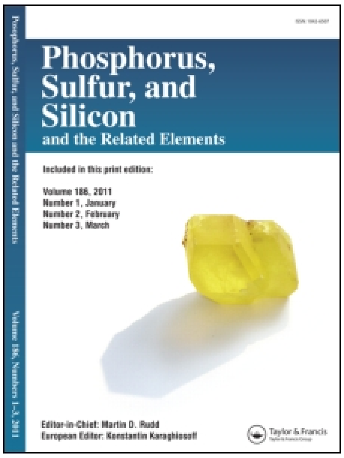


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Studies on the Crystal Structure and Properties of N-(2-ethoxyphenyl)-N'-(4-ethoxybenzoyl)-thiourea

Jing-Han Hu[a]; Li Xu[a]; Jun Wang[b]; Tai-Bao Wei[b]
[a] College of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu, P. R. China [b] Department of Chemistry, Northwest Normal University, Lanzhou, Gansu, P.R. China

To cite this Article Hu, Jing-Han , Xu, Li , Wang, Jun and Wei, Tai-Bao(2008) 'Studies on the Crystal Structure and Properties of N-(2-ethoxyphenyl)-N'-(4-ethoxybenzoyl)-thiourea', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 7, 1584 — 1591

To link to this Article: DOI: 10.1080/10426500701693495

URL: http://dx.doi.org/10.1080/10426500701693495

Phosphorus, Sulfur, and Silicon, 183:1584–1591, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701693495

Taylor & Francis
Taylor & Francis Group

Studies on the Crystal Structure and Properties of N-(2-ethoxyphenyl)-N′-(4-ethoxybenzoyl)-thiourea

Jing-Han Hu,[1] Li Xu,[1] Jun Wang,[2] and Tai-Bao Wei[2]
[1]College of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu, P. R. China
[2]Department of Chemistry, Northwest Normal University, Lanzhou, Gansu, P.R. China

The N-(2-ethoxyphenyl)-N′-(4-ethoxybenzoyl)-thiourea has been synthesized under phase transfer catalysis at room temperature. The compound was characterized via IR, ^{1}H NMR, ^{13}C NMR, elemental analysis, and the structure of the compound was determined by X-ray diffraction analysis. Its crystal belongs to nonoclinic space group, with $a = 2.0236(5)$ *nm,* $b = 1.4543(4)$ *nm,* $c = 1.4067(3)$ *nm and* $\alpha = 90.00°$, $\beta = 119.21(1)°$, $\gamma = 90.00°$ *and* $Z = 8$. *The compound exhibits selective recognition for* $H_2PO_4^-$, AcO^-, *and* F^- *in* Me_2SO. *In addition, the compound is also a considerable plant-growth regulator.*

Keywords Anion recognition property; biological activity; crystal structure; thiourea

INTRODUCTION

Studies of N-aryl-N′-benzoyl-thiourea have attracted increasingly considerable attention due to their potential use in agriculture, extraction, separation, medicine and analytical chemistry.[1–4] And N-acyl-thiourea derivatives are associated with various kinds of biological activities.[5] The crystal structures of those compounds have revealed many significant structural phenomena, including inter-, intra-molecular hydrogen bonds, and $\pi - \pi$ interactions between phenyl groups. Recently, thiourea and its derivatives as neutral receptors have been growing in the field of host-guest chemistry.[6–8] Among a variety of possible H-bond donor groups, systems employing thiourea moieties have been proven

Received 5 May 2007; accepted 27 August 2007.

