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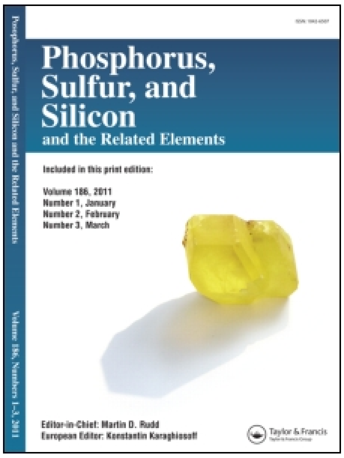

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis and Structure of N-Ethoxycarbonyl-N'-O-Methoxyphenylthiourea

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N-ethoxycarbonyl-N′-o-methoxyphenylthiourea was synthesized and characterized by elemental analysis, TG-DTA analysis, IR, and ^1H NMR spectrum, and single crystal X-ray diffraction analysis. The compound crystallizes as a planar molecule in the monoclinic space group P2(1)/c, with $a = 9.690(2)$ Å, $b = 8.595(2)$ Å, $c = 15.944(4)$ Å, $\alpha = 90°$, $\beta = 106.467(4)°$, $\gamma = 90°$, and $D_{calc} = 1.326\ g/cm^3$ for $Z = 4$. Intramolecular H-bonds promote the stability of the title compound and change the coordination ability of the thiourea ligand. Intermolecular N—H...S H-bonds link pairs of two molecules.

Keywords Molecular structure; single crystal; thiourea; X-ray diffraction

INTRODUCTION

Thiourea derivatives are "old" ligands that were synthesized and well documented in previous works;[1] but in recent years these kind of compounds have been paid special attention because thiourea derivatives have antitumor and antifungal bioactivities and active chemical properties etc. They also have been widely applied in many research fields

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such as the extraction of trace metals and the separation of platinum group metal and may be applied in a coordination reaction etc.[2–4] Of all the thiourea derivatives, both the carbonyl thiourea derivatives have received the most attention because the existence of carbonyl and thiocarbonyl groups in these ligands enhances the coordination ability. They also readily form supramolecular structures via hydrogen bonds.[5,6]

In our previous works,[7–11] the carbonyl thiourea derivatives and the corresponding coordination compounds with Cu(I) were synthesized and characterized, and the influence of intramolecular hydrogen bonds in the ligands on the coordination behaviors of ligands was discussed. In order to probe deeply into the hydrogen bonding actions in the coordination reaction of the carbonyl thiourea derivatives with transition metals, the synthesis, characterization, thermodynamic properties and single crystal structure of the compound (I), *N*-ethoxycarbonyl-*N*′-*o*-methoxyphenylthiourea, are reported herein.

RESULTS AND DISCUSSION

The TG-DTA data of compound (I) show that there are two absorption peaks, which have a melting peak at 141.6°C and a decomposition peak at 202.4°C.

The IR spectrum of compound (I) shows two bands at 3134 and 3435 cm^{-1} due to NH stretching. Because C=O is locked into the hydrogen bond, the carbonyl stretch appears at 1726 cm^{-1}. A strong band at 1252 cm^{-1} is assigned as the thiocarbonyl group.

The details concerning data collection and refinement of X-ray diffraction analysis are given in Table I and the data on the hydrogen bonds are listed in Table II. A molecular structural view is shown in Figure 1 and molecular packing diagram is shown in Figure 2.

In the molecular structure of compound (I), the carbonyl and thiocarbonyl moieties point in approximately opposite directions. Both N—H atoms participate in the formation of hydrogen bonds. Two intramolecular hydrogen bonds exist between N1, O1 and N1, O2 (Table II). They make this molecule form two six-numbered hydrogen bond rings, which are almost coplanar with the substituted benzene ring with a mean deviation of 0.0652 Å from the least squares plane formed by the previously mentioned hydrogen bond rings and the benzene ring. The formation of coplanar hydrogen rings promotes the stability of the thiourea compound and probably leads to the observed shortening of the C1—N1 single bond involved in hydrogen bonding to 1.327(3) Å, which is close to the double bond length of C=N 1.28 Å.[12] Thus the single bond of C1—N1 shows a little double bond character. However, the single bond length of C1—N2 on the other side of the thiocarbonyl group C=S is 1.384(3) Å.

