

# Synthesis, Spectral Properties and Structure of New Novel 3,3'-Dibenzoyl-1,1'-(propan-1,3-diyl)-bisthiourea

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**Abstract** A new 3,3'-dibenzoyl-1,1'-(propan-1,3-diyl)bisthiourea was synthesized by using benzoylisothiocyanate with 1,3-diaminopropane in aprotic solvent. The structure was determined by means of FT-IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  and mass spectroscopic techniques. The crystal structure of 3,3'-dibenzoyl-1,1'-(propan-1,3-diyl)bisthiourea has also been examined by using X-ray crystallographic techniques and found to be crystallized in the monoclinic space group  $P2_1/c$  with the unit cell parameters:  $a = 5.968(1) \text{ \AA}$ ,  $b = 19.471(2) \text{ \AA}$ ,  $c = 16.585(2) \text{ \AA}$ ,  $\beta = 98.32(1)^\circ$ ,  $V = 1907.0(4) \text{ \AA}^3$ ,  $D_x = 1.395 \text{ g cm}^{-3}$ , and  $Z = 4$  respectively.

**Keywords** Bisthiourea · Crystal structure determination · Spectroscopic studies · FT-IR

## Introduction

The  $N,N$ -dialkyl- $N'$ -aroyl-thioureas,  $\text{ArCONHCSNR}'\text{R}'$ , have long been known since their first synthesis by Neucki

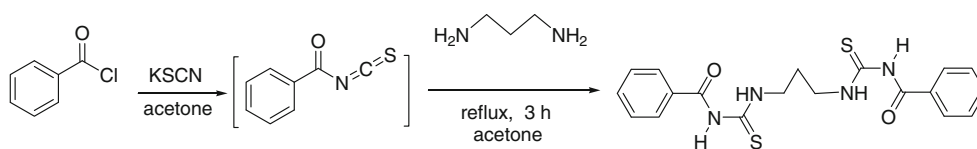
in 1873 [1]. The synthesis of monoalkylfuroylthioureas,  $\text{ArCONHCSNHR}$ , was already described by Douglass and Daws in 1934 [2]. Recently, many thioureas such as  $N$ -alkyl- $N'$ -acyl(aroyl)thioureas,  $\text{R/ArCONHCSNHR}'$ , and  $N,N$ -dialkyl- $N'$ -acyl(aroyl) thioureas,  $\text{R/ArCONHCSNR}'\text{R}'$ , have been synthesised. They are largely important in synthesis of heterocyclic compounds and many of these substrates have interesting biological activities [3–5]. Aroyl thioureas which have at least three potential donor atoms (N, O, S), have been found to display a remarkably rich coordination chemistry, showing a more varied coordination behaviour than the structurally related  $\beta$ -diketones, which have been thoroughly investigated [6–8]. Early reports revealed that these compounds containing carbonyl and thiocarbonyl groups have confirmed the utility among organic reagents as potential donor ligands for transition metal ions by the research groups [9]. Thiourea derivatives can be regarded as model compounds for different intra- and intermolecular interactions involving S atoms [10–13]. Metal complexes of these type ligands containing oxygen and sulfur as donor atoms are known to possess antifungal and antibacterial activities. Furthermore, some thiourea derivatives have been used in commercial fungicides. Both thiourea derivatives and their metal complexes display a wide range of biological activity including antibacterial, antifungal, insecticidal, herbicidal, and plant-growth regulator properties [5, 14–16].

In the present study, a new 3,3'-dibenzoyl-1,1'-(propane-1,3-diyl)bisthiourea was synthesized (Scheme 1) and its structure was determined by using different spectroscopic methods (Scheme 2). In addition, the crystal structure of title compound was also examined by means of X-ray crystallographic techniques (Fig. 1).

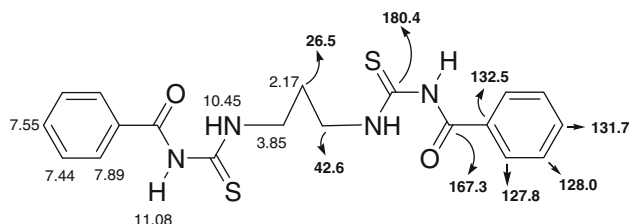
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**Scheme 1** Synthesis route of title compound



**Scheme 2** The  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR data for the title compound

spectra were recorded on a Bruker AVANCE DPX NMR spectrometer operating at 400 and 101.6 MHz. Elemental analyses were performed on a Carlo-Erba 1106 Elemental Analysis instrument. LC mass spectrum was recorded on an AGILENT 1100 MSD spectrometer with an ion source temperature of 240 °C using the impact mode (70 eV). All chemicals used for the preparation of the compounds were of reagent grade quality.

