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Synthesis, spectral characterization and crystal structure of 2-benzoylpyridine *N*(4)-cyclohexylthiosemicarbazone

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Abstract

The synthesis, characterization, molecular and crystal structure of 2-benzoylpyridine *N*(4)-cyclohexylthiosemicarbazone is reported. IR analysis was done and NMR assignments using COSY homonuclear and HMQC heteronuclear correlation techniques were carried out. The electronic structure of the compound was revealed by solid state reflectance studies and in chloroform solution. The infrared spectrum gives evidence for the compound in the thione form, which is consistent with the observed bond lengths from the crystal structure. The compound crystallizes into a monoclinic lattice with space group $P2_1/n$. The non-coplanarity of the two benzene rings in the compound is confirmed from the dihedral angles. Puckering analysis and least square planes calculations point out to chair conformation of the cyclohexyl ring.

Keywords: Thiosemicarbazone; 2-Benzoylpyridine; ^{1}H NMR; ^{13}C NMR; COSY; HMQC; Crystal structure

1. Introduction

Thiosemicarbazones are thiourea derivatives and the studies on their chemical and structural properties have received much attention due to the widespread application in the chemotherapeutic field [1,2]. Thiosemicarbazones, with the general formula $R^1R^2C=N-NH-CS-NR^3R^4$ usually react as chelating ligands with transition metal ions by bonding through the sulphur and the hydrazinic nitrogen atom. The group N–C=S is of considerable chemotherapeutic interest and is responsible for the pharmacological activity. Thiosemicarbazones of α-(*N*)-heterocyclic aldehydes and ketones possess a broad spectrum of potentially useful chemotherapeutic activities such as antimalarial, antibacterial, antiviral and antileishmanial activities [3,4]. We have recently reported spectral and structural studies of copper(II) complexes of 2-benzoylpyridine *N*(4), *N*(4)-(butane-1,4-diyl)thiosemicarbazone [5]. Thiosemicarbazones derived from 2-acetylpyridine have been extensively studied [6–10], but there are fewer reports on the studies of *N*(4)-substituted 2-benzoylpyridine thiosemicarbazones and their metal complexes [11–13]. Thiosemicarbazones exist in the tautomeric thione (A) and thiol (B) forms (Fig. 1).

The thione form acts as a neutral bidentate ligand while the thiol form can deprotonate and act as an anionic ligand [14]. As a part of our studies on *N*(4)-substituted thiosemicarbazones [15–24], we now report the spectral and crystal studies of 2-benzoylpyridine *N*(4)-cyclohexylthiosemicarbazone (Fig. 2).

2. Experimental

2.1. Materials

Cyclohexyl isothiocyanate (Fluka), hydrazine hydrate (Lancaster) and 2-benzoylpyridine (Lancaster) were used as received. Carbon, hydrogen and nitrogen analyses were done on a Heraeus elemental analyzer at Central Drug Research Institute, Lucknow, India. The infrared spectra were recorded on a Shimadzu DR 8001 series FTIR instrument as KBr pellets in the range 4000–400 cm^{-1}. The ^{1}H NMR, ^{13}C NMR, COSY and HMQC spectra were

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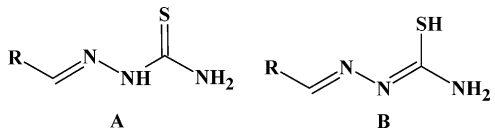

Fig. 1. Tautomers of thiosemicarbazone.

recorded using Bruker DRX 500, with $CDCl_3$ as solvent and TMS as standard at Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India. The solid state reflectance spectrum was recorded on Ocean Optics, SD2000 Fiber Optic Spectrometer. The electronic spectrum in $CHCl_3$ solution was recorded on a Shimadzu 160A UV/Vis Spectrophotometer.

2.2. X-ray data collection, structure solution and refinement

Slow evaporation of the ligand in methanol yielded single crystals suitable for X-ray analysis. A pale yellow crystal of HL was mounted on a glass fiber with epoxy cement for the crystallographic study. The crystallographic data and structure refinement parameters for the compound at 293 K are given in Table 1. The data were collected using a SMART CCD diffractometer equipped with graphite-monochromated Mo Kα radiation, with a detector distance of 5 cm and swing angle of $-35°$. A hemisphere of the reciprocal space was covered by combination of three sets of exposures. Each set had a difference of angle (0, 88, 180°) and each exposure of 10 s covered 0.3° in ω. The structures were solved by direct methods and refined by least-square on F_0^2 using the SHELXTL software package [25]. The collected data were reduced using SAINT program [26] and the empirical absorption were carried out using the SADABS program. The graphics tool was PLATON for windows [27]. All the hydrogen atoms were fixed geometrically and treated as riding on their parent C and N atoms, with C–H distances in the range 0.87–1.08 Å. The non-hydrogen atoms were refined with anisotropic thermal parameters. The selected bond lengths and bond angles are listed in Table 2.

