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STRUCTURE OF ORGANIC COMPOUNDS

Synthesis, Characterization, and Crystal Structure of Bis[4-(3'-benzoyl)thiocarbamidophenyl]ether[1]

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Abstract—The title compound, bis[4-(3'-benzoyl)thiocarbamidophenyl]ether, was synthesized by the reaction of benzoylisothiocyanate with 4,4'-diaminodiphenylether in aprotic solvent. The structure was determinated by means of elemental analysis and FT—IR, ^{1}H—NMR, ^{1}3C—NMR and MS spectroscopic techniques. The crystal structure was characterized by X-ray syngle crystal analysis: orthorhombic, sp. gr. *Pnna*, $Z = 4$. In crystal packing, there are intramolecular hydrogen bond N—H···O generating S(6) motif, and intermolecular hydrogen bond N—H···S forming $R_2^2(8)$ ring.

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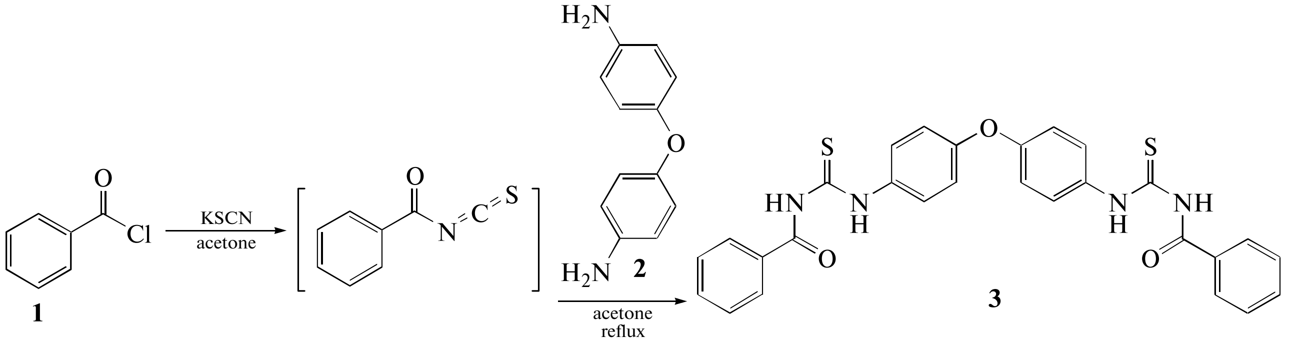
INTRODUCTION

In recent years, N-alkyl- and N,N-dialkyl-N'-acyl/aroyl thiourea compounds and their derivatives have been widely used in extraction, separation, medicine, agriculture and analytical chemistry [1–8]. They have a long history as ligands in coordination chemistry and also attracted considerable attention because of their coordination ability with transition metal ions such as Pt, Cu, Ni, Co *via* sulfur and oxygen [9–12]. These hard and soft donor atoms provide a multitude of bonding possibilities [13]. Hydrogen bonding behavior of some thioureas have been investigated and it is found that intramolecular hydrogen bonds between the carbonyl oxygen and a nitrogen atom is common [14]. Recently, bis-thiourea derivatives have been reported to be the symmetrical bipodal ligands for the coordination chemistry [15, 16]. Apart from the coordination properties, they appear biological activities [17]. Thus, some acyl thioureas have been found to possess pesticidal activities and promote plant growth [18]. They are important intermediates in organic synthesis [19]. They are also of current interest in supramolecular chemistry and host-guest chemistry [20, 21]. Furthermore, the corrosion of some metals can be determined using thiourea and its derivatives [22].

In this present study, we have synthesized a new bis-thiourea derivative (Scheme 1) and characterized it by MS, FT—IR, ^{1}H—NMR, ^{13}C—NMR, UV—visible spectroscopic techniques. The crystal structure of Bis[4-(3'-benzoyl)thiocarbamidophenyl]ether (**3**) was also determined using X-ray single crystal analysis in order to reveal the hydrogen bonding.



Scheme 1. Synthesis of the title compound **3**.