## Experimental Section

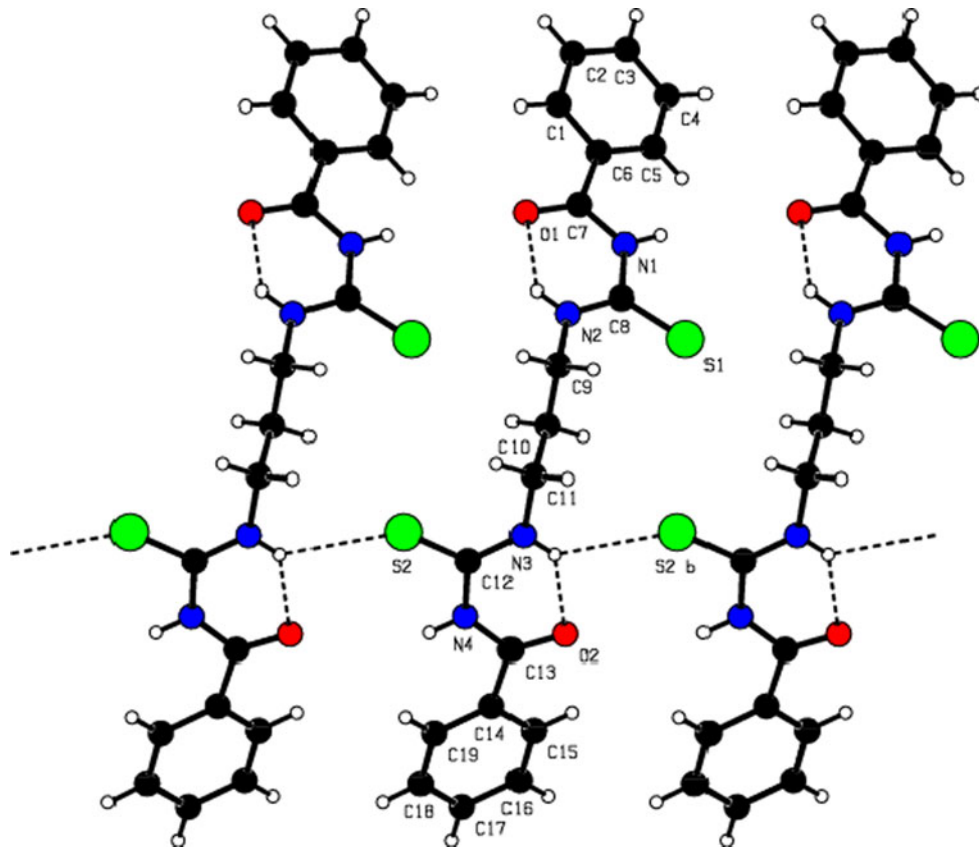
### Reagents and Techniques

Melting points were measured on an Electro Thermal IA 9100 apparatus using a capillary tube. Infrared absorption spectra, which were obtained through the use of with KBr pellets, were recorded in the range 4000–400  $\text{cm}^{-1}$  on a Perkin-Elmer BX II spectrometer. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR

### Preparation of Title Compound

A solution of benzoyl chloride (2.34 mL, 2.81 g, 20 mmol) in acetone (20 mL) was added dropwise to a suspension of potassium thiocyanate (1.94 g, 20 mmol) in acetone (20 mL). The reaction mixture was refluxed with stirring for 0.5 h to obtain white colour benzoyl isothiocyanate and then cooled to room temperature. A solution of 0.084 mL (0.074 g, 10 mmol) of 1,3-diaminopropane in 20 mL acetone was added dropwise to the benzoyl isothiocyanate and