2.3. Synthesis of HL

The thiosemicarbazone (HL) was prepared by adopting the reported procedure of Klayman [28]. Cyclohexyl isothiocyanate (0.706 g, 5 mmol) and hydrazine hydrate (0.250 g, 5 mmol), each dissolved in 10 ml methanol were mixed with constant stirring. The stirring was continued for 30 min and the white product, *N*(4)-cyclohexylthiosemicarbazide formed was washed with methanol and dried. A solution of the *N*(4)-cyclohexylthiosemicarbazide (0.865 g, 5 mmol) in 10 ml methanol was refluxed with a

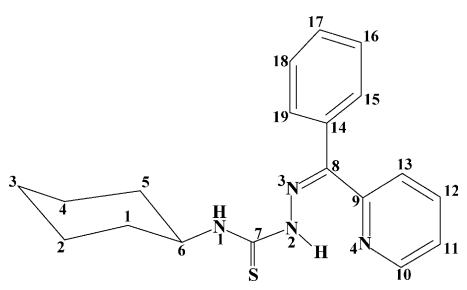

Fig. 2. Structure of compound *N*(4)-cyclohexylthiosemicarbazone (HL).

Table 1
Summary of crystal data and structural refinement for HL

Empirical formula	$C_{19}H_{22}N_4S$
Formula weight (M)	338.47
Temperature (*T*) (K)	293(2)
Wavelength (Mo Kα) (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Lattice constants	
a (Å)	6.1522(3)
b (Å)	17.9701(8)
c (Å)	16.9023(7)
α (°)	90.00
β (°)	94.423(1)
γ (°)	90.00
Volume *V* (Å^3)	1863.08(15)
Z	4
Calculated density (ρ) (mg m^{-3})	1.207
Absorption coefficient (μ) (mm^{-1})	0.181
F(000)	720
Crystal size (mm)	0.86 × 0.38 × 0.32
Θ Range for data collection	2.42–28.30
Limiting indices	$-7 = h = 8$, $-19 = k = 23$, $-22 = l = 21$
Reflections collected	4559
Unique reflections	3581 ($R_{int} = 0.0169$)
Completeness to θ	28.29 (91.1%)
Max. and min. transmission	0.9444 and 0.8599
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4559/0/297
Goodness-of-fit on F^2	1.047
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0452$, $wR_2 = 0.1228$
R indices (all data)	$R_1 = 0.0587$, $wR_2 = 0.1374$
Largest difference peak and hole (eÅ^{-3})	0.298 and −0.233

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

C(1)–C(6)	1.499(3)	N(1)–C(6)–C(5)	109.43(14)
C(5)–C(6)	1.525(2)	N(1)–C(6)–C(1)	111.57(15)
C(6)–N(1)	1.452(19)	C(6)–N(1)–C(7)	125.92(13)
C(7)–N(1)	1.328(19)	N(1)–C(7)–S(1)	125.62(11)
C(7)–S(1)	1.675(15)	N(2)–C(7)–S(1)	118.87(11)
C(7)–N(2)	1.364(18)	N(1)–C(7)–N(2)	115.51(13)
N(2)–N(3)	1.367(17)	N(2)–N(3)–C(8)	120.14(12)
C(8)–N(3)	1.290(18)	N(3)–C(8)–C(9)	126.94(13)
C(8)–C(14)	1.489(2)	C(9)–C(8)–C(14)	118.95(12)
C(8)–C(9)	1.488(2)	N(4)–C(9)–C(8)	118.25(13)
C(9)–N(4)	1.345(2)	C(8)–C(9)–C(13)	120.04(14)
C(10)–N(4)	1.337(2)	N(4)–C(9)–C(13)	121.62(14)
C(9)–C(13)	1.391(2)	C(8)–C(14)–C(19)	119.82(13)
C(14)–C(15)	1.393(2)	C(8)–C(14)–C(15)	121.17(14)
C(14)–C(19)	1.384(2)	C(15)–C(14)–C(19)	118.99(14)

methanolic solution of 2-benzoylpyridine (0.916 g, 5 mmol) continuously for 5 h after adding 1–2 drops of acetic acid. On cooling the solution pale yellow crystals separated, which were filtered and washed with methanol. The crystals were recrystallised from ethanol and dried over P_4O_{10} in vacuo. (m.p. 170 °C). Yield 1.425 g (80%). The empirical formula given for the compound $C_{19}N_4H_{22}S$ was confirmed by elemental analysis: found (calcd): C, 67.63 (67.45); H, 6.70 (6.50); N, 16.54 (16.57).

