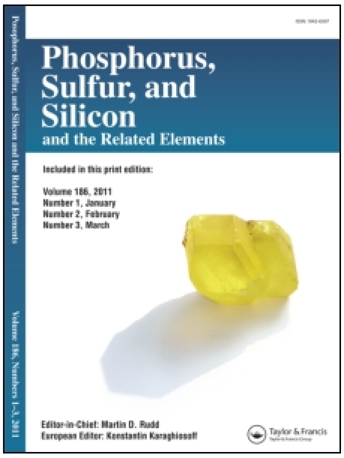

**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# Weak Interaction and Supramolecular Structure of <i>N</i>-ethoxycarbonyl-<i>N</i>'-arylthiourea

Qi Lin[a]; Tai-Bao Wei[a]; You-Ming Zhang[a]
[a] College of Chemistry and Chemical Engineering, Gansu Key Laboratory of Polymer Materials, Northwest Normal University, Lanzhou, Gansu, P.R. China

**To cite this Article** Lin, Qi , Wei, Tai-Bao and Zhang, You-Ming(2007) 'Weak Interaction and Supramolecular Structure of <i>N</i>-ethoxycarbonyl-<i>N</i>'-arylthiourea', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 4, 863 — 871

**To link to this Article: DOI:** 10.1080/10426500601087392

**URL:** http://dx.doi.org/10.1080/10426500601087392

*Phosphorus, Sulfur, and Silicon*, 182:863–871, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500601087392

# Weak Interaction and Supramolecular Structure of *N*-ethoxycarbonyl-*N′*-arylthiourea

**Qi Lin**
**Tai-Bao Wei**
**You-Ming Zhang**
College of Chemistry and Chemical Engineering, Gansu Key Laboratory of Polymer Materials, Northwest Normal University, Lanzhou, Gansu, P.R. China

*Two kinds of N-ethoxycarbonyl-N′-arylthiourea were synthesized, and their structure was determined by X-ray diffraction. There are inter- and intramolecular hydrogen bonds in these compounds. In the crystals, the compounds were assembled to one-dimensional catenulate supramolecular structure by intermolecular hydrogen bonds.*

**Keywords** Hydrogen bond; supramolecular; thiourea

## INTRODUCTION

Thiourea derivatives have been found to possess many important biological activities;[1] many of them are used as heribicides,[2,3] insecticides[4,5] and plant-growth regulators.[6] In addition, owning to their strong coordination ability,[7,8] N-substituted- N′-ethoxycarbonyl thioureas are extensively utilized as the collector for some precious metals.[9] Recently, these compounds have attracted considerable attention for their potential uses as artificial receptors in supramolecular chemistry because of their characteristic behavior based on strong hydrogen-bond donors.[10,11] In fact, the biological activity and the

Received June 26, 2006; Accepted September 20, 2006.

The authors gratefully acknowledge the support of the Natural Science Foundation of China (No. 20371040), the Key Scientific and Technical Research Project of Ministry of Education of China (205161), and the Youth Foundation of Gansu province (3YS051-A25-010). At the same time, the authors thank the Key Laboratory of Eco-Environment-Related Polymer Materials (Northwest Normal University), Ministry of Education of China, for financial support.

Address correspondence to You-Ming Zhang, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, 730070, Gansu, P.R. China. E-mail: zhangnwnu@126.com.