**Fig. 1** The molecular structure of the title compound



refluxed with stirring ca. 3 h. The progress of reaction was controlled by TLC. As the reaction was completed, the solution was poured into water containing ice (100 mL). Then, the resulting yellow precipitate was filtered and washed with 10 mL water at four times, dried in under vacuum. Finally, the crude product was recrystallized from tetrahydrofuran: ethanol (V:V, 3:1) to give the product. The physical and spectral data of title compound are given follow: Colourless crystal, yield 85%, m.p. 159–160 °C. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3404 (N–H), 3218 (N–H), 3060 (C–H<sub>arom.</sub>), 2929 (C–H<sub>aliphatic</sub>), 1670 (C=O), 1250 (C=S), 1514 (N–CO), 1317 (SC–N), 1180 (C=O<sub>stretching</sub>), 724 (C=S<sub>stretching</sub>); <sup>1</sup>H NMR (400 MHz,  $\delta$ ppm, DMSO-*d*6): 11.08 (s, 1H, NH), 10.45 (s, 1H, NH), 7.89 (d, 4H, ph-H), 7.55 (t, 2H, ph-H), 7.44 (t, 4H, ph-H), 3.85 (q, 4H, –NH–CH<sub>2</sub>), 2.17 (m, 2H, –CH<sub>2</sub>–); <sup>13</sup>C NMR (100 MHz,  $\delta$ ppm): 180.41 (C=S), 167.33 (C=O), 132.57, 131.77, 128.08, 127.81 (C<sub>arom.</sub>), 42.62 and 26.51 (C<sub>aliphatic</sub>), MS (*m/z*): 400.10 (M<sup>+</sup>). Anal. calcd. for C<sub>19</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 56.98; H,

5.03; N, 13.99, S: 16.01, %. Found: C, 56.86; H, 5.09; N, 13.95, S: 16.06%.

#### X-Ray Structure Determination

The crystal of title molecule was mounted on goniometer of a STOE IPDS 2 diffractometer with a graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data

**Table 1** Crystallographic data and refinement parameter for the title compound

CCDC number	780265
Empirical formula	C <sub>19</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>
Compound weight	400.51
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
Crystal dimension	0.12 × 0.18 × 0.34 mm <sup>3</sup>
<i>Unit cell parameters</i>	
<i>a</i>	5.968(1) Å
<i>b</i> , $\beta$	19.471(2) Å, 98.32(1)°
<i>c</i>	16.585(2) Å
<i>V</i>	1907.0(4) Å <sup>3</sup>
<i>Z</i>	4
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.395
$\mu$ (MoK $\alpha$ )	0.302 mm <sup>-1</sup>
<i>F</i> (000)	840
2 $\theta$ <sub>max</sub>	51.98°
<i>h</i> , <i>k</i> , <i>l</i> range	–7 ≤ <i>h</i> ≤ 7 –24 ≤ <i>k</i> ≤ 24 –20 ≤ <i>l</i> ≤ 20
Measurement	STOE IPDS 2
Program system	STOE X-AREA
Structure determination	SHELXS-97
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Reflections collected	31,180
Independent reflections	3,755
Data/restraints/parameters	3,755/0/244
Goodness of fit on <i>F</i> <sup>2</sup>	1.174
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0991, <i>wR</i> <sub>2</sub> = 0.1064
( $\Delta\rho$ ) <sub>max</sub> , ( $\Delta\rho$ ) <sub>min</sub>	0.186, –0.211 e Å <sup>-3</sup>

**Table 2** Some selected bond lengths (Å), bond angles (°) and torsion angles (°)

<b>Bond lengths (Å)</b>	
S1–C8	1.672(4)
N3–C12	1.317(5)
N2–C8	1.324(5)
N1–C7	1.374(5)
O2–C13	1.228(5)
S2–C12	1.658(4)
N3–C11	1.449(5)
N2–C9	1.454(5)
N1–C8	1.384(5)
O1–C7	1.224(5)
<b>Bond angles (°)</b>	
C12–N3–C11	123.5(4)
C7–N1–C8	129.6(4)
C13–N4–C12	130.3(4)
N1–C8–S1	118.3(3)
O2–C13–N4	121.1(4)
N2–C9–C10	114.9(4)
C8–N2–C9	124.2(4)
N1–C7–C6	115.6(4)
N2–C8–S1	123.9(4)
N3–C12–S2	125.2(4)
N3–C11–C10	112.4(4)
N4–C13–C14	117.3(4)
<b>Torsion angles (°)</b>	
C8–N1–C7–C6	179.9(4)
C13–N4–C12–S2	–178.2(4)
C8–N2–C9–C10	85.4(5)
O2–C13–C14–C19	–165.0(5)
O2–C13–C14–C15	17.4(6)
C12–N4–C13–O2	–6.3(7)
C7–N1–C8–S1	–178.0(4)
C9–N2–C8–S1	–3.5(6)
C9–N2–C8–N1	175.5(4)
C11–N3–C12–S2	2.2(6)
N3–C11–C10–C9	179.4(3)
C12–N3–C11–C10	106.5(5)