3. Results and discussion

3.1. Spectral studies

In the solid state reflectance spectrum of HL, bands observed at 34,730 and 28,730 cm^{-1} are assigned to the thiosemicarbazone moiety and the $n \rightarrow \pi^*$ transitions of the pyridyl ring, respectively [29], whereas the $\pi \rightarrow \pi^*$ transitions are observed at 38,610 cm^{-1} (Fig. 3). In the spectra from DMF solution, these bands are shifted in energy to 34,810, 29,410 and 39,010 cm^{-1} having log ε values 4.13, 3.32 and 4.20, respectively.

The IR spectrum of HL (Fig. 4) shows a broad band at 3334 cm^{-1} corresponding to the NH moiety linked to the cyclohexyl group. The other bands observed in the spectrum at 833 and 1582 cm^{-1} are due to ν(C=S) and ν(C=N), respectively, whereas the band at 1435 cm^{-1} is due to the cyclohexane ring [8,30]. A ring deformation band of pyridine is observed at 607 cm^{-1}. The absence of ν(S–H) band around 2700 cm^{-1} suggests that HL remains in the thione form in the solid state [31,32]. This thiosemicarbazone is found to act as a tridentate ligand in its copper(II) complexes [33].

The one-dimensional and two-dimensional nuclear magnetic resonance spectra are used in resolving the carbon and hydrogen atoms. The ^1H resonances were assigned on the basis of the chemical shift values,

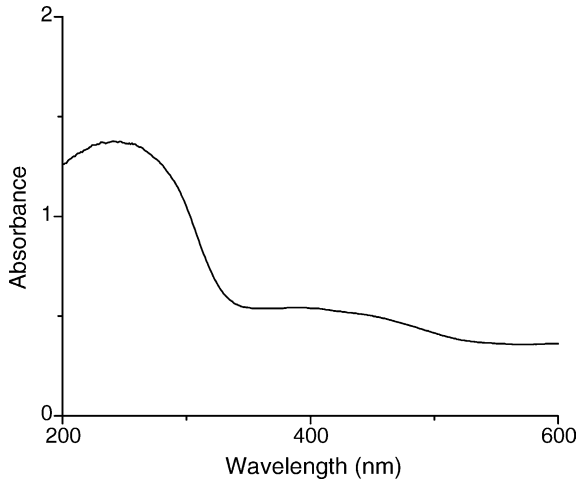

Fig. 3. Electronic spectrum of HL.

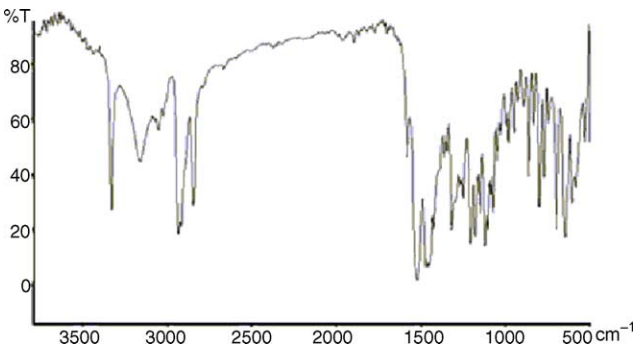

Fig. 4. IR spectrum of HL.

multiplicities and coupling constants and connectivity from ^1H and ^1H–^1H correlation experiments [31,34]. These give insight into the average effective magnetic fields present, interaction of the nuclear spin with the adjacent atoms and the number of equivalent protons.