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EXPERIMENTAL

Reagents and techniques. Melting point was measured on an Electro Thermal IA 9100 apparatus using a capillary tube. FT–IR spectra was recorded by a Perkin Elmer BX–II spectrometer and reported in cm^{-1} units. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE DPX NMR spectrometer operating at 400 and 101.6, using DMSO(*d*). The mass spectrum was obtained on an AGILENT 1100 LC/MSD spectrometer with an ion source temperature of 240°C. 4,4'-Diaminodiphenylether, benzoyl chloride, potassium thiocyanate, acetone, tetrahydrofurane were purchased from Merck.

Synthesis of title compound (3). Potassium thiocyanate (1.94 g, 20 mmol) was added slowly to an acetone solution (20 mL) containing benzoyl chloride (**1**) (2.32 mL, 20 mmol). A mixture was refluxed with stirring for 30 min at ambient temperature, then, a solution of 4,4'-diaminodiphenylether (**2**) (2.00 g, 10 mmol) as symmetrical diamine in acetone (20 mL) was added dropwise to the benzoyl isothiocyanate and refluxed with stirring for 4 hours. The course of reaction was controlled by TLC. When the reaction was completed, the solution was poured into a beaker containing some ice. The white precipitate was filtered off and washed with distilled water. After drying under vacuum, it was recrystallized from tetrahydrofuran to give the product (**3**, Scheme 1). The physical and spectral data of compound are as follow: colourless crystal, yield 83% m.p. 221–222°C.

Table 1. Crystallographic characteristics and the X-ray-data collection and structure-refinement parameters for ($C_{28}H_{22}N_4O_3S_2$)

System, sp. gr., *Z*	Orthorhombic, *Pnna*, 4
a, *b*, *c*, Å	12.2679(9), 13.6360(9), 15.7626(13)
V, Å^3	2636.8(3)
D_x, Mg cm^{-3}	1.327
Radiation, λ, Å	MoK_α, 0.71073
μ, mm^{-1}	0.24
T, K	293
Sample size, mm	0.59 × 0.31 × 0.15
Diffractometer	STOE IPDS II
Scan mode	ω
Absorption correction, $T_{\min}$, $T_{\max}$	0.909, 0.971
$\theta_{\max}$, deg	26
h, *k*, *l* ranges	$-14 \le h \le 15, -14 \le k \le 16, -19 \le l \le 19$
Number of reflections: measured/unique (*N*1), R_{int}/with $I > 2\sigma(I)$ (*N*2)	15882/2602,0.204/1429
Refinement method	Full matrix least squares on F^2
Number of refined parameters	168
R1/*wR*2 relative to *N*1	0.1695/0.1298
*R*1/*w*R2 relative to *N*2	0.0874/0.1092
S	1.089
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e/Å^3	–0.33, 0.23
Programs	X-AREA Version 1.18, X-RED32 Version 1.04 [24], SHELX97 [25]

IR (KBr pellet, ν; cm^{-1}): 3205 (N–H), 3133 (N–H), 3021 (C–H$_{\text{arom}}$), 1514 (N–CO), 1331 (SC–N), 1659 (C=O), 1268 (N–C = S, thioureido), 1222 (*Ar*–O), 709 (C=S$_{\text{stretching}}$); ^{1}H NMR (400 MHz, δ, ppm, DMSO–*d*6): 12.57 (s, 1H, NH), 11.58 (s, 1H, NH), 8.00 (d, 2H, *Ar*–H), 7.59 (t, 2H, *Ar*–H), 7.65 (t, 1H, *Ar*–H), 7.53 (d, 2H, *Ar*'–H), 7.10 (d, 2H, *Ar*'–H) [*Ar* = phenyl, *Ar*' = terephthoyl]; ^{13}C NMR (100 MHz, δ, ppm) 180.82 (C=S), 169.76 (C=O), 165.02, 134.88, 134.42, 133.44, 129.95, 129.71, 127.58, 119.89 (C$_{\text{aromatic}}$); MS (EI) (*m*/*z*): 526.11 (M^{+1}), 492, 404, 349. Anal. calcd. for $C_{28}H_{22}N_4O_3S_2$: C, 63.86; H, 4.21; N, 10.64, S: 12.18, %. Found: C, 63.81; H, 4.20; N, 10.69, S: 12.22%.