TABLE I X-Ray Diffraction Analysis Data

$C_{11}H_{14}N_2O_3S$	$D_x = 1.326$ Mg m^{-3}
$Mr = 254.30$	Mo$K\alpha$ radiation (0.71073 Å)
Monoclinic, $P2_1/c$	Cell parameters from 903 reflections
a = 9.690(2) Å	$\theta = 2.66^\circ - 26.32^\circ$
b = 8.595(2) Å	$\mu = 0.253$ mm^{-1}
c = 15.944(4) Å	$T = 293(2)$ K
$\beta = 106.467(4)^\circ$	Block, Colorless
$V = 1273.4(5)$ Å^3	Crystal size 0.4 × 0.3 × 0.2 mm
$Z = 4$	
Data Collection	
Bruker SMART diffractometer	$R_{int} = 0.0209$
ϕ/ω scans	$\theta_{max} = 26.4^\circ$
7164 measured reflections	$h = -8 \rightarrow 12$
2603 independent reflections	$k = -10 \rightarrow 8$
1830 reflections with $I > 2\delta$ (I)	$l = -19 \rightarrow 19$
Refinement	
Refinement on F^2	164 parameters
$R[F^2 > 2\delta(F^2)] = 0.043$	$\omega = 1/[\delta^2(F_0^2) + (0.0454P)^2 + 0.0.6655P]$
$R(F^2) = 0.119$	where $P = (F_0^2 + 2F_c^2)/3$
$S = 1.02$	$\Delta\rho_{max} = 0.357$ e Å^{-3}
2603 reflections	$\Delta\rho_{min} = -0.337$ e Å^{-3}

The difference in the lengths of the C—N bonds close to the thiocarbonyl group will influence the attack of a nucleophilic reagent, e.g. $NaOCH_3$, on the thiourea ligand and the formation of C=N and oxazoline ring in the desulfurisation.[5,11]

Because the carbonyl O atom is involved in hydrogen bonding, it is often difficult for the carbonyl O atom of thiourea derivatives to participate in the coordination with metal ions.[7,8] However, in disubstituted thiourea derivatives, the carbonyl O atom commonly takes part in the coordination reaction.[13]

Because of the formation of hydrogen bonds, the ^{1}H NMR chemical shift of H1 on N1 appears in the low field. The chemical shift $\delta = 8.49$

TABLE II Hydrogen-Bonding Geometry (Å,°)

D—H···*A*	*D*—H	H—*A*	D···*A*	*D*—H···*A*
N2—H2···S*	0.86	2.55	3.39	167
N1—H1···O1	0.87	2.10	2.54	111
N1—H1···O2	0.87	1.93	2.68	143
C7—H7···S1	0.93	2.60	3.23	126

*Symmetry codes: 1-x, −y, 2-z

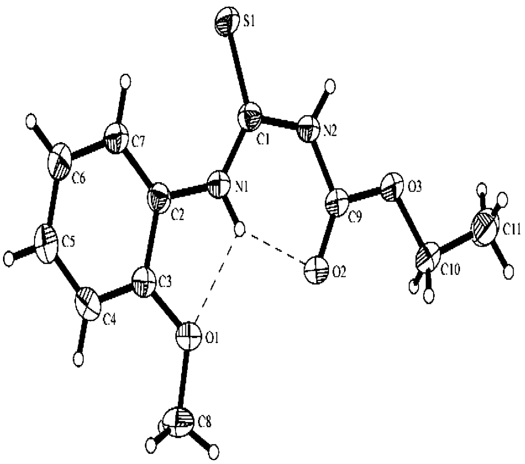

FIGURE 1 View of compound (I) showing the atom labelling. Intramolecular H-bonds are indicated by dashed lines.

of H7 on the benzene ring is in a lower field compared with the other hydrogen atoms on benzene; this is also due to the weak intramolecular hydrogen bond between C7—H7···S1.

Between thiocarbonyl S atom and H2 on N2, there is also an intermolecular hydrogen bond (1−x, −y, 2−z) by which two ligand molecules

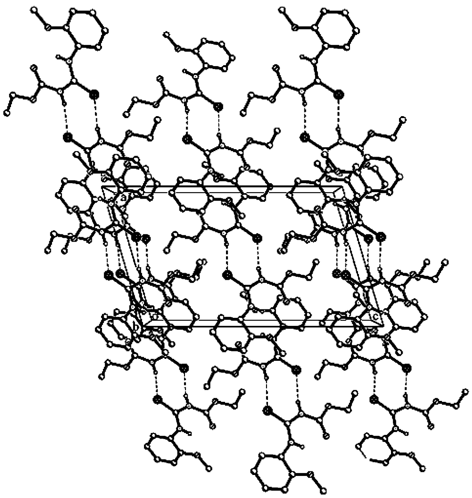

FIGURE 2 Packing diagram.

are connected into a dimer with a eight-numbered hydrogen ring between them.