The NMR spectral assignments are given in Figs. 5–7. The ^1H NMR spectrum reveals four signals for the pyridyl moiety, multiplet for the phenyl moiety and seven well resolved peaks for the cyclohexyl moiety. The signals at $\delta = 13.48$ and 7.63 ppm are assigned to the ^{2}NH and ^{1}NH protons, respectively. The intensity of these peaks decreases on addition of D_2O, which suggests that they are easily exchangeable. These protons are shifted downfield because they are attached to heteroatoms and so are easily subjected to hydrogen bonding and are decoupled by the electrical quadrupole effects. The proton attached to ^{2}N appears as singlet as expected since the NH protons are decoupled from the nitrogen atoms and the protons from the adjacent atoms. But contrary to this, ^{1}NH shows coupling with the adjacent hydrogen H6 and hence give a doublet. This coupling is clear in COSY, which can be attributed to the low NH exchange rate. The peak at 8.80 ppm is assigned to be due to the H10 proton. This proton is very sensitive to the electron densities as it is close to the pyridyl nitrogen and is observed to be deshielded due to the electronic effect of the phenyl ring. The phenyl moiety appears as a multiplet at about 7.45 ppm where the chemical shift values are very close, hence very difficult to be resolved. The complexity of the COSY predicts that the spectrum is not strictly of the first order. The peak (7.3 ppm) corresponding to the solvent ($CDCl_3$) appears to be superimposed with that of the phenyl protons. The cyclohexyl moiety forms a chair conformation and hence the hydrogens exist in two different electronic environments, viz. axial and equatorial, and hence give seven well-resolved peaks. The equatorial protons 2.08 ppm (H5e) are found to resonate at a slightly higher frequency compared to that of the axial protons 1.27 ppm (H5a). A multiplet present at 4.32 ppm is attributed to the H6, which is deshielded by the adjacent electronegative nitrogen.

Fig. 8 shows the ^1H–^1H-correlation spectrum of the compound. The COSY spectrum separates out the interactions among the protons and establishes the proton–proton couplings. The proton spectrum is

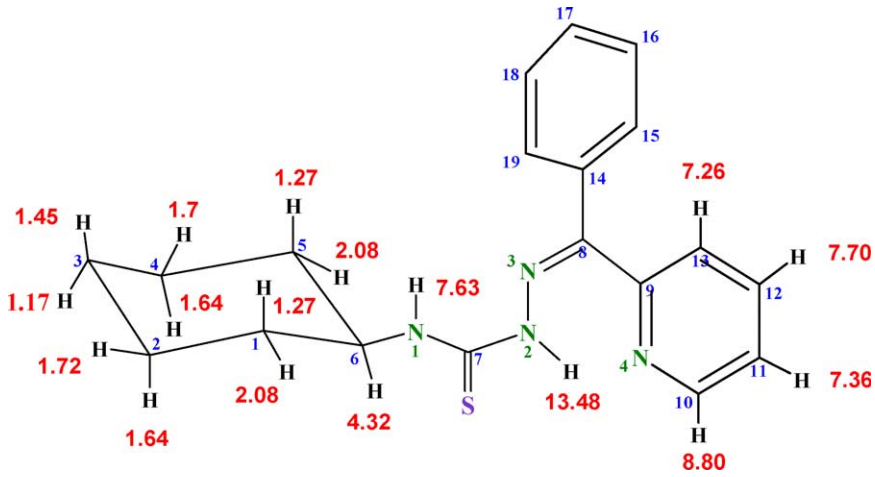

Fig. 5. ^{1}H NMR assignments of HL.

plotted along the *X* and *Y*-axes and can be seen as contours in diagonal. In the proton NMR spectrum, we have already identified a doublet at 8.80 ppm as of the pyridyl proton H10. If we extend horizontal and vertical lines from this point, it will eventually encounter off-diagonal cross peaks at 7.36 ppm, which is assigned as peak due to the H11. That is, the peak of the proton H10 is split by that of the proton at H11. Similarly by extending the lines from the spot at 7.36 ppm it will encounter off diagonal spots at 8.80 ppm (H10) and 7.70 ppm (H12). The multiplet at 7.36 ppm is related to the number of possible orientations these neighboring protons can adopt. The H12 proton is also split by the H13 proton and vice versa. In the spectrum around δ 7.40 ppm, the contours are seen ambiguous and the multiplet is assigned to the protons of the phenyl moiety. The chemical shifts are very close, so this spectrum is not strictly first order. The peak at 2.08 ppm is assigned to the equatorial proton on the carbon atom C5. From the COSY, it is shown to interact with three other protons H6, H5a and H4e. The couplings are of diequatorial and axial/equatorial type. The coupling constants agree well with those corresponding to the chair conformation of cyclohexane. Similarly H5e and H4e protons split the peak of the axial proton H5a. In the ^{1}H NMR, the multiplet at 1.72 ppm is already assigned to the H4e proton which interacts with five other protons H5a, H5e, H4a, H3e and H3a where interaction with H3a is very weak. All these couplings are of vicinal type. The multiplet at 1.64 ppm is formed by the coupling of H4a protons with the neighboring H4e, H3a and H3e protons. The proton shows no coupling with the H5e and H5a protons. The coupling between the H3a and H4a protons give *J* values around 11 Hz, which is consistent with diaxial type coupling constants. Even though, the coupling in the region 1.5 ppm is intricate to resolve as the chemical shift values of H3a, H3e and H5a are very close, it is clearly evident from the spectrum that the H3a proton couples with H4a and H3e. Similarly H3e is coupled with the H3a, H4e and H4a protons. The same coupling is observed for the protons at C1 and C2, which are magnetically equivalent to the C5 and C4 protons. The H6 proton interacts with the ^{1}NH and also with two protons of C1 and C5.