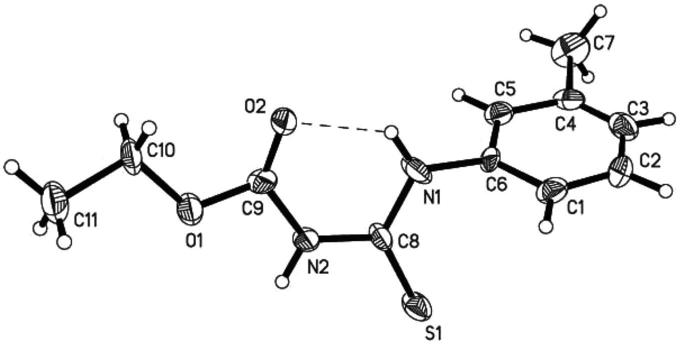

**FIGURE 1** The crystal structure of *N*-ethoxycarbonyl-*N*′-3-methylphenylthiourea.

coordination ability of these kinds of compounds are closely related to their structure. In view of this and as a part of our research on supramolecular weak interaction and molecular recognition characteristic of thiourea derivatives,[12–14] we synthesized two kinds of *N*-ethoxycarbonyl-*N*′-arylthiourea and obtained its unambiguous structure by X-ray analysis. There are inter- and intramolecular hydrogen bonds in these compounds. In the crystals, the compounds were assembled to a One-Dimensional (1D) catenulate supramolecular structure by intermolecular hydrogen bonds.

## RESULTS AND DISCUSSION

The molecular structure of *N*-ethoxycarbonyl-*N*′-3-methylphenylthiourea (**a**) and *N*-ethoxycarbonyl-*N*′-4-fluorophenylthiourea (**b**) are

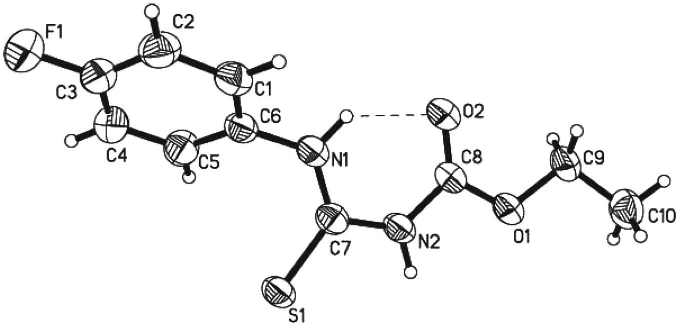

**FIGURE 2** The crystal structure of *N*-ethoxycarbonyl-*N*′-4-fluorophenylthiourea.

**TABLE I Crystal Data and Structure Refinement for a and b**

| Compounds | **a** | **b** |
|---|---|---|
| Formula | $C_{11}H_{14}N_2O_2S$ | $C_{10}H_{11}FN_2O_2S$ |
| Formula weight | 238.30 | 242.27 |
| Crystal system | triclinic | Monoclinic |
| Crystal color | colorless | colorless |
| Space group | $P1$ | $P2_1/n$ |
| $a$ (Å) | 5.8380(10) | 9.718(2) |
| $b$ (Å) | 9.441(2) | 25.712(5) |
| $c$ (Å) | 11.595(2) | 9.878(2) |
| $\alpha$ (deg) | 77.15(3) | 90.00 |
| $\beta$ (deg) | 87.89(3) | 109.86(3) |
| $\gamma$ (deg) | 86.22(3) | 90.00 |
| $V$ (Å$^3$) | 621.6(2) | 2321.4(8) |
| $D_{calcd}$. (g·cm$^{-3}$) | 1.273 | 1.213 |
| $\mu$ (mm$^{-1}$) | 0.248 | 0.244 |
| Total no. of reflns | 1296 | 2263 |
| No. of unique data | 1138 | 1378 |
| No. of params | 290 | 290 |
| $R$ | 0.0275 | 0.0402 |
| $R_w$ | 0.0694 | 0.0837 |
| Goodness of fit on $F^2$ | 1.059 | 1.058 |
| Largest peak/Hole in final diff map (e Å$^{-3}$) | 0.070, −0.059 | 0.068, −0.061 |

shown in Figures 1 and 2. Unit-cell data are listed in Table I and, selected bond distances and angles are listed in Tables II and III. Coordinates and equivalent isotropic thermal parameters for nonhydrogen atoms in the structure of **a** and **b** are listed in Table IV.

