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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 monocleinic system with space group of $P2_1/c$ *and t*he unit cell dimension for the compounds I and II are a = 21.819(5) Å, b = 4.8005(12) Å c = 15.539(4) Å , β =96.163(4) and a = 14.117(3) Å, b =7.0048(14) Å, c = 17.690(3) Å , β =107.960(3)° , 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[1]. Disubstituted thiourea derivatives are very useful building blocks for the synthesis of a wide range of aliphatic macromolecular and heterocyclic compounds[2,3]. Thiourea derivatives are well known for their complexation capacity towards transition metals[4,5] and display high biological activities as herbicides with low toxicity and low residue content[6,7]. Thiourea compounds are used extensively as pesticides, fungicides and regulating agents of plant growth in the agrochemical industry[8,9]. Therefore for these potential application of thiourea derivatives have driven the growth for synthesize 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 β-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 cm^{-1}**)** and at (2929.2, 3035.1cm^{-1}) referring to ν(N-H) and ν(O-H) for compounds I and II, respectively. The absorptions at 1320, 1305 due to NCS in the compounds, respectively. The absorptions at 1537 cm^{-1} duo to ν (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) Å, b = 4.8005(12) Å c = 15.539(4) Å, β =96.163(4) and a = 14.117(3) Å, b =7.0048(14) Å, c = 17.690(3) Å, β =107.960(3)°, 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

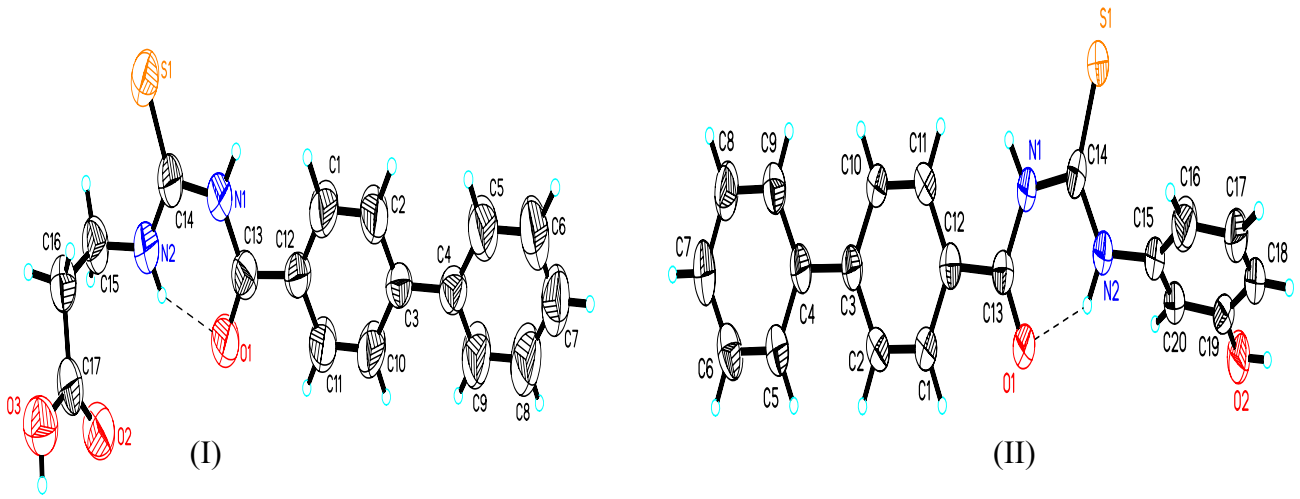

Fig.-1 :The molecular structure of 3-(3-biphenylcarbonylthioureido)propanoic acid and *N*-(4-biphenylcarbonyl)-*N'*-(3-hydroxyphenyl)thiourea(II)) with 50% probability displacement ellipsoids The dashed line indicates the intramolecular hydrogen bond

The central thiourea moieties (S1/N1/N2/C14) in both compounds I and II makes angles of 70.98(10) and 53.04(9)° 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[10,11] Table 2 and 3.