Crystal structure determination. To get single crystal, tetrahydrofuran solution of **3** was subjected to slow evaporation. The details on data collections and structure calculations are given in Table 1. The structure was determined by direct method. All H atoms were refined using a riding model, with C–H = 0.93°, U_{iso}(H) = 1.2U_{eq}(C) for aromatic C atoms, and N–H = 0.86°, U_{iso}(H) = 1.2U_{eq}(N) for N atoms.

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, no. CCDC 892994.

RESULTS AND DISCUSSION

FT–IR, ^{1}H NMR, ^{13}C NMR spectroscopy. In the IR spectra of title compound **3**, the two N–H stretching vibrations were observed at 3205 and 3133 cm^{-1}, as an intense broad band (Fig. 1), The sharp absorption

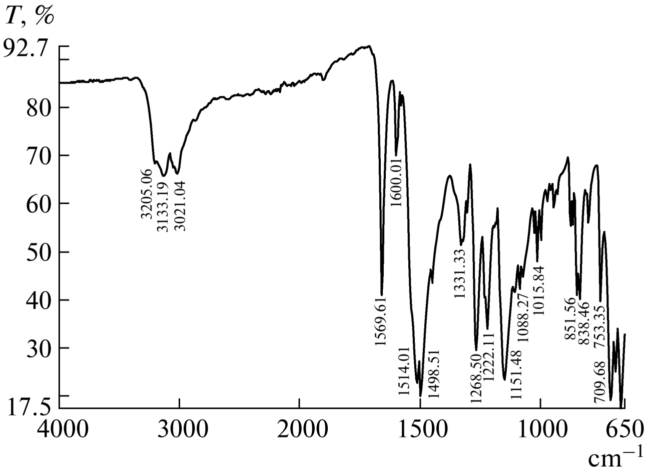


Fig. 1. FT–IR spectrum of **3**.