In the molecule of compound **a**, there is an intramolecular hydrogen bond, N1-H···O2, which forms a six-membered ring with C9, N2,

**TABLE II Selected Bond Length (nm) for a and b**

| **a** | | | | **b** | | | |
|---|---|---|---|---|---|---|---|
| S1—C8 | 0.1618(3) | N1—C8 | 0.1400(8) | S1—C7 | 0.1678(4) | N1—C6 | 0.1427(7) |
| O1—C9 | 0.1350(9) | N2—C8 | 0.1395(8) | O2—C8 | 0.1211(9) | N2—C7 | 0.1366(8) |
| O2—C9 | 0.1176(9) | N2—C9 | 0.1429(7) | O1—C8 | 0.1326(8) | N2—C8 | 0.1381(7) |
| O1—C10 | 0.1434(9) | N1—C6 | 0.1428(6) | O1—C9 | 0.1456(6) | N1—C7 | 0.1331(8) |
| C4—C7 | 0.1598(1) | C11—C10 | 0.1517(1) | F1—C3 | 0.1353(9) | C9—C10 | 0.1489(9) |
| C1—C6 | 0.1404(9) | C5—C6 | 0.1376(9) | C1—C6 | 0.1372(9) | C5—C6 | 0.1376(9) |
| C1—C2 | 0.1376(9) | C2—C3 | 0.1388(2) | C1—C2 | 0.1389(9) | C2—C3 | 0.1396(2) |
| C3—C4 | 0.1230(2) | C4—C5 | 0.1414(1) | C3—C4 | 0.1371(2) | C4—C5 | 0.1372(9) |

**TABLE III Selected Bond Angle (°) and Torsion Angle (°)**

| a | | b | |
|---|---|---|---|
| N1—C8—S1 | 126.4(5) | N1—C7—S1 | 124.6(4) |
| N1—C8—N2 | 113.8(6) | N2—C7—S1 | 118.1(4) |
| N1—C6—C1 | 119.8(6) | N1—C6—C1 | 118.7(5) |
| N2—C8—S1 | 119.8(4) | N1—C7—N2 | 117.3(4) |
| O2—C9—N2 | 127.6(6) | O2—C8—N2 | 125.7(6) |
| O1—C9—O2 | 126.9(6) | O1—C8—O2 | 125.4(5) |
| O1—C9—N2 | 105.4(5) | O1—C8—N2 | 108.8(5) |
| C9—O1—C10 | 114.8(5) | C8—O1—C9 | 116.3(5) |
| C8—N2—C9 | 127.4(5) | C7—N2—C8 | 127.2(5) |
| C6—N1—C8 | 119.5(6) | C6—N1—C7 | 126.1(4) |
| C5—C4—C7 | 113.1(7) | C2—C3—F1 | 119.0(7) |
| C3—C4—C7 | 123.3(7) | C4—C3—F1 | 119.5(8) |
| C4—C5—C6 | 116.8(6) | C6—C5—C4 | 120.2(6) |
| C4—C3—C2 | 120.3(6) | C4—C3—C2 | 121.4(7) |
| C6—N1—C8—S1 | 5.3(10) | C6—N1—C7—S1 | −3.4(7) |
| C9—N2—C8—S1 | 179.0(6) | C8—N2—C7—S1 | −176.4(4) |
| C8—N1—C6—C1 | −79.1(9) | C7—N1—C6—C1 | 131.5(5) |
| C7—C4—C5—C6 | −179.9(7) | F1—C3—C4—C5 | −179.7(7) |
| C9—N2—C8—N1 | 0.6(10) | C8—N2—C7—N1 | 3.1(8) |
| C8—N2—C9—O2 | −6.2(12) | C7—N2—C8—O2 | −8.3(9) |
| C8—N2—C9—O1 | 177.8(6) | C7—N2—C8—O1 | 172.9(5) |