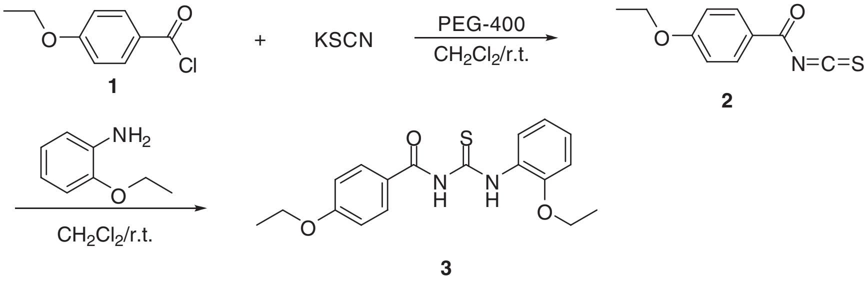
We gratefully acknowledge the support of the Key Project of Gansu Provincial Science and Technological Department (No. 2GS057-A52-001-04), National Natural Science Foundation of China (No. 20671077).

Address correspondence to Jing-Han Hu, College of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu, 730070, P. R. China. E-mail: hujinghan62@163.com

to be very efficient in the design of neutral anion binding receptors.[9–13] Moreover, it is well demonstrated that phenyl substituted thiourea compounds exhibit strong binding ability[13] as compared with that of alkyl substituted ones. In continuation of our earlier work,[14] we report the preparation of the title compound and study its properties. The results show that it can be used as anion sensor in DMSO, owing to its ability to act as classical H-bond donor. At the same time, by investigating the biological activity of the title compound, we found that the compound has high plant growth regulating activity at low concentration.

RESULTS AND DISCUSSION

N-(2-ethoxyphenyl)-N′-(4-ethoxybenzoyl)-thiourea has been synthesized according to the previous papers[15–16] in high yield under PEG-400 as the phase-transfer catalyst (Scheme 1). And, it was characterized by element analysis, IR, ^{1}H NMR, ^{13}C NMR, and X-ray single crystal diffraction.



SCHEME 1

Structure Determination

Intensity data of title compound was collected 296(2) K on the Bruker SMART diffractometer and used graphite monochromatic MoKα radiation ($\lambda = 0.71073$ Å). A total of 3365 unique reflections (R(int) = 0.0197) were collected in the range of $1.81^\circ < \theta < 25.50^\circ$ ($0 \leq h \leq 24$, $1 \leq k \leq 17$, $-17 \leq l \leq 14$) with Φ-ω scans mode, in which 1572 reflections are $1 < 2\sigma(I)$. Empirical absorption correction was applied to the raw intensities by using SADABS program.[17] The structure was solved by direct methods and full-matrix least-squares method based on F^2 using SHELXTL program package.[18] Non-hydrogen atoms were subjected to anisotropic refinement. The data collection and refinement processes for $C_{18}H_{20}N_2O_3S$ are summarized in Table I.

TABLE I The Crystal Data of the Title Compound

Empirical formula	$C_{18}H_{20}N_2O_3S$
Formula weight	344.43
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 2.0236(5)$ nm $\alpha = 90.00^\circ$ $b = 1.4543(4)$ nm $\beta = 119.21(1)^\circ$ $c = 1.4067(3)$ nm $\gamma = 90.00^\circ$
Volume	3.6135(19) nm^{-3}
Z	8
Density (calculated)	1.274 mg/cm^3
Absorption correction	empirical
F(000)	1465
Absorption coefficient	0.198 mm^{-1}
Reflections collected	3365
Independent reflections	1572 [R(int) = 0.0197]
Data/restraints/parameters	3365 /0 / 231
Final R indices [I > 2sigma(I)]	R1 = 0.0437, wR2 = 0.0827
R indices (all data)	R1 = 0.1061, wR2 = 0.0918
Goodness of fit on F^2	0.974
Largest diff. Peak and hole	0.196 and −0.181 e. $Å^{-3}$

Crystal Structure

The structure of the title compound is shown in Figure 1. Selected bond distances and angles are listed in Table II. As presented in Figure 1, the N1-H pendant arm extends towards the carbonyl O atom and forms an intramolecular hydrogen bond between them (Table III). The six atoms N(1)-C(7)-N(2)-C(8)-O(2) in the hydrogen-bonded ring structure are almost coplanar, the mean deviation from plane is 0.0253Å. And, this six-membered ring forms a dihedral angle of 13° and 152.9° with the plane O(2), C(8), C(9), C(14), and C(6), C(7), N(1), C(1), O(1), respectively.