The ^{13}C NMR spectrum was assigned on the basis of the proton-decoupled ^{13}C and the HMQC spectrum (Fig. 9). The HMQC experiment provides the correlation between

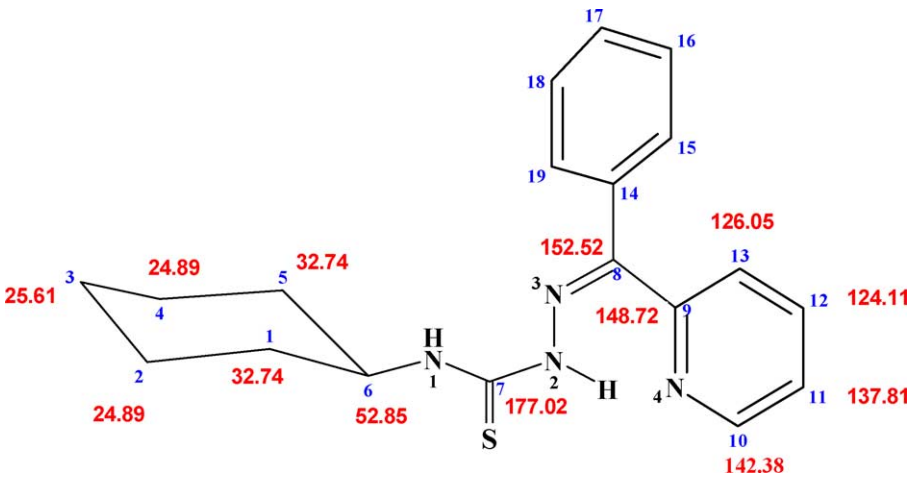

Fig. 6. ^{13}C NMR assignments of HL.

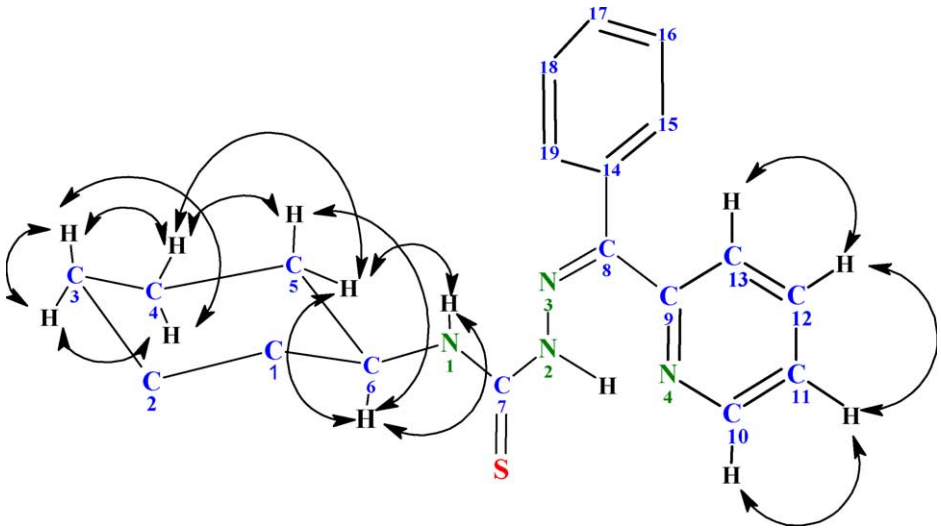

Fig. 7. $^{1}H-^{1}H$ COSY assignments of HL.

the protons and their attached heteronuclei through the heteronuclear scalar coupling. The decoupled ^{13}C spectrum of the compound contains 15 peaks corresponding to the fifteen magnetically unique atoms. The signal from ^{13}C is much weaker than that of the corresponding proton NMR. From the HMQC spectrum, it is evident that the peaks at 177.02, 152.52 and 148.72 ppm are of the non-protonated carbons and they correspond to the S = C7, N = C8 and C9 carbon atoms, respectively. The carbon atom closest to the electronegative atom is farthest downfield. The carbon atoms on the pyridyl ring can be assigned as C10, 142.38; C11, 137.81; C12, 124.11; C13, 126.05. Aromatic carbons of the phenyl ring appear around 129 ppm and it is very difficult to be resolved. The peaks at 32.74, 24.89, 25.61 and 52.85 ppm are assigned to C1, C2, C3 and C6 carbons, respectively. The C4 and C5 are chemically equivalent with C2 and C1 carbons and hence have the values 24.89 and 32.74 ppm, respectively.