collection, reduction and corrections for absorption and decomposition were achieved using X-AREA, X-RED software [17]. The structure was solved by SHELXS-97 and refined with SHELXL-97 [18, 19]. The positions of the H atoms bonded to C atoms were calculated (C–H distance 0.86, 0.93 and 0.97 Å), and refined using a riding model. The H atom displacement parameters were restricted to be  $1.2U_{eq}$  of the parent atom. The details of the X-ray data collection, structure solution and structure refinements are given in Table 1. Selected bond distances and angles are listed in Table 2. The molecular structure with the atom-numbering scheme is shown in Fig. 1. Crystallographic data (excluding structure factors) for the structures reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 780265<sup>1</sup>.

## Results and Discussion

### FT-IR Studies

Infrared spectra of title compound reveal all the expected frequency region of the  $\nu$  (N–H),  $\nu$  (C=O),  $\nu$  (C=S),  $\nu$  (CO–N),  $\nu$  (CS–N). The band at N–H 3405 and 3218  $\text{cm}^{-1}$ , correspond to the stretching  $\nu$  (NH) vibrations of the hydrogen bond NH groups in the bis-thiourea group. These assignments were supported by the literature that N(2)–H(2)···(O1) can be seen at above 3200  $\text{cm}^{-1}$  and the N(3)–H(3)···(O3, S1) can be found at above 3000  $\text{cm}^{-1}$  have been examined due to the existence of inter- and intramolecular hydrogen bonding [20]. The strong absorb  $\nu$  C=O band in the IR spectra of the compound appears at about 1670  $\text{cm}^{-1}$ , apparently decreasing in frequencies comparing with the ordinary carbonyl absorption (1700  $\text{cm}^{-1}$ ). This is interpreted as being a result of its conjugated resonance with the phenyl ring due to a delocalized pi-bond in it and the possible formation of intramolecular hydrogen bonding with N–H [21]. In addition, the abnormal intensity ratio between  $\nu$  (C=O) and 1550 and 1514  $\text{cm}^{-1}$  bands revealed that intramolecular hydrogen bonding might exist in this compound as observed in the X-ray analysis. The  $\nu$  (C–N) stretching frequencies have been found at around 1334–1317  $\text{cm}^{-1}$ . In fact, these vibrational frequencies have been assigned by comparison with the assignments of acylthiourea derivatives at 1400–1000  $\text{cm}^{-1}$ . The bands at ca. 1300  $\text{cm}^{-1}$ , such as 1317  $\text{cm}^{-1}$ , are assigned to the vibration of –N–C=S as

known thioureido. The  $\nu$  (C=S) stretching vibration can be observed at 609–724  $\text{cm}^{-1}$  range that are in close agreement with previously studied of other thiourea derivatives [22–25] (Fig. 2).

### NMR Studies

The experimental <sup>1</sup>H-NMR data of the title compound corresponds to those of similar compounds. The <sup>1</sup>H NMR signal for N<sub>1</sub>–H<sub>1</sub> and N<sub>3</sub>–H<sub>3</sub> shifted downfield to about 11.08 (s, 1H, NH) ppm and 10.45 (s, 1H, NH) ppm, while that N–H appeared at about ~8.00 and ~4.00 ppm, respectively. The resonance values of the phenyl protons were confirmed 7.89 (d, 4H, ph-H), 7.55 (t, 2H, ph-H), 7.44 (t, 4H, ph-H). The <sup>1</sup>H-NMR spectra of compound (C–H) peaks is observed at 3.85 ppm (q, 4H, CH<sub>2</sub>), 2.17 ppm (m, 2H, CH<sub>2</sub>) due to the difference in the interaction of the CSNH group with the aliphatic groups. The most de-shielded <sup>13</sup>C-NMR signals correspond to C=O and C=S groups. The carbon atoms of thiocarbonyl show the highest value such as 180.41 ppm, due to the lower excitation energy  $n-\pi^*$ . It is possible that very strong electron-withdrawing neighbors reduce the nucleophilic character of the C=S group. The <sup>13</sup>C-NMR signal of the carbonyl groups in compound appeared at 167.3 ppm due to the existence of the intra-molecular hydrogen bond related to the carbonyl oxygen atom (Figs. 3, 4).