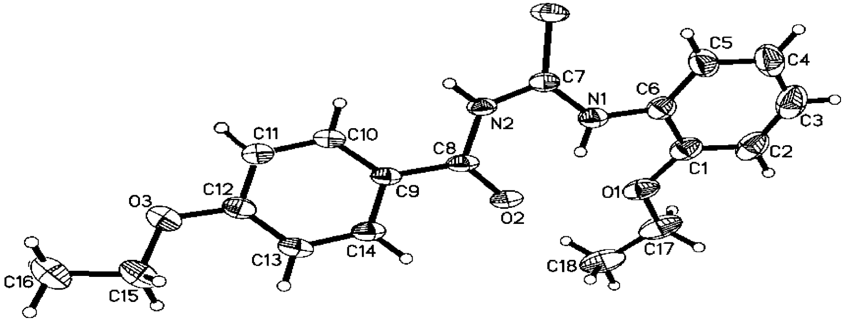


FIGURE 1 The crystal structure of the title compound.

TABLE II Selected Bond Distances (nm) and Bond Angles (°) for the Compound

Bond lengths			
S-C(7)	1.658(2)	O(1)- C(1)	1.365(3)
O(1)-C(17)	1.415(3)	O(2)-C(8)	1.217(2)
O(3)-C(12)	1.359(3)	O(3)-C(15)	1.423(3)
N(1)-C(7)	1.337(3)	N(1)-C(6)	1.421(3)
N(2)-C(7)	1.379(3)	N(2)-C(8)	1.384(2)
C(1)-C(6)	1.389(3)	C(1)-C(2)	1.407(4)
Bond angles			
C(1)-O(1)-C(17)	118.5(3)	C(7)-N(1)-C(6)	130.5(2)
O(2)-C(8)-N(2)	120.5(2)	C(12)-O(3)-C(15)	118.7(2)
O(2)-C(8)-C(9)	122.9(2)	C(7)-N(2)-C(8)	130.1(2)
O(1)-C(1)-C(6)	115.3(3)	O(1)-C(1)-C(2)	124.2(3)
C(6)-C(1)-C(2)	120.5(3)	C(3)-C(2)-C(1)	117.3(4)
C(4)-C(3)-C(2)	122.8(4)	C(3)-C(4)-C(5)	120.0(4)

From Figure 2, in the crystal structure ,we can see that each pair of molecules is connected with a dimer by two intermolecular N—H· · ·S hydrogen bonds (Figure 3).

Anion Recognition Properties

The binding ability of receptor **3** towards different anions (tetra(n-butyl) ammonium were used for counter cations) was investigated through UV-Vis titration experiment in DMSO. Data from UV-Vis titrations were processed through a non-linear least-squares procedure[19] in order to determine association constants K. The result indicated that the receptor **3** exhibited selective recognition for F^-, AcO^-, and $H_2PO_4^-$ in DMSO. However, the addition of other anions scarcely showed spectral changes.

Upon addition of AcO^- from 0 to 200 equiv., the peak at 298 nm decreases while a new peak of 325 nm increases and appears two isosbestic points, which suggested the formation of complex between receptor **3** and AcO^-, as shown in Figure 4. The association constant and correlation coefficient of receptor **3** with AcO^- were 1.1 10^4, 0.9965,

TABLE III Data of Hydrogen Bond(nm) and Angle (°) of Title Compound

D—H· · ·A	D—H	H· · ·A	D· · ·A	∠DHA	Symmetry code
N(1)-H(1)· · ·O(2)	0.086	0.191	0.2628(2)	139.80(1)	
N(2)-H(2)· · ·N	0.086(2)	0.2730(1)	0.3514(1)	152.90(19)	x +1/2, y+1/2,Z

