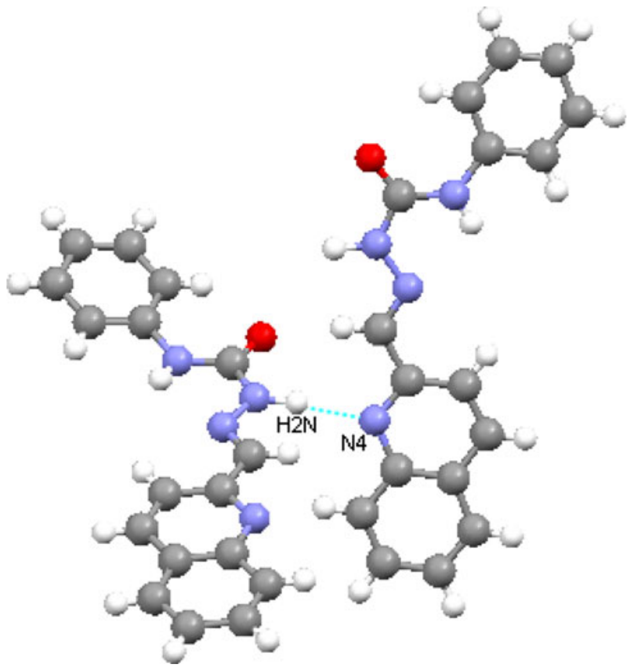


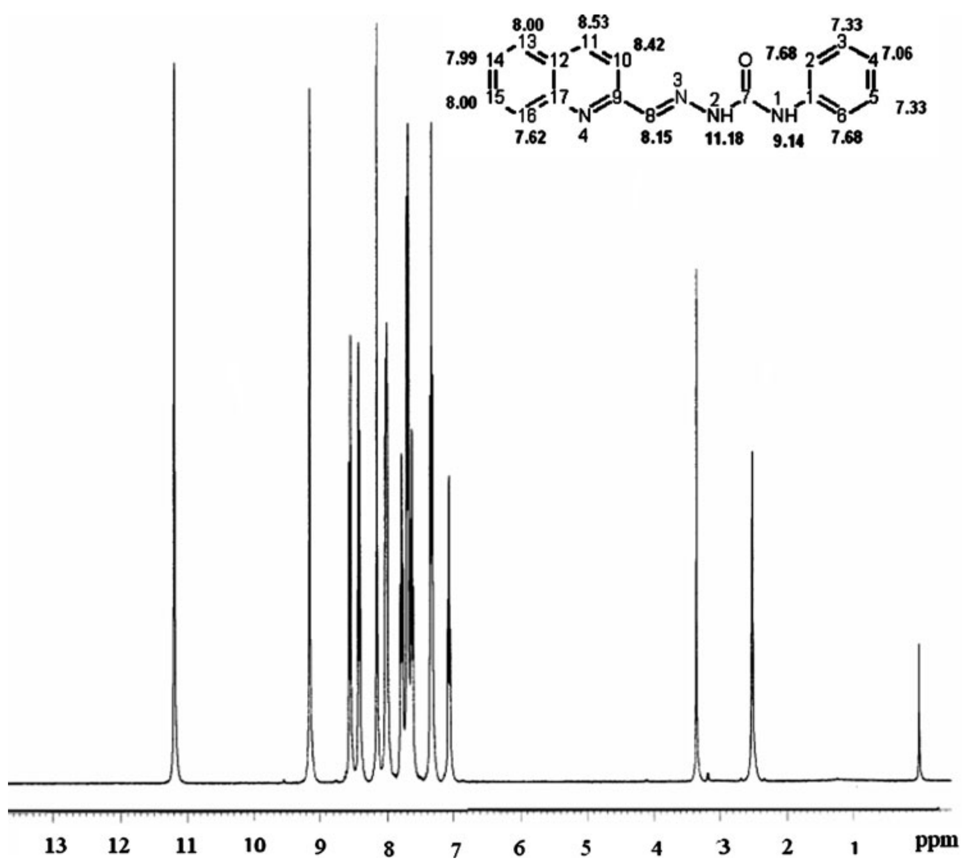
Fig. 4 Intermolecular hydrogen bonding interaction

Spectral Studies

The ^{1}H NMR spectrum of the compound along with the spectral assignments is given in Fig. 5. The signals at $\delta = 11.187$ and 9.141 ppm are assigned to ^{2}NH and ^{1}NH protons respectively. These protons are shifted downfield because they are attached to hetero atoms and so are easily subjected to hydrogen bonding and are decoupled by the electrical quadrupole effects. The protons attached to ^{2}N and ^{1}N appear as singlets as expected since these NH protons are decoupled from the nitrogen atoms and the protons from the adjacent atoms. Absence of any coupling interactions by C(8)H proton due to availability of protons on neighbouring atoms render singlet peak at $\delta = 8.157$ ppm. Two doublets at $\delta = 8.537$ and 8.423 ppm are assigned to the C(11)H and C(10)H protons. At $\delta = 8.007$, we got a quartet which is assigned to be a merged form of one triplet and a doublet corresponding to C(15)H and C(13)H protons. Another triplet at $\delta = 7.998$ ppm is assigned to C(14)H proton. The resonances for the C_6H_5-group appear as a doublet at $\delta = 7.685$ ppm (ortho) and as triplets at $\delta = 7.334$ and 7.060 ppm corresponding to meta and para phenyl protons. All the assignments made above are in good agreement with previous reports [16, 17] (Fig. 5).