3.2. Crystal structure of HL

The molecular structure of HL along with the atomic numbering scheme is given in Fig. 10. The compound crystallizes into a monoclinic lattice with space group $P2_1/n$ and the molecule shows an Z configuration with respect to the C8=N3 bond. A torsion angle value of $-174.31°$ corresponding to the S1–C7–N2–N3 moiety confirms the trans configuration of the thiocarbonyl S1 atom with respect to the hydrazine nitrogen atom N3 [35]. Similarly, the N2–N3 bond length (1.367 Å) is closer to single bond length (1.45 Å) than to double bond length (1.25 Å) [36]. The C7–S1 bond distance (1.675 Å) is close to that expected of a C=S double bond (1.60 Å) [36] and the C8–N3 bond length (1.290 Å) is nearly the same as that of the C=N double bond (1.28 Å) [37]. These bond distances are in strong support of the existence of 2-benzoylpyridine *N*(4)-cyclohexylthiosemicarbazone in the thione form in

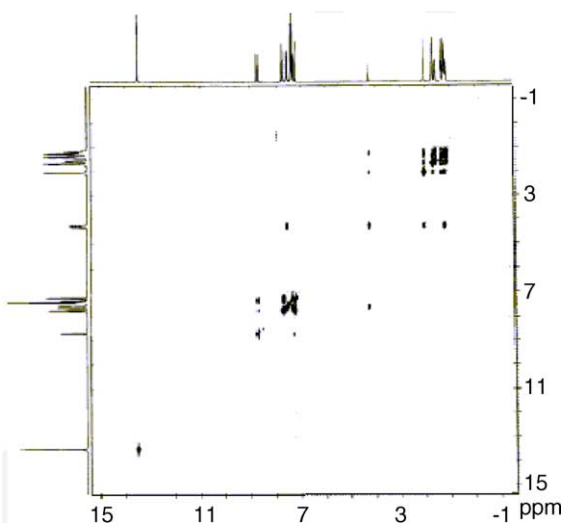

Fig. 8. $^{1}H-^{1}H$ COSY spectrum of HL.

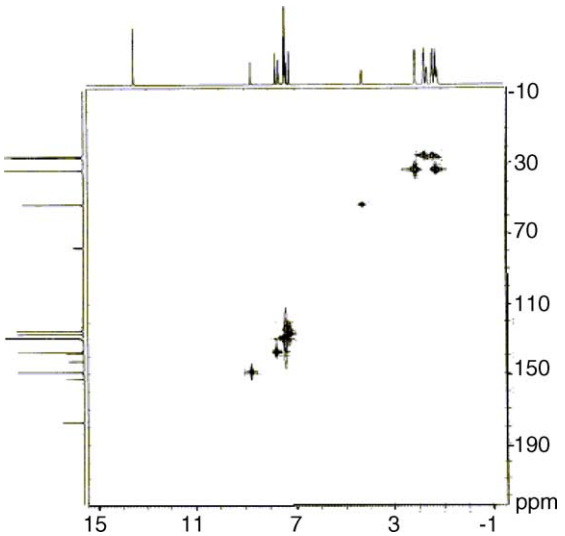

Fig. 9. $^{13}C-^{1}H$ HMQC spectrum of HL.