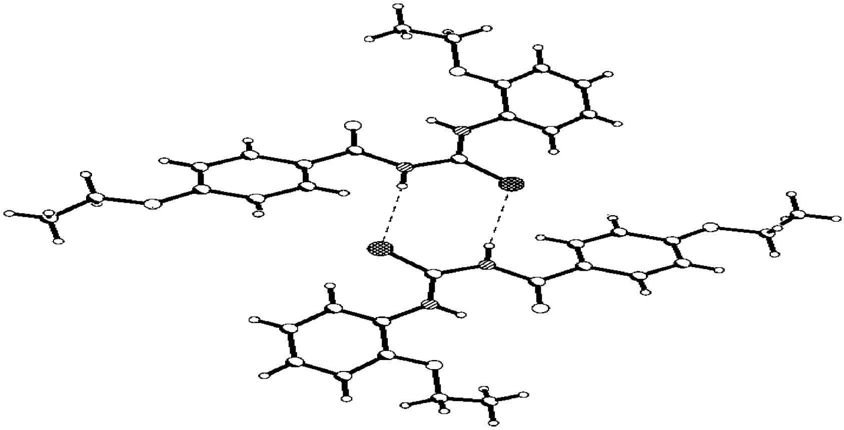


FIGURE 2 A view of the intermolecular hydrogen bonds N—H· · ·S.

respectively. The results illustrated the 1:1 stoichiometry complex was formed by hydrogen bonding, as show in Figure 5. The anion-binding properties of F^- and $H_2PO_4^-$ in DMSO are similar to it of AcO^-, the association constant were 2.7×10^4, 1.0×10^3, respectively. These results demonstrate that receptor **3** can be used for sensing F^- and AcO^- over $H_2PO_4^-$.

Biological Activity

We also investigated plant growth regulation activity. Here, we adopted the method of plate culture. The compound was collected to the solution

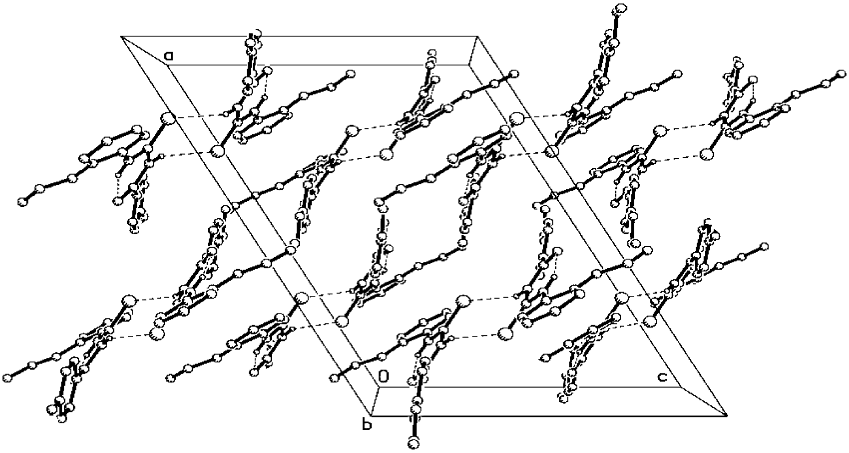


FIGURE 3 Packing diagram of the title compound.