and C8 atoms (Figure 1); the mean deviation from the best plane of the five non-H atoms is 0.0203 Å. Moreover, the carbonyl and the thiocarbonyl moieties point approximately in opposition. The compound adopts a cis-trans configuration, where the phenyl group and the ethoxycarbonyl moiety lie, respectively, cis and trans relative to the S atom across the thiourea C—N bonds. The torsion angles of C6-N1-C8-S1 and C9-N2-C8-S1 are 5.34° and 179.04°. This configuration facilitates the formation of the two pairs of centrosymmetric intermolecular hydrogen-bonds N—H···S′, N′—H′···S, and N′—H′···O, N—H···O′ (Figure 3), which connect the molecules into a 1D catenulate supramolecular structure along the *b* axis direction. Moreover, from Figure 3 we can find the parallel packing of the phenyl rings in the crystal of compound **a**; however, the distance between the centers of two parallel phenyl rings is 0.5838 nm, which is out of the accepted range of the intermolecular $\pi - \pi$ interaction.[15]

In the crystal of compound **b**, there is a six-membered ring formed by intramolecular hydrogen bond N1-H···O2 alike compound **a** (Figure 2). The mean deviation from the best plane of the five non-H atoms is 0.0205 Å. The compound also adopts a cis-trans configuration, the torsion angles of C6-N1-C7-S1 and C8-N2-C7-S1 are −3.44° and 3.14°,

**TABLE IV Final Atomic Coordinates (× $10^4$) for all Non-Hydrogen Atoms and Equivalent Thermal Parameters (× $10^5$ nm$^2$) of a andb**

| **a** | | | | | **b** | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Atom | *x* | *y* | *z* | *U* (eq) | Atom | *x* | *y* | *z* | *U* (eq) |
| C1 | 1332(11) | 12677(9) | 856(6) | 51.6(15) | C1 | 3350(7) | 2066(3) | 3511(7) | 74.6(14) |
| C2 | 2106(12) | 13669(10) | −112(9) | 63.3(19) | C2 | 3861(9) | 2575(3) | 3658(9) | 85.3(17) |
| C3 | 941(16) | 14018(8) | −1170(8) | 61.4(19) | C3 | 5354(8) | 2658(3) | 4361(8) | 76.7(15) |
| C4 | 918(11) | 13507(3) | −1245(5) | 47.0(13) | C4 | 6294(8) | 2254(3) | 4917(9) | 82.3(16) |
| C5 | 1899(10) | 12457(8) | 331(6) | 46.0(13) | C5 | 5757(7) | 1756(3) | 4794(7) | 74.7(13) |
| C6 | 717(9) | 12047(6) | 707(5) | 37.9(12) | C6 | 4294(6) | 1662(2) | 4067(5) | 61.0(12) |
| C7 | 2418(19) | 13911(17) | −2411(8) | 8.5(3) | C7 | 4249(5) | 732(2) | 3475(5) | 60.5(11) |
| C8 | −911(11) | 9665(6) | 2056(5) | 42.2(13) | C8 | 2368(5) | 176(2) | 3885(6) | 62.7(12) |
| C9 | 4193(10) | 9313(7) | 3561(5) | 19.8(6) | C9 | 721(7) | −485(3) | 4003(8) | 77.9(15) |
| C10 | 6877(16) | 8348(8) | 7296(2) | 66(2) | C10 | 282(9) | −1007(3) | 3343(11) | 923(19) |
| C11 | −701(2) | 7087(11) | 6101(12) | 82(3) | F1 | 5882(9) | 3149(2) | 4475(10) | 11.07(18) |
| O1 | −4830(10) | 8125(6) | 4360(5) | 53.5(12) | O1 | 1961(4) | −315.8(19) | 3602(5) | 71.9(11) |
| O2 | −5049(8) | 10500(6) | 3426(5) | 52.2(12) | O2 | 1783(5) | 491(2) | 4421(7) | 84.7(13) |
| N1 | −1772(12) | 11110(7) | 1693(6) | 58.7(17) | N1 | 3720(4) | 1146(2) | 3939(5) | 64.2(11) |
| N2 | −2177(10) | 8843(6) | 2981(5) | 48.7(13) | N2 | 3584(5) | 265.4(19) | 3494(5) | 65.6(11) |
| S1 | 1362(2) | 8930.8(13) | 1530.5(12) | 61.3(7) | S1 | 5659.6(15) | 744.9(5) | 2860.0(16) | 70.1(8) |