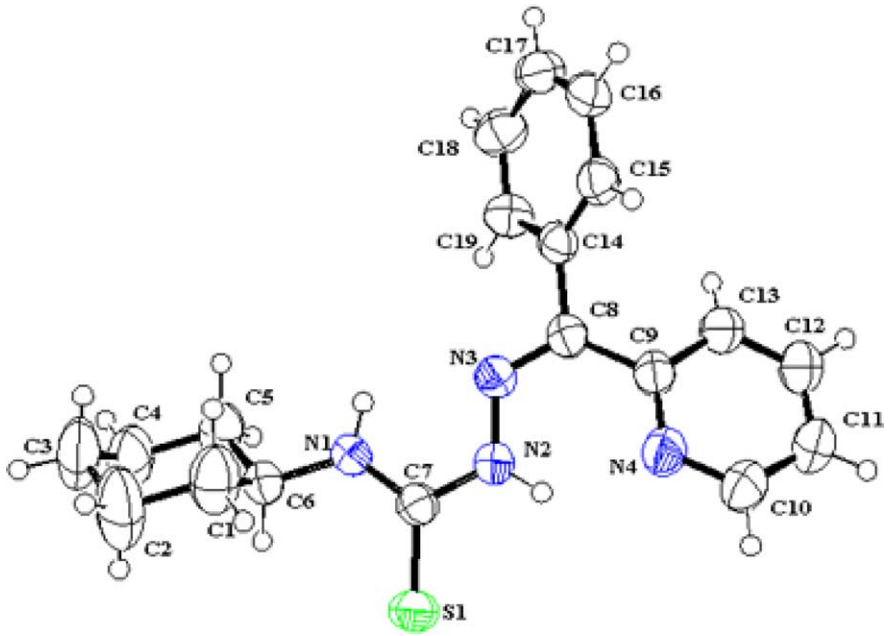

Fig. 10. ORTEP diagram for HL, displacement ellipsoids are drawn at 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radii.

the solid state. A collection of the data observed in our study on the various bond distances in the crystal structures of thiosemicarbazones is presented in Table 3. The mean plane deviation calculations show that the pyridyl ring Cg(1) is planar with a max deviation of −0.0096 Å. The thiosemicarbazone moiety also is planar with a maximum mean plane deviation value of −0.0596 Å and a torsion angle value of 3.65° for N2–N3–C8–C9 confirms that the C8–C9 bond is in the same plane of the thiosemicarbazone moiety. Also, the atoms C9, N4, C10, C11, C12, C13 and C8 are coplanar as evidenced from the maximum deviation value of −0.0205 Å from the plane. The dihedral angle formed by the two least square planes Cg(3) and Cg(1) is equal to 67°, which confirms the non-coplanarity of the two rings. The intramolecular hydrogen bonding interaction N(1)–H(1)N(1)–N(3) leads to the formation of a five membered ring comprising of N(1), H(1)N(1), C(7), N(2) and N(3). A similar six membered ring involving N(2), H(1)N(2), N(3), C(8), C(9) and N(4) is also developed by the N(2)–H(1)N(2)–N(4) intramolecular hydrogen bonding interaction in the compound. The axial substitution of the cyclohexyl ring at the N1 nitrogen of the thiosemicarbazone is confirmed by a torsion Cg(3) = C(14), C(15), C(16), C(17), C(18), C(19) value of −178.26° for the N2–C7–N1–C6 bond. Ring puckering analysis and least square planes calculations show that the cyclohexyl ring, Cg(2) adopts a chair conformation (Q_T = 0.5701 Å). The atoms C1, C2, C4 and C5 constitute the best fitting plane of the cyclohexyl ring, and the atoms C3 and C6 deviate by 1.2462 and −1.2358 Å, respectively, on either side of this plane.

The packing of the molecule in a unit cell is shown in Fig. 11. The unit cell is viewed down the '*a*'-axis and four molecules of the compound are arranged in the unit cell. It is evident from the figure that the unit cell as a whole is packed in a centrosymmetric manner especially at the center, where two units each comprising of two molecules are symmetrically packed in a 'face-to-face' manner. The self-assembly of the molecules in the crystal lattice in this manner is effected by the π–π interaction between the two pyridyl rings, i.e. the Cg(1) of the two neighboring units are observed at a distance of 3.8582 Å whereas these are observed at an average distance 5.7295 Å between the Cg(1) of one unit with the phenyl ring Cg(3) of the adjacent molecule (Table 4). The C–H–π interaction, viz. C3–H3B–Cg(3), also contributes to the stability of the crystal lattice, where Cg(3) is the cyclohexyl ring of the adjoining molecular unit.

Table 3
A comparison of the selected bond lengths (Å) observed in various thiosemicarbazones

Compound	Bond distances (Å)				
	N1–C7	C7–S1	C7–N2	N2–N3	N3–C8
HL	1.328(19)	1.675(15)	1.364(18)	1.367(17)	1.290(18)
BpytTsc	1.343(4)	1.681(3)	1.360(4)	1.366(3)	1.295(4)
ApytTsc	1.347(6)	1.692(4)	1.349(6)	1.364(5)	1.293(6)
DpktTsc	1.349(5)	1.671(4)	1.386(4)	1.371(4)	1.308(4)
DpkpTsc	1.339(3)	1.676(2)	1.362(2)	1.357(2)	1.286(2)
DpkmpTsc	1.349(2)	1.6686(18)	1.377(2)	1.362(2)	1.295(2)
MbTsc	1.3238(18)	1.6987(15)	1.3398(18)	1.3886(17)	1.271(2)

BpytTsc, 2-benzoylpyridine 3-tetramethyleneiminyl thiosemicarbazone [19]; ApytTsc, 2-acetylpyridine 3-tetramethyleneiminyl thiosemicarbazone [20]; DpktTsc, Di-2-pyridyl ketone 3-tetramethyleneiminyl thiosemicarbazone [21]; DpkpTsc, di-2-pyridyl ketone N(4)-phenyl thiosemicarbazone [22]; DpkmpTsc, di-2-pyridyl ketone N(4)-methyl N(4)-phenyl thiosemicarbazone [23]; MbTsc, *p*-methoxybenzaldehyde thiosemicarbazone [24].