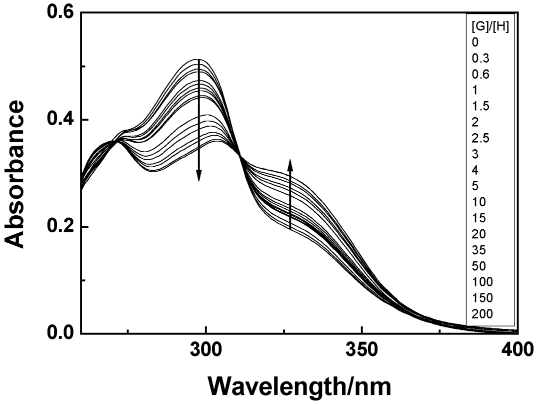


FIGURE 4 UV-vis spectra of **3** (2×10^{-5}) in DMSO after the addition of 0→200 equiv. of AcO^-.

in concentration of 100 ppm, 50 ppm, 10 ppm, and coleseed was cultured in a 10 cm Petri dish with 10 mL different solution and a circular filter paper. After growing at room temperature for 4 days, the root length was gained and the percentage plant growth activity was calculated according to the following equation:

$$\text{Percentage plant growth activity} = (N - N1)/N1 \times 100\% \qquad (1)$$

In Eq. (1), N is the root length cultured in compound solution and N1 is the root length cultured in the distilled water under the same condition. The data are shown in Table IV.

From the results summarized in Table IV, compared with heteroauxing, the compound exhibited root elongation activity, and with the

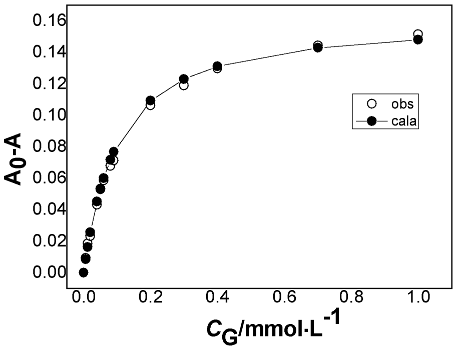


FIGURE 5 Plot of the absorbance of receptor **3** at 298 nm vs. equivalents of AcO^- in DMSO.

TABLE IV Plant Growth Regulating Activity Data (Rape)

	% Plant growth activity [a]		
Compound	100 ppm	50 ppm	10 ppm
3	20.15	31.55	37.76
Heteroauxing	−81.7	−63.1	−30.9

[a] The solution was prepared in the proportion of H_2O:DMF = 99.5:0.5, and 0.1 g Tween-80 was added to promote the compound to dissolved.

concentration was decreased from 100 ppm to 10 ppm, the root elongation activity becomes strengthener gradually. It is evident that the compound show good plant-growth regulation activity.

CONCLUSIONS

In summary, we have synthesized N-(2-ethoxyphenyl)-N′-(4-ethoxybenzoyl)- thiourea based anion receptor and determined IR, ^{1}H NMR, ^{13}C NMR, and X-ray diffraction analysis. The compound crystallizes in nonoclinic space group and each pair of molecules is connected with a dimer by two intermolecular N—H···S hydrogen bonds. The anion-binding properties have been studied by UV-Vis, which is shown to be capable of strongly binding for F^- and AcO^- over $H_2PO_4^-$ through hydrogen bonding interaction in DMSO and formed a 1:1 stoichiometry complex with basic anions. In addition, investigation of biological activity shows the compound show good plant-growth regulation activity.

EXPERIMENTAL

Material and Methods

Melting points were measured on a X-4 digital melting-point apparatus and were uncorrected. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury plus-400 MHz spectrometer.

General Procedure for the Preparation of Compounds 3

Powdered potassium thiocyanate 0.73 g (7.5 mmol) 4-ethoxybenzoyl chloride 0.92 g (5 mmol), PEG-400 (3% With respect to ammonium thiocyanate), and 20 mL of dichloromethane were placed in a dried round-bottomed flask containing a magnetic stirrer bar and stirred at room temperature for 1 h; then 2-ethoxybenzenamine 0.69 g (5 mmol) was added, and the mixture was stirred for additional 0.5 h. The corresponding thiosemicarbazide precipitates immediately. The product is filtered, washed with water to remove inorganic salts, dried, and recrystallized from DMF-EtOH-H_2O to give the title compound.