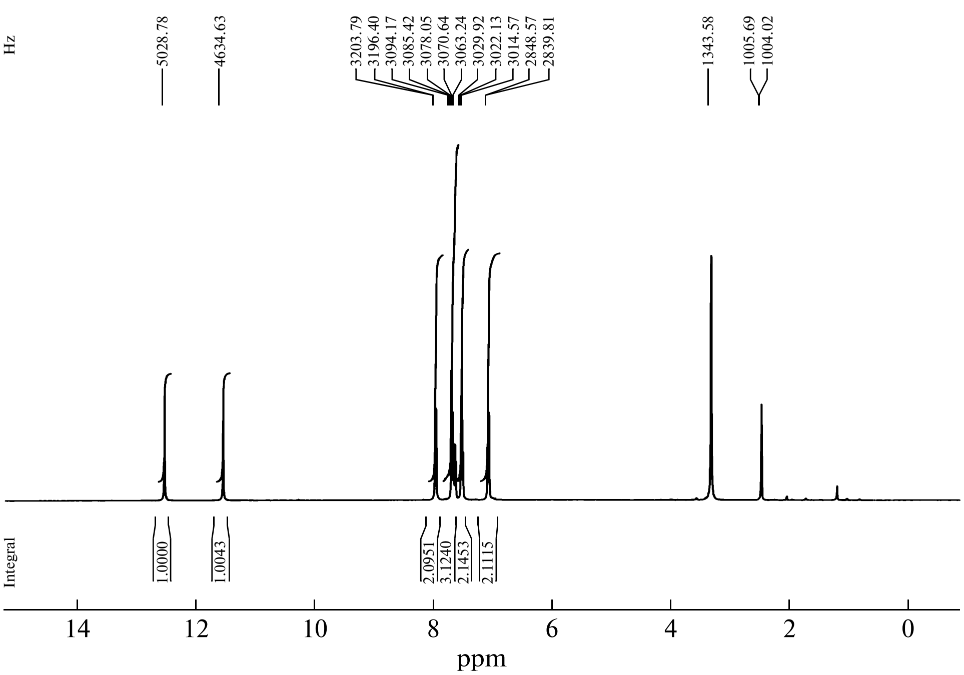


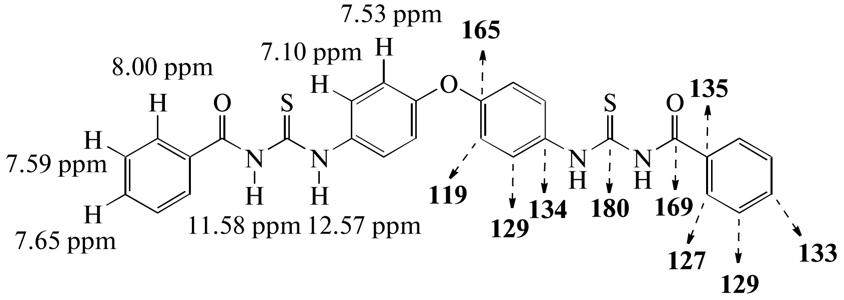
Fig. 2. ^{1}H NMR spectrum of **3** in DMSO.

band was seen at 1659 cm^{-1}, belonging to the carbonyl function of the benzoyl groups. Decreasing in frequencies compared with ordinary carbonyl absorption (ca. 1710 cm^{-1}) was interpered as being a result of its conjugation with the phenyl ring and formation of intramolecular hydrogen bond with N–H group. The strong bands at 1268 cm^{-1} and 709 cm^{-1} were assigned to the thioureido (N–C=S) and thiocarbonyl (C=S) stretching vibrations, respectively. The C–H aromatic stretching vibration was observed at 3021 cm^{-1}. Typical bands corresponding to diaryl ether at 1268–1222 cm^{-1} for the antisymmetric vibration and at 1151 cm^{-1} for the symmetric vibration are observed. The bands of ca. 1500–1514 cm^{-1} were assigned to the amide group (CO–N) (Fig. 1).

The experimental 1H–NMR data of the title compound correspond to those of similar compounds [8–14]. The N–H protons exhibited two characteristic broad singlets at 12.57 and 11.58 ppm, due to resonance with the carbonyl and thiocarbonyl groups and intra- and intermolecular hydrogen bonds, while amide N–H appeared at about ~8.00 ppm. Signals for the *para* substituted phenyl protons were also noted about 7–8 ppm (Fig. 2).

The most deshieldled ^{13}C–NMR signals at 180.82 and 169.76 ppm correspond to C=O and C=S groups. These values are the highest due to the lower excitation energy n–π* and due to the existence of the intramolecular hydrogen bond related to the thionyl sulfur atom [23]. It is possible that very strong electron-withdrawing neighbors reduce the nucleophilic character of the C=S group.

The ^{13}C–NMR signal of the carbonyl group in **3** appeared at 169.76 ppm (Fig. 3) because of the existence of the intramolecular hydrogen bond related to the carbonyl oxygen atom according to X-ray crystal structure (Fig. 4). All aromatic carbon peaks appeared at about 140–120 ppm (Fig. 3 and Scheme 2).



Scheme 2. ^{1}H and ^{13}C NMR chemical schifs of the title compound in DMSO.