^{13}C NMR spectrum of ligand HL was recorded in $CDCl_3$. The proton decoupled ^{13}C spectrum of the compound contains 15 peaks corresponding to the 15 magnetically unique carbon atoms. The signals from ^{13}C spectrum are much weaker than that of the corresponding proton

Fig. 5 ^{1}H NMR spectrum



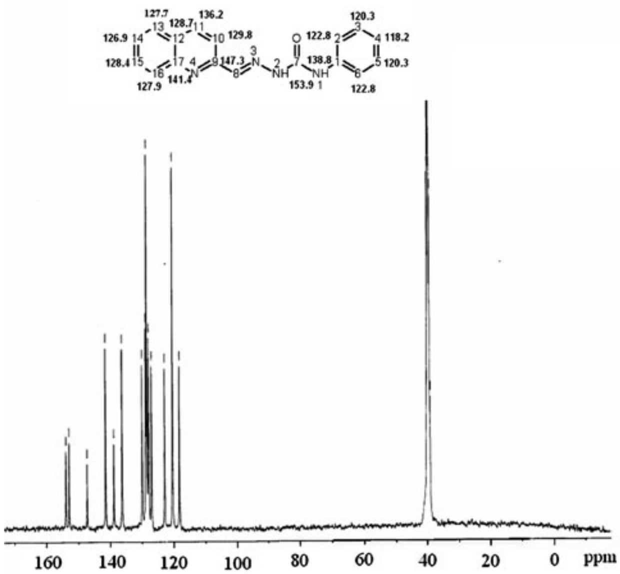


Fig. 6 ^{13}C NMR spectrum

NMR spectrum. Assignment of different resonant peaks to respective carbon atoms is presented in Fig. 6. The peaks at 152.863, 147.314 and 141.422 ppm correspond to the C(8), C(9) and C(17) carbon atoms respectively. The carbon atom at para position to the heteroatom viz. C(11) resonate at lower field value when compared to the meta positioned carbon atom C(10). The non-protonated carbon C(7) is showing more downfield shift due to increased electron density resulting from the presence of electronegative oxygen and conjugative effect of the N(3)–N(2)–C(O)–N(1)– semicarbazone skeleton. The ^{13}C peaks are assigned as follows. C(1), 138.857 ppm; C(2), 122.810 ppm; C(3), 120.326 ppm; C(4), 118.205 ppm; C(5), 120.326 ppm; C(6), 122.810 ppm; C(7), 153.900 ppm; C(8), 152.863 ppm; C(9), 147.314 ppm; C(10), 129.895 ppm; C(11), 136.245 ppm; C(12), 128.751 ppm; C(13), 127.763 ppm; C(14), 126.989 ppm; C(15), 128.458 ppm; C(16), 127.924 ppm; C(17), 141.422 ppm. The downfield shift of C(8) carbon is due to the π electron delocalization on the C(8)=N(3) bond [18] (Fig. 6).

The IR spectrum of the compound HL was recorded as KBr pellets in the 4000–400 cm^{-1} range. A medium band observed at 3380 cm^{-1} is assigned to the ν_a(NH) of the imino group. The presence of a band at 1702 cm^{-1} assigned to ν(CO) stretching vibration which reveals the presence of only keto form in the solid state. The azomethine stretching vibrations are observed at 1592 cm^{-1}. A band at 1526 cm^{-1} due to the interactions between N–H bending and C–N stretching vibrations of the C–N–H group of the amide function [19]. A weak band at 1269 cm^{-1} also results from the N–H bending and C–N stretching interactions. The spectrum of the compound, HL has a band at 1150 cm^{-1}is due to ν(N–N). The bands at 1225 and 1113 cm^{-1} correspond to the in-plane vibrations of the quinoline ring while the out-of-plane vibrations are observed at 749 and 689 cm^{-1} [20, 21].

Electronic spectrum of the ligand in DMF shows bands at 31400 and 29900 cm^{-1} which are assigned to the n-π^* of azomethine and carbonyl groups of semicarbazone moiety respectively. The band observed at 36900 cm^{-1} is attributed to intraligand π–π^* transition of the imine function of the semicarbazone moiety [22].

Supplementary Material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data center, CCDC 689742 for compound **HL**. Copies of this information may be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2, IEZ, UK; Fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk

Acknowledgements M.R.P. Kurup is thankful to the Council of Scientific & Industrial Research, New Delhi, India for the financial assistance. The authors are thankful to the National Single Crystal X-ray diffraction Facility, IIT, Bombay, India for providing single crystal XRD data.

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