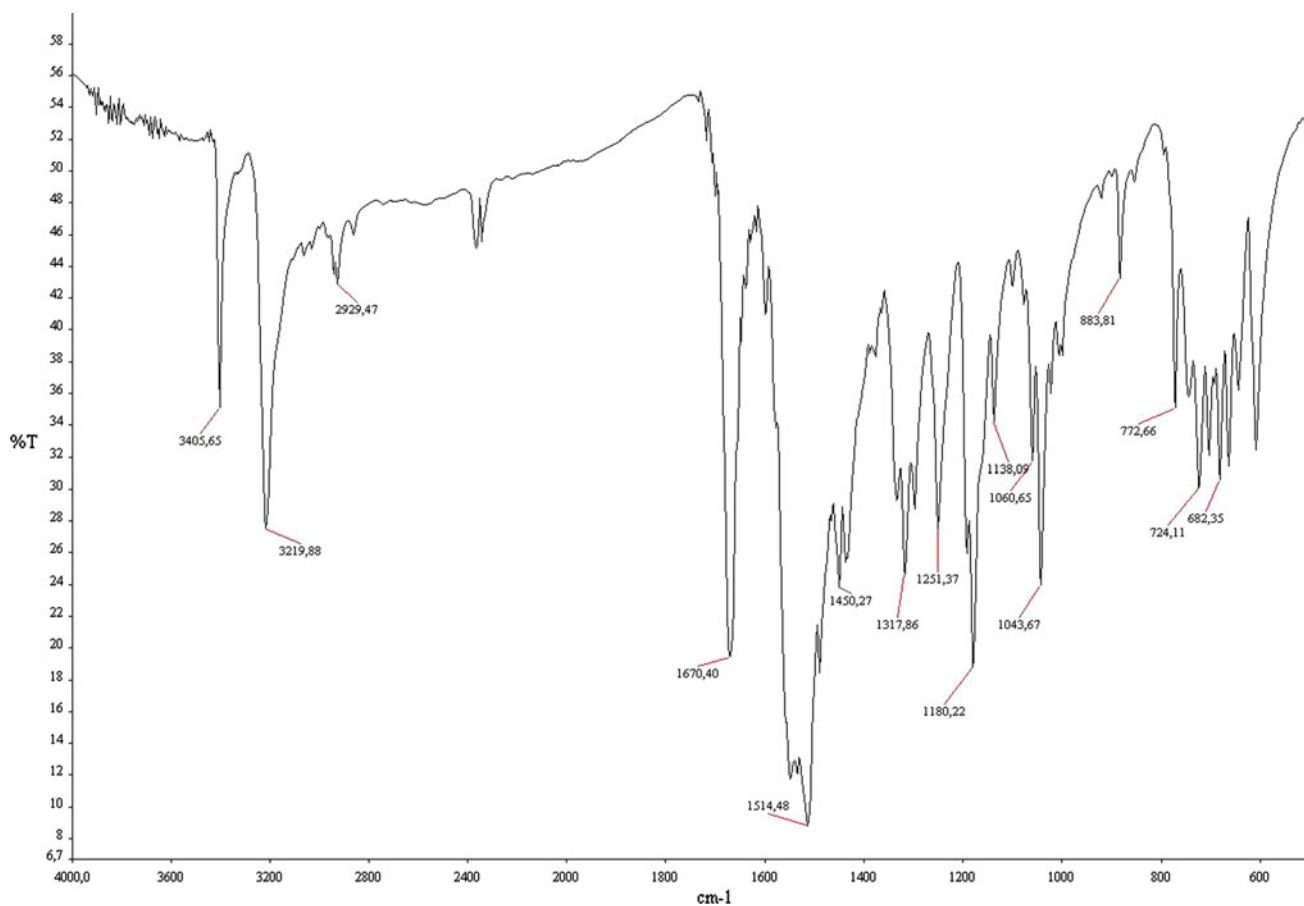
### Crystallographic Study

3,3'-Dibenzoyl-1,1'-(propan-1,3-diy)-bisthiourea consists of three parts. The part **A** [C1, C2, C3, C4, C5, C6, C7, C8, O1, N1 and S1; planar with a maximum deviation of 0.3422(8) Å for the S1 atom] and another part **B** [C19, C18, C17, C16, C15, C14, C13, C12, N4, O2 and S2; planar with a maximum deviation of 0.1289(12) Å for the N2 atom] are inclined at an angle of 10.07(3)°. However, it is accepted that it is essentially planar with the only significant deviation for the N1–C8–S1 and N4–C12–S2 moiety.