EXPERIMENTAL

The infrared spectrum was recorded in the range of 4000–400 cm^{-1} on a Nicolet NEXUS 670 FT-IR spectrometer, using KBr pellets. The ^1H NMR spectrum was obtained on an INOVA-400 MHz superconduction spectrometer. DMSO-d_6 was used as the solvent and TMS as the internal standard. Chemical shifts are expressed as δ. Elemental analyses were carried out on a PE-2400 CHN instrument. Melting point determination was performed in an open capillary tube and is uncorrected. The TG-DTA DT-40 analysis was carried on a (Japan Shimadzu) thermalyzer. Experimental data: heating rate, 10 K min^{-1}; atmosphere, nitrogen; flow rate of furnace, 60 mL min^{-1}; crucible, platinum; sample size, 4 mg; references substance, α-Al_2O_3.

Single crystal X-ray data were collected on a Bruker SMART diffractometer using monochromated Mo Kα radiation. The structure was solved by direct Fourier methods. Full-matrix least-squares refinement was based on F^2. Programs used for calculations were SHELXTL.[14,15]

All chemicals used for the preparation of the compound were of reagent grade quality. The compound was obtained in CH_2Cl_2 using the method reported in the previous works.[10] The single crystals were obtained after one week by slow evaporation of a chloroform solution.

N-ethoxycarbonyl-*N*′-*o*-methoxyphenylthiourea color: white, Yield: 85%, m.p. 138–139°. Anal. required for $C_{11}H_{14}N_2O_3S$: C, 51.95; H, 5.55; N, 11.02. Found: C, 51.88; H, 4.78; N, 10.56. IR (KBr pellet, cm^{-1}): ν = 3435 (NH), 3134 (NH), 1726 (C=O), 1567, 1536, 1498 (C=C), 1252 (C=S). ^1H NMR (δ) ppm: 1.24 (t, 3H, CH_3); 3.84 (s, 3H, $ArOCH_3$); 4.20 (q, 2H, CH_2); 6.93–8.49 (m, 4H, ArylC_6H_4); 11.27 (s, 1H, NH); 11.90 (s, 1H, NH).

A fully completed Crystallographic Information File deposited with the CCDC is available (CCDC No. 260880).

REFERENCES

[1] D. C. Schroeder, *Chem. Rev.*, **55,** 181 (1955).
[2] K. R. Koch, *Coord. Chem. Rev.*, **216–217,** 473 (2001).
[3] O. Foss, S. Husebye, K.W. Törnroos, and P. E. Fanwick, *Polyhedron*, **23,** 3021 (2004).
[4] P. Bombicz, I. Mutikainen, M. Krunks, T. Leskelä, J. Madarász, and L. Niinistö, *Inorg. Chim. Acta*, **357,** 513 (2004).
[5] X. Shen, X. Shi, B. Sheng, Y. Tong, Y. Liu, L. Gu, Q. Liu, and Y. Huang, *Polyhedron*, **18,** 33 (1998).
[6] K. R. Koch, J. D. S. Miller, and O. Seidelmann, *Inorg. Chim. Acta*, **331,** 136 (2002).

[7] B. Q. Su, L. Xian, H. B. Song, and L. Sheng, *Acta Cryst.*, **C60,** m661 (2004).
[8] L. Xian, T. B. Wei, and Y. M. Zhang, *J. Coord. Chem.*, **57,** 453 (2004).
[9] Y. M. Zhang, T. B. Wei, L. Xian, and L. M. Gao, *Phosphorus, Sulfur, and Silicon*, **179,** 2007 (2004).
[10] Y. M. Zhang, L. Xian, T. B. Wei, and L. X. Cai, *Acta Cryst.*, **E59,** o817 (2003).
[11] Y. M. Zhang, L. Xian, T. B. Wei, and K. B. Yu, *J. Chem. Res.*, **12,** 798 (2003).
[12] M. Gómez, G. Muller, and M. Rocamora, *Coord. Chem. Rev.*, **193–195,** 769 (1999).
[13] C. Sacht and M. S. Datt, *Polyhedron*, **19,** 1347 (2000).
[14] G. M. Sheldrick, SHELXL97. University of Göttingen, Germany. (1997).
[15] G. M. Sheldrick, *Acta Cryst.*, **A46,** 467 (1990).