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

Bond	Length, A	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)		

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····O1 (Table 6). In the crystal structure, the molecules are linked by N1–H1····O2, O3–H3····S1, C1–H1A····O2 and C5–H5····O1 intermolecular hydrogen bonds, forming a one dimensional chain along the *a* axis (Fig. 2)

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

D—H---A	D—H	H---A	D---A	D—H---A
N2—H2····O1	0.86	1.92	2.609(3)	136
N1—H1····O2^{i}	0.86	2.38	3.233(3)	173
C1—H1A····O2^{i}	0.93	2.23	3.134(4)	165
C5—H5····O1^{ii}	0.93	2.52	3.352(4)	149
O3—H3····S1^{iii}	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

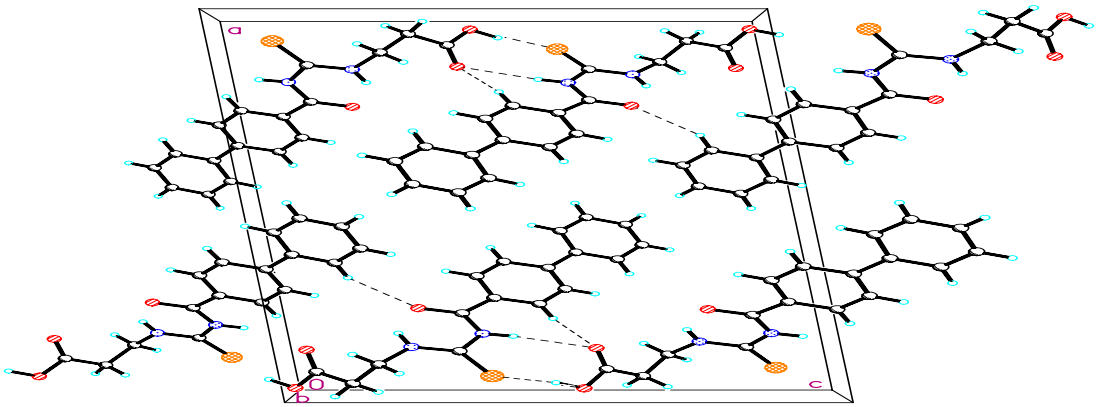

Fig.-2: Molecular packing of 3-(3-biphenylcarbonylthioureido)propanoic acid (I) viewed down the *b* axis. Dashed lines denote C—H···· O, O—H····S and N—H····O hydrogen bonds

In the compound (II), there is also one inramolecular hydrogen bonds N2—H2B···O1 in the molecule. In the crystal structure, the molecules are linked by N1—H(1A)···O2 and O2—2H···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---A	D—H	H---A	D---A	D—H---A
N2—H2B···O1	0.86	1.89	2.5969	139
N1—H1A···O2^{i}	0.86	2.31	3.1244	158
O2—2H···S1^{ii}	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

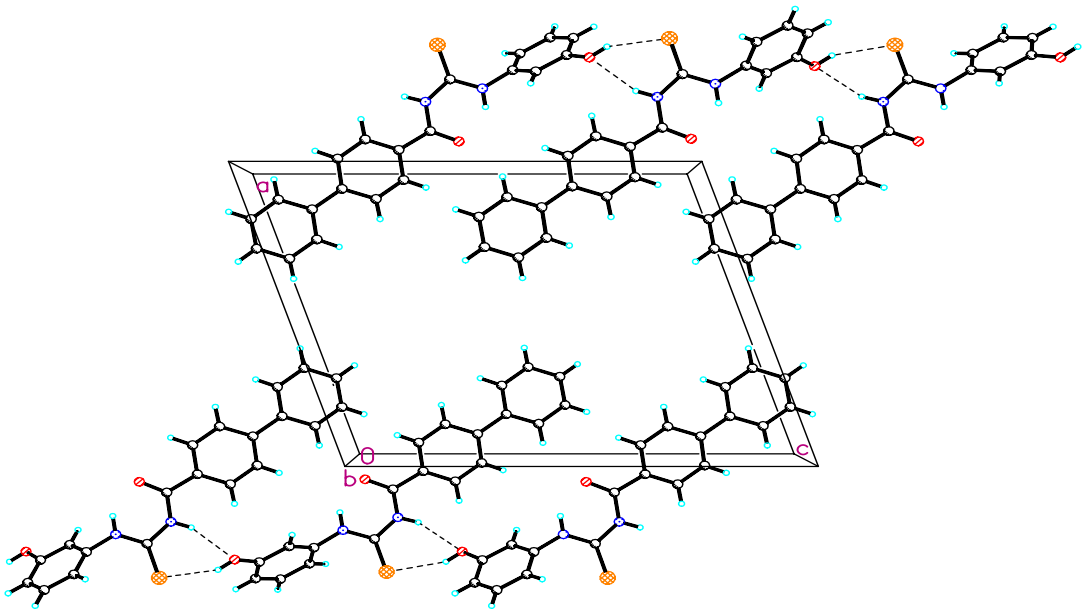

Fig.-3: Molecular packing of *N*- (4-biphenylcarbonyl)-*N`*-(3-hydroxyphenyl)thiourea (II) viewed down the b axis. Dashed lines denote N—H···O and O—H···S hydrogen bonds

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