The conformation of the compound with respect to the thiocarbonyl and carbonyl moieties is twisted, as reflected by the torsion angles O2–C13–C14–C19 and C11–N3–C12–S2, –165.0°, 2.2° and benzoyl moiety is almost planar, as reflected by the torsion angles O2–C13–C14–C15, C7–N1–C8–N2, C12–N4–C13–O2 17.4°, –178.0°, –6.3° respectively. Symmetrical thiourea moiety is flexible due to C8–N2–C9–C10 and C12–N3–C11–C10, 84.5°, 106.5°, respectively.

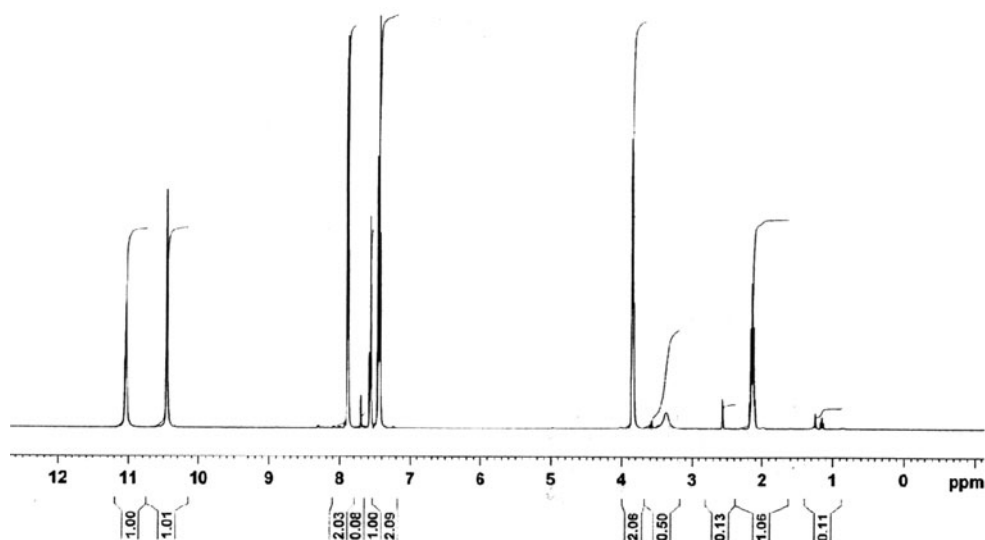
X-ray structure determinations revealed that thio-keto form is favoured over the thiol-imine form. This is evident from the observed C8=S1 bond distance of 1.672(4) Å,

<sup>1</sup> Further information may be obtained from: Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository number CCDC-780265. E-mail: deposit@ccdc.cam.ac.uk



