



# SYNTHESIS AND X-RAY STRUCTURE STUDY OF *CIS-TRANS* 3-(3-BIPHENYL CARBONYLTHIOUREIDO)PROPANOIC ACID(I) AND *N*-(4-BIPHENYL CARBONYL)-*N'*-(3-HYDROXYPHENYL)THIOUREA(II)

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## ABSTRACT

Benzoylthiourea derivatives can be synthesized from the reaction between benzoyl- isothiocyanate and amine compounds. Consequently, with a biphenyl carbonoyl derivative can be obtained. Both compounds **I** and **II** have been characterized by microelemental analysis, IR and X-ray diffraction. Single crystal X-ray investigation showed that the compounds crystallized in monoclinic system with space group of  $P2_1/c$  and the unit cell dimension for the compounds I and II are  $a = 21.819(5) \text{ \AA}$ ,  $b = 4.8005(12) \text{ \AA}$ ,  $c = 15.539(4) \text{ \AA}$ ,  $\beta = 96.163(4)^\circ$  and  $a = 14.117(3) \text{ \AA}$ ,  $b = 7.0048(14) \text{ \AA}$ ,  $c = 17.690(3) \text{ \AA}$ ,  $\beta = 107.960(3)^\circ$ , respectively.

**Keywords:** Benzoylthiourea, microelemental analysis, benzoyl- isothiocyanate.

## INTRODUCTION

In recent years, thiourea derivatives have been studied for their potential use in agriculture, medicine and analytical chemistry<sup>1</sup>. Disubstituted thiourea derivatives are very useful building blocks for the synthesis of a wide range of aliphatic macromolecular and heterocyclic compounds<sup>2,3</sup>. Thiourea derivatives are well known for their complexation capacity towards transition metals<sup>4,5</sup> and display high biological activities as herbicides with low toxicity and low residue content<sup>6,7</sup>. Thiourea compounds are used extensively as pesticides, fungicides and regulating agents of plant growth in the agrochemical industry<sup>8,9</sup>. Therefore for these potential application of thiourea derivatives have driven the growth for synthesise of new thiourea derivatives. The X-ray crystal structure analysis of both compounds were carried out as part of our studies on thiourea derivatives.

## EXPERIMENTAL

An acetone solution (40 mL) of  $\beta$ -alanine (0.03 mol, 2.67 g) or 3-aminophenol (0.03 mol, 3.273 g) were added dropwise into a two-necked round-bottomed flask containing biphenyl-4-carbonylisothiocyanate (0.03 mol). The mixtures were refluxed for about 5 h and then filtered into a beaker containing ice cubes. The yellow precipitates obtained were washed with cold distilled water and recrystallized from ethanol.

## RESULTS AND DISCUSSION

The microelemental analysis CHNS-O data (Table1) are in agreement with the formula of the compound I and II. The IR spectrum of both compounds I and II showed the presence of the characteristic frequencies at  $(3246.8, 3356.09 \text{ cm}^{-1})$  and at  $(2929.2, 3035.1 \text{ cm}^{-1})$  referring to  $\nu(\text{N-H})$  and  $\nu(\text{O-H})$  for compounds I and II, respectively. The absorptions at 1320, 1305 due to NCS in the compounds, respectively. The absorptions at  $1537 \text{ cm}^{-1}$  duo to  $\nu(\text{C=C})$  of phenyl rings in both compounds.

The X-ray investigation of compound (I) and (II) showed that compounds crystallized in monoclinic system with space group of  $P2_1/c$ . The unit cell dimension are  $a = 21.819(5) \text{ \AA}$ ,  $b = 4.8005(12) \text{ \AA}$ ,  $c = 15.539(4) \text{ \AA}$ ,  $\beta = 96.163(4)^\circ$  and  $a = 14.117(3) \text{ \AA}$ ,  $b = 7.0048(14) \text{ \AA}$ ,  $c = 17.690(3) \text{ \AA}$ ,  $\beta = 107.960(3)^\circ$ , respectively. Both molecules (I) and (II) adopt *cis-trans* configuration with respect to the position of the propionic acid or 3-hydroxyphenyl and biphenylcarbonyl groups relative to the S atom across the C14-N2 and C14-N1 bonds, respectively. Figure 1 showed the molecular structure with the numbering scheme.