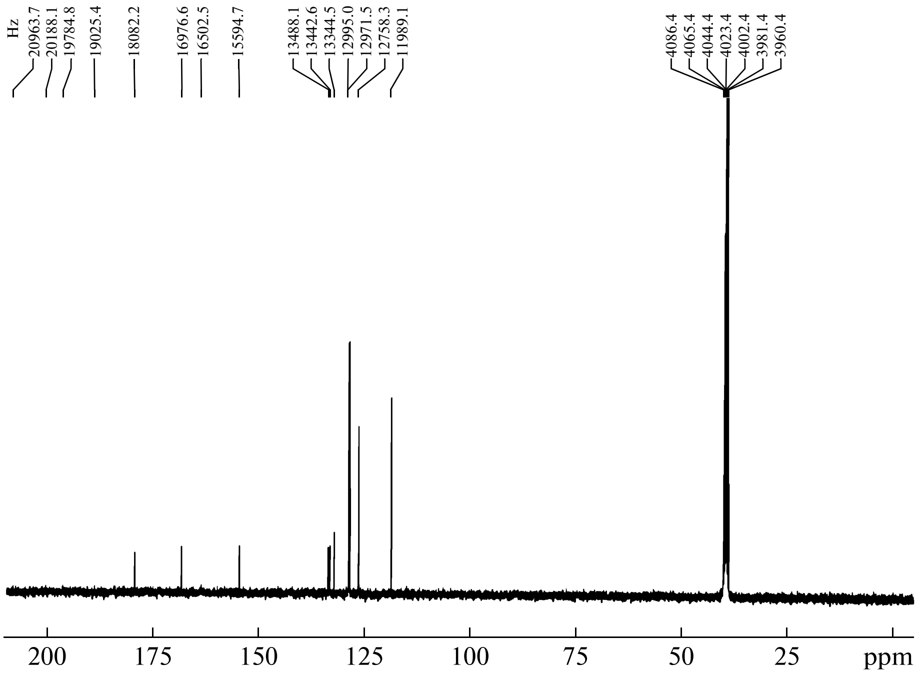


Fig. 3. ^{13}C NMR spectrum of **3** in DMSO.

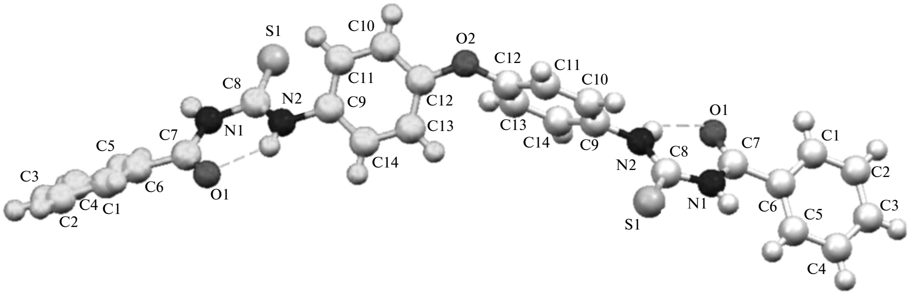


Fig. 4. The molecular structure of **3**, showing 10% probability displacement ellipsoids and the atomic numbering scheme. Intramolecular hydrogen bonds are shown as dashed lines.

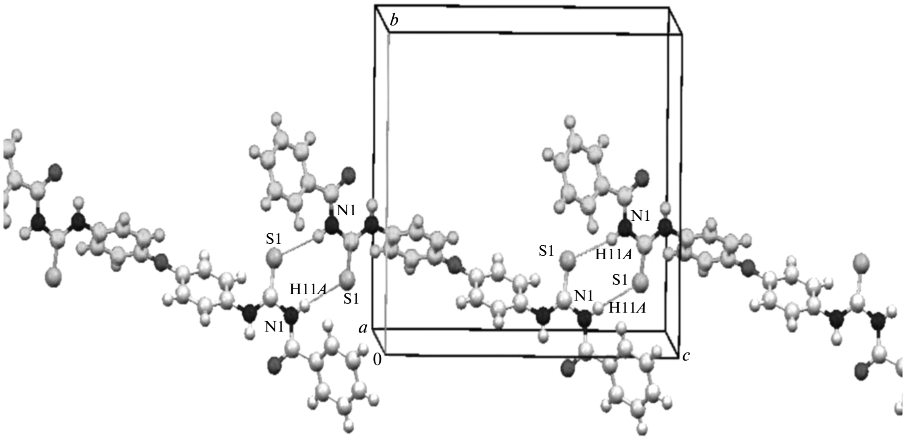


Fig. 5. A molecular chain running parallel to the [001]. The intermolecular hydrogen bonds are indicated by dashed lines.