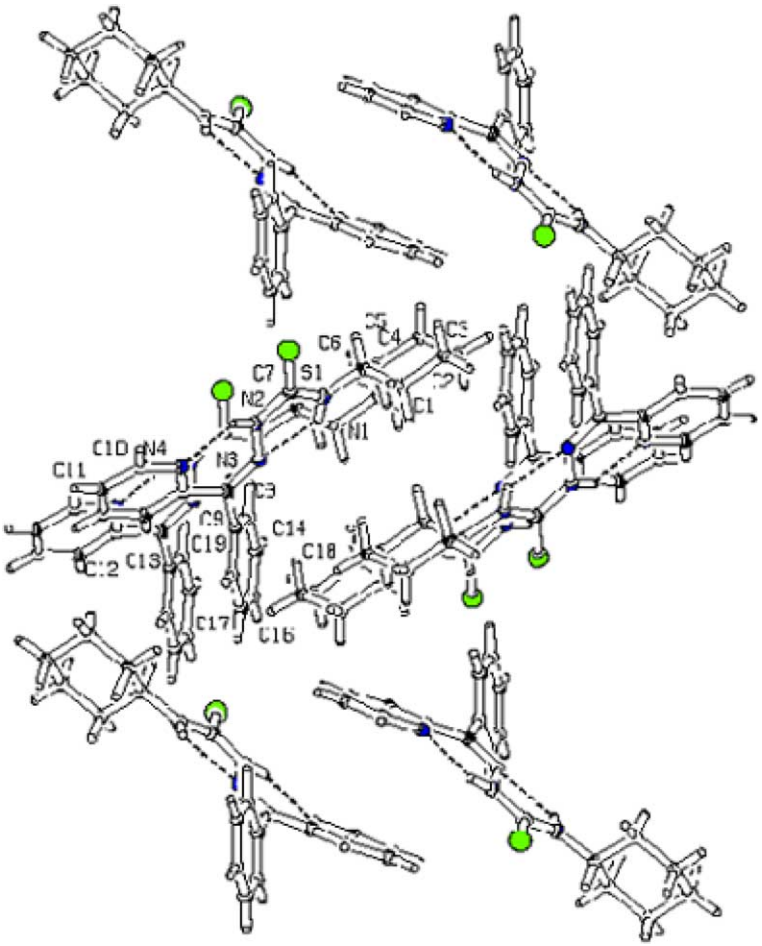

Fig. 11. Unit cell packing diagram of HL, viewed down the '*a*'-axis.

Table 4
H bonding, π−π and CH−π interactions of HL

H bonding (Å, Å)				
D–H–A	D–H	H–A	D–A	D–H–A
N1–H1N1–N3	0.87	2.15	2.5905	117
N2–H1N2–N4	0.90	2.01	2.6853	131
π–π interactions				
Cg(I)–Res(I)–Cg(J)	Cg–Cg (Å)		α (Å)	β (Å)
Cg(1) [1]–Cg(1)[a]	3.8582		0.00	13.64
Cg(1) [1]–Cg(3)[b]	5.4642		67.00	53.66
Cg(3) [1]–Cg(1)[c]	5.9949		69.28	48.82
			Cg(1) = N(4),C(9), C(10), C(11),C(12),C(13)	
			Cg(2) = C(1)0, C(2), C(3), C(4), C(5), C(6)	
			Cg(3) = C(14), C(15), C(16), C(17), C(18), C(19)	
CH–π interactions				
X–H(I)–Cg(J)		H–Cg (Å)	X–H–Cg (°)	X–Cg (Å)
C(3)–H(3B)–Cg(3)[d]		2.8680	139.71	3.6608

D, Donor; A, acceptor, Cg, centroid; α, dihedral angles between planes *I* and *J*; β, angle Cg(1)–Cg(J); equivalent position codes: $a = -x, 1-y, -z$, $b = -1+x, y, z$, $c = 1/2, 1/2-y, 1/2+z$, $d = -x, 1-y, 1-z$.

4. Supplementary data

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data center, CCDC for compound HL. Copies of this information maybe obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2, IEZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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