Table-1: Microelemental analysis and melting points of the compound (I) and (II)

Compound	m.p(K)	C%	H%	N%	S%	O%
$C_{17}H_{16}N_2O_3S$ (I)	442.1-443.2	61.80	4.48	8.29	8.77	16.66
			(62.18) (4.91)		(8.53) (9.76)	(14.62)
$C_{20}H_{16}N_2O_2S$ (II)	483-484	69.01	4.57	8.15	8.53	9.74
			(68.94) (4.63)		(8.04) (9.20)	(9.18)

The calculated values are in the bracket

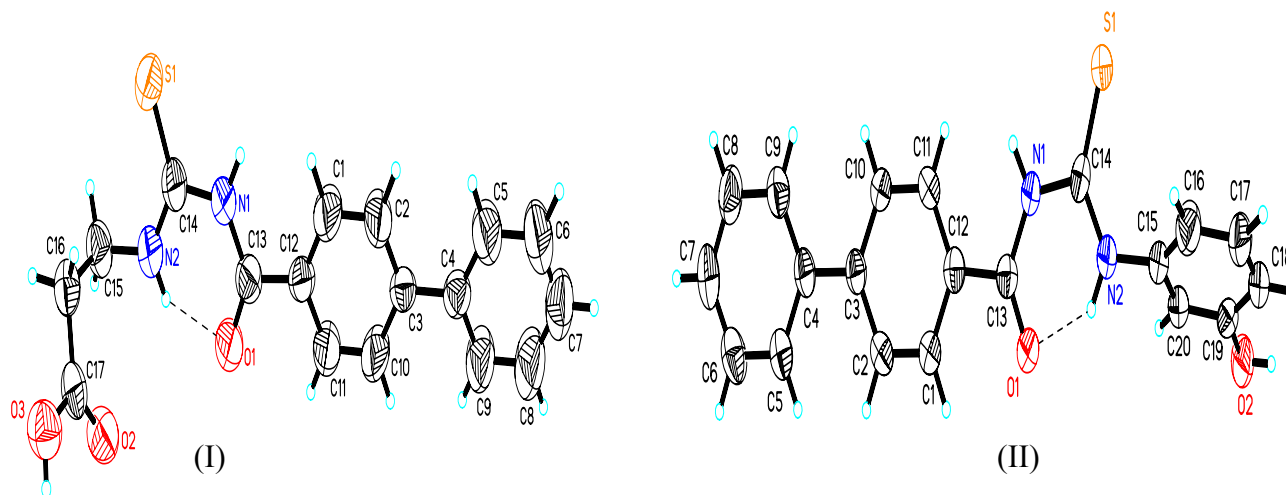


Fig.-1 :The molecular structure of 3-(3-biphenylcarbonylthioureido)propanoic acid and *N*-(4-biphenylcarbonyl)-*N'*-(3-hydroxyphenyl)thiourea(II) with 50% probability displacement ellipsoids The dashed line indicates the intramolecular hydrogen bond

The central thiourea moieties (S1/N1/N2/C14) in both compounds I and II makes angles of  $70.98(10)$  and  $53.04(9)^\circ$  with propionic acid and phenol ring, respectively. The benzene rings of biphenyl are a coplanar at an angles of  $5.99(16)$  and  $4.24(16)$ , respectively in the compounds I and II. The bond lengths and angles in both compound are in normal ranges<sup>10,11</sup> Table 2 and 3.