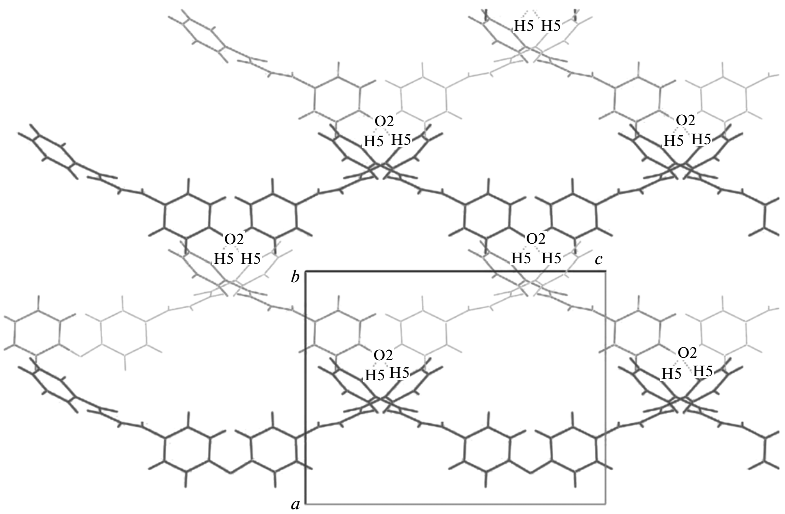


Fig. 6. Projection of crystal structure of 3 along *a* showing nonclassical bifurcated C5–H5···O2 hydrogen bonds (dashed lines).

Table 2. Selected bond distances *d*, Å, bond angles ω, deg, and torsion angles, τ, deg

Bond	*D*	Bond	*d*
S1–C8	1.665(4)	O1–C7	1.223(5)
O2–C12	1.389(4)	C8–N2	1.326(5)
N1–C7	1.383(5)	N2–C9	1.427(5)
N1–C8	1.397(5)		
Bond angle	Ω	Bond angle	ω
N1–C8–S1	118.5(3)	O1–C7–N1	121.7(4)
$C12^{i}$–O2–C12	122.2(4)	C8–N2–C9	125.9(4)
C7–N1–C8	128.5(4)	N2–C8–S1	126.3(3)
N2–C8–N1	115.2(4)		
Torsion angle	τ	Torsion angle	τ
C7–N1–C8–N2	0.7(6)	12^{i}–O2–C12–C11	–177.8(4)
C7–N1–C8–S1	179.5(3)	$C12^{i}$–O2–C12–C13	–148.2(5)
C8–N1–C7–O1	2.3(7)	N1–C8–N2–C9	–174.6(3)
S1–C8–N2–C9	6.8(6)		

Symmetry code: (i) $x, -y + 1/2, -z + 1/2$.

Table 3. Geometric details of intra- and intermolecular hydrogen bonds in the structureof the title compound

D–H···*A*	Distances, Å			*D*–H···*A* angle, deg
	D···*A*	*D*–H	H···*A*	
N2–H2A···O1	0.86	1.92	2.622(5)	137
N1–H11A···$S1^{ii}$	0.86	2.67	3.443(4)	150
C5–H5···$O2^{iii}$	0.93	2.50	3.411(5)	165
C5–H5···$O2^{iv}$	0.93	2.50	3.411(5)	165

Symmetry codes: $^{ii}\ x, -y + 1/2, -z + 3/2$; $^{iii}\ x - 1/2, y, -z + 1$; $^{iv}\ x - 1/2, -y + 1/2, z + 1/2$.

Crystal structure. The molecular structure of **3** is presented in Fig. 4, while their packing in crystal is shown in Fig. 5 and 6. The molecule is situated on twofold axis. Selected bond distances and bond angles are listed in Table 2. The two thiourea groups are thus *anti* relative to one another, as indicated by the twofold rotation axis as a result of bipodal structure.

In crystal 3, an intra- and two intermolecular hydrogen bonds exist (Table 3). The intramolecular hydrogen bond N2–H2···O1 generates S(6) motif as in the case of similar compounds [26]. Intermolecular hydrogen bonds N1–H11A···S1 forming a $R_2^2(8)$ motif connect the molecules into the chains parallel to [001]. Similar interactions were found in another compound [27–29] (Fig. 5). C5 atom forms bifurcated hydrogen bond C5–H5···O2 (Fig. 6).

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