**Fig. 2** FT-IR spectrum of title compound

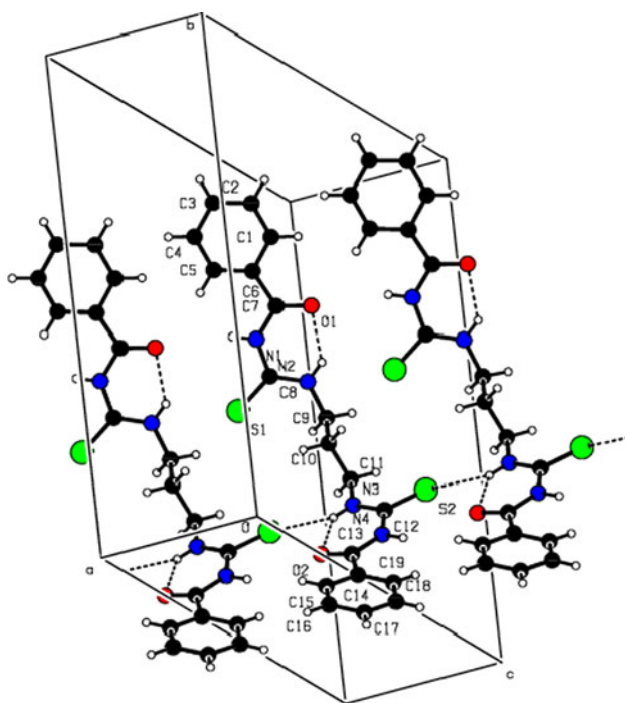
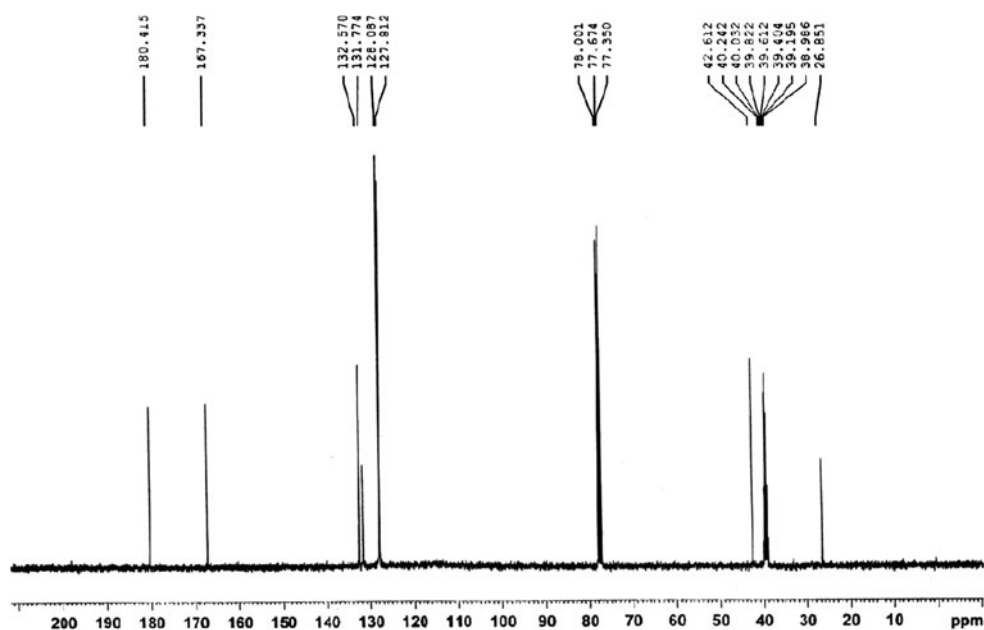
**Fig. 3**  $^1\text{H-NMR}$  spectrum of title compound



which is consistent with the  $\text{C}=\text{S}$  double bond; similarly the  $\text{N1-C8}$  and  $\text{N2-C8}$  distance of 1.384(5) and 1.324(5) Å and they are also consistent with the  $\text{N-C}$  single bonding. The  $\text{C}=\text{S}$  double bond length of 1.672(5) is in agreement with similar related compounds (see footnote 1). The

$\text{N1-C8} = 1.384(5)$  Å and  $\text{N2-C8} = 1.324(5)$  Å bond length differ significantly from each other, and the  $\text{N2-C8}$  bond length is shorter than the  $\text{N1-C8}$  bond length. This may be due to the strong intramolecular hydrogen  $[\text{O}\cdots\text{H}-\text{N}]$  bonding (see Fig. 5) between the keto( $\text{C}=\text{O}$ ) group and

**Fig. 4**  $^{13}\text{C}$ -NMR spectrum of title compound



**Fig. 5** In the crystal structure a perspective view of the molecule, the intermolecular and intramolecular hydrogen bonds have been indicated by *dashed lines*

the amine ( $-\text{NH}-$ ) nitrogen. The bond  $\text{C8}-\text{S1} = 1.672(5) \text{ \AA}$  is significantly longer than a  $\text{C}-\text{S}$  double bond. The determined  $\text{C}-\text{S}$  distance is smaller than single  $\text{C}-\text{S}$  bond distance of  $1.82 \text{ \AA}$ , however, bigger than double  $\text{C}-\text{S}$  bond of  $1.56 \text{ \AA}$  [21, 22, 26]. Consequently, the  $\text{C}-\text{S}$  bond in these compounds possesses only partial double-bond

character. The bond lengths and angles are in good agreement with those of other thiourea derivatives. According to the obtained results, the different packing arrangements of benzoylthiourea derivatives are all based on the formation of characteristic dimers and can be described in terms of the packing of the dimers.

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