Table-2: The selected bond lengths and angles of 3-(3-biphenylcarbonylthioureido) propanoic acid

Bond	Length, \AA	Bond	Angles, $^\circ$
S1-C14	1.656(3)	C13-N1-C14	128.6(2)
N1-C14	1.392(4)	C14-N2-C15	126.3(3)
N2-C14	1.327(4)	O1-C13-N1	121.9(3)
N2-C15	1.431(4)	O1-C13-C12	121.6(3)
N1-C13	1.373(4)	N1-C13-C12	116.5(3)
O1-C13	1.218(3)	N2-C14-N1	114.3(3)
O2-C19	1.361(4)	N2-C14-S1	125.8(2)
N1-C14-S1	119.9(2)		

C16-C15-N2	121.1(3)	C20-C15-N2	117.8(3)
C1-C12-C11	117.7(3)		
C1-C12-C13	117.3(3)		

Table-3: The selected bond lengths and angles of *N*-(4-biphenylcarbonyl)-*N'*-(3-hydroxy phenyl) thiourea (II)

Bond	Length, Å	Bond	Angles, °
S1-C14	1.656(3)	C13-N1-C14	128.6(2)
N1-C14	1.392(4)	C14-N2-C15	126.3(3)
N2-C14	1.327(4)	O1-C13-N1	121.9(3)
N2-C15	1.431(4)	O1-C13-C12	121.6(3)
N1-C13	1.373(4)	N1-C13-C12	116.5(3)
O1-C13	1.218(3)	N2-C14-N1	114.3(3)
O2-C19	1.361(4)	N2-C14-S1	125.8(2)
N1-C14-S1	119.9(2)	C20-C15-N2	117.8(3)
C16-C15-N2	121.1(3)		
C1-C12-C11	117.7(3)		
C1-C12-C13	117.3(3)		

In compound (I) there is one intramolecular hydrogen bond N2–H2<sup>⋯</sup>O1 (Table 6). In the crystal structure, the molecules are linked by N1–H1<sup>⋯</sup>O2, O3–H3<sup>⋯</sup>S1, C1–H1A<sup>⋯</sup>O2 and C5–H5<sup>⋯</sup>O1 intermolecular hydrogen bonds, forming a one dimensional chain along the *a* axis (Fig. 2)

Table-4: Hydrogen geometric parameters (Å, °) of 3-(3-biphenylcarbonyl thioureido)propanoic acid (VI)

D—H <sup>⋯</sup> A	D—H	H <sup>⋯</sup> A	D <sup>⋯</sup> A	D—H <sup>⋯</sup> A
N2—H2 <sup>⋯</sup> O1	0.86	1.92	2.609(3)	136
N1—H1 <sup>⋯</sup> O2 <sup>i</sup>	0.86	2.38	3.233(3)	173
C1—H1A <sup>⋯</sup> O2 <sup>i</sup>	0.93	2.23	3.134(4)	165
C5—H5 <sup>⋯</sup> O1 <sup>ii</sup>	0.93	2.52	3.352(4)	149
O3—H3 <sup>⋯</sup> S1 <sup>iii</sup>	0.82	2.30	3.109(2)	171

Symmetry codes: (i)  $x, 5/2 - y, 1/2 + z$ , (ii)  $x, 3/2 - y, 1/2 + z$ , (iii)  $x, 5/2 - y, -1/2 + z$

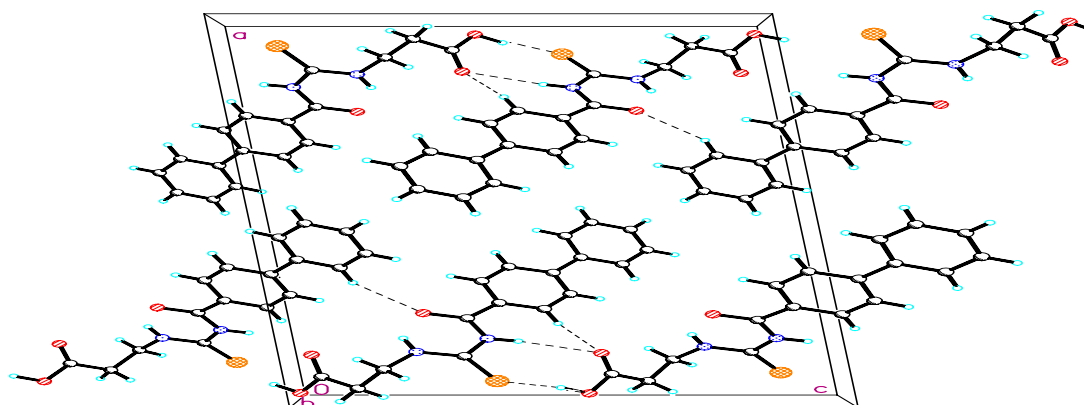


Fig.-2: Molecular packing of 3-(3-biphenylcarbonylthioureido)propanoic acid (I) viewed down the *b* axis. Dashed lines denote C—H<sup>⋯</sup>O, O—H<sup>⋯</sup>S and N—H<sup>⋯</sup>O hydrogen bonds