Yield, 78%; m.p. 119–121°C; ^{1}H NMR(DMSO-d_6, 400MHz) δ: 13.27 (s, 1H, NH), 11.34(s, H, NH), 6.99 ~8.76(m, 8H, ArH), 4.11(dd 2H, CH_2), 4.15(dd 2H, CH_2), 1.35(t, 3H, CH_3), 1.42 (t, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 400MHz) δ: 14.50, 14.59, 63.61, 64.33, 112.26, 114.12(2C), 119.72, 122.47, 123.64, 126.30, 127.35, 131.02(2C), 149.59, 162.52, 167.54, 177.63; IR (KBr, cm^{-1})υ: 3307, 3039 (NH), 2977, 2931 (CH), 1602, 1549, 1499 (Ar), 1675 (C=O), 1155 (C=S); 1249(-O-); Anal. calcd. for $C_{18}H_{20}N_2SO_3$: C: 62.77, H: 5.85, N: 8.13; found C: 62.70, H: 5.90, N: 8.07.

REFERENCES

[1] D. C. Schroeder, *Chem. Rev.,* **50,** 185 (1955).

[2] A. Irving, K. R. Koch and M. Matoetoe, *Inorg. Chim. Acta,* **206,** 193–199 (1993).

[3] X. Shen, X. Shi, B. Kang, Y. Liu, H. Jiang, and K. Chen, *Plyhedron*, **17,** 4049 (1998).

[4] M. S. Sheridana, D. R. Nagaraj, D.Fornasieroa, and J. Ralstona, *Minerals Engineering,* **5,** 333 (2002).

[5] K. S. Uppal and S. K. Baneji, Indian J. *Agric. Chem.*, **18,** 85 (1985).

[6] D. A. Amilan, D. K. Kumar, B. Ganguly, and A. Das, *Org. Lett.*, **6,** 3445–3448(2004).

[7] F. M. Pfeffer, T. Gunnlaugsson, P. Jensen, and P. E. Kruger, *Org. Lett.*, **7,** 5357–5360 (2005).

[8] L. S. Evans, P. A. Gale, M. E. Light, and R. Quesada, *Chem. Commun.*, 965–967 (2006).

[9] Y. M. Zhang, J. D. Qin, Q. Lin, and T. B. Wei, *J. Flu. Chem.*, **127,** 1222-1227 (2006).

[10] D. H. Lee, H. Y. Lee, K. H. Lee, J. I. Hong, *Chem. Commun.*, 1188–1189 (2001).

[11] J. L. Wu, Y. B. He, Z. Y. Zeng, L. H. Wei, L. Z. Meng, and T. X. Yang, *Tetrahedron*, **60,** 4309–4314 (2004).

[12] S. I. Kondo, M. Nagamine, and Y. Yano, *Tetrahedron Lett.*, **44,** 8801–8804 (2003).

[13] P. Buhlmann, S. Nishizawa, K. P. Xiao, Y. Umezawa, *Tetrahedron*, **53,** 1647–1654 (1997).

[14] J. H. Hu, L. C. Wang, H. Liu, and T. B. Wei, *Phosphorus, Sulfur, and Silicon*, **181,** 2691 (2006).

[15] S. J. Xie, S. Y. Ke, T. B. Wei, L. P. Duan, and Y. L. Guo, *J. Chin. Chem. Soc.*, **51,** 1013–1018 (2004).

[16] T. B. Wei, Q. Lin, Y. M. Zhang, and W. Wei, *Synth. Commun.,* **34,** 181–186 (2004).

[17] G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.

[18] G. M. Sheldrick, *SHELXTL:Structure Determination Software Program* (Bruker Analytical X-ray System, Inc., Madison, WI, 1997).

[19] Y. Liu, B. Li, and B. H. Han, *J. Chem. Soc. Perkin Trans.,* **2,** 563–568 (1999).