In the compound (II), there is also one intramolecular hydrogen bonds N2—H2B $\cdots$ O1 in the molecule. In the crystal structure, the molecules are linked by N1—H1A $\cdots$ O2 and O2—2H $\cdots$ S1 intermolecular hydrogen bonds (Table 5) to form one dimensional chain (Fig.3).

Table-5: Hydrogen geometric parameters (A, °) of *N*-(4-biphenylcarbonyl)-*N'*-(3-hydroxyphenyl) thiourea (II)

D—H $\cdots$ A	D—H	H $\cdots$ A	D $\cdots$ A	D—H $\cdots$ A
N2—H2B $\cdots$ O1	0.86	1.89	2.5969	139
N1—H1A $\cdots$ O2 <sup>i</sup>	0.86	2.31	3.1244	158
O2—2H $\cdots$ S1 <sup>ii</sup>	0.82	2.45	3.2068	153

Symmetry codes: (i)x, 3/2 -y, -1/2 +z, (ii)x, 3/2 -y, 1/2 +z

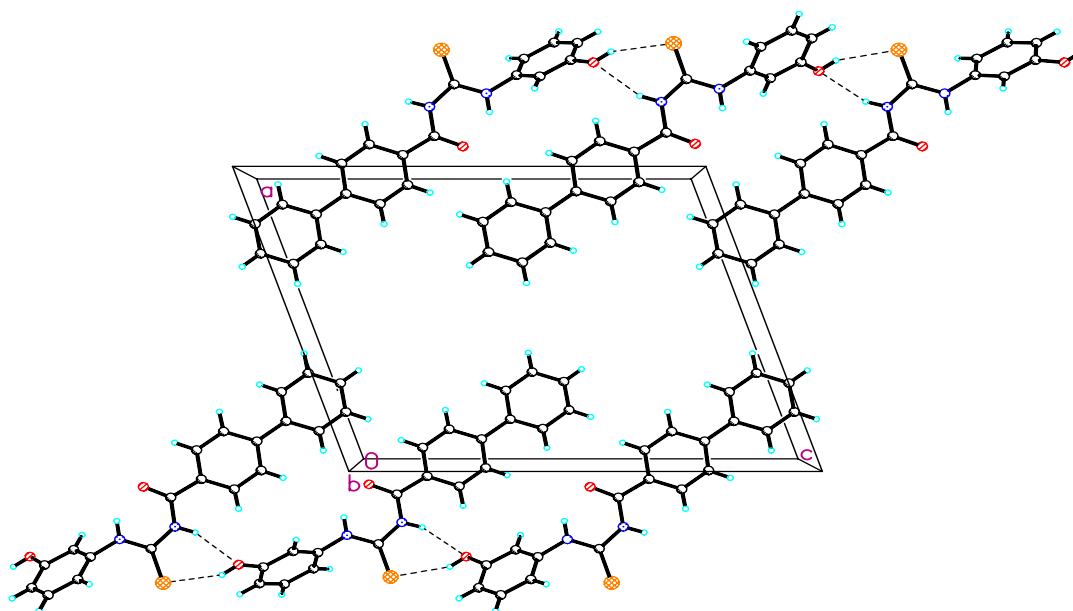


Fig.-3: Molecular packing of *N*-(4-biphenylcarbonyl)-*N'*-(3-hydroxyphenyl)thiourea (II) viewed down the b axis. Dashed lines denote N—H $\cdots$ O and O—H $\cdots$ S hydrogen bonds

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(Received: 13 August 2009

Accepted: 26 August 2009

RJC-431)

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