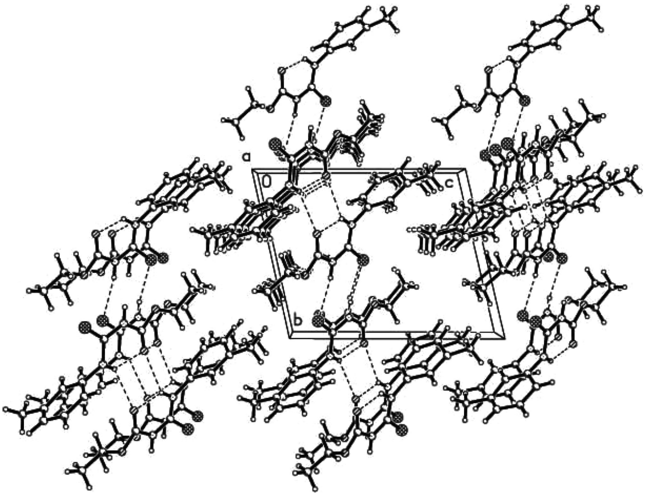

**FIGURE 3** The 1D catenulate supramolecular structure of compound **a**.

respectively. However, unlike compound **a**, the molecules of **b** only form one pair of centrosymmetric intermolecular hydrogen bonds, N—H···S′ and N′—H′···S, which connect compound **b** to dimers, and these dimers are linked together by another intermolecular hydrogen bond, C—H···F,′ and form a 1D zigzag catenulate supramolecular structure (Figure 4). It is obvious that from the hydrogen-bonding geometry

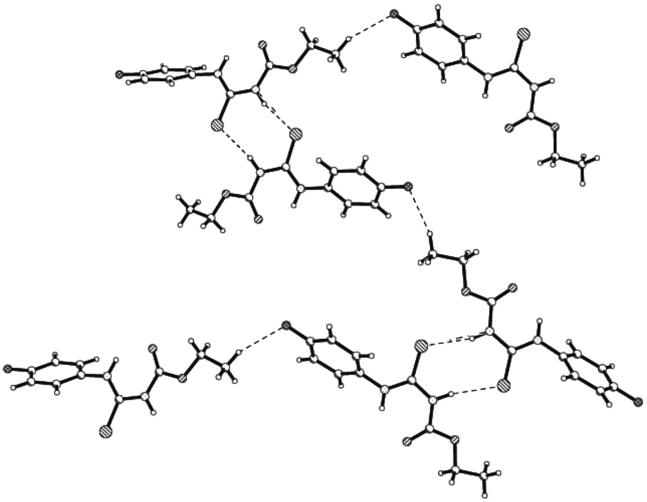

**FIGURE 4** The 1D zigzag catenulate superamolecular structure of compound **b**.

**TABLE V Data of Hydrogen Bond for a and b**

| Compounds | D—H···A | D—H/ nm | H···A/ nm | D···A/ nm | D—H···A/ deg | Symmetry code |
|---|---|---|---|---|---|---|
| **a** | N1—H1···O2 | 0.0900 | 0.2013 | 0.2715 | 133.90 | |
| | N1—H1···O2 | 0.0900 | 0.2498 | 0.3183 | 133.25 | $x-1, y+1, z$ |
| | N2—H2···S1 | 0.0900 | 0.2468 | 0.3352 | 167.23 | $x+1, y-1, z$ |
| **b** | N1—H1···O2 | 0.0900 | 0.1975 | 0.2686 | 134.89 | |
| | N2—H2···S1 | 0.0900 | 0.2490 | 0.3376 | 168.22 | $x+1/2, -y+1/2, z+1/2$ |
| | C10—H2···F1 | 0.0960 | 0.2540 | 0.3447 | 157.50 | $-x+1/2, y+3/2, -z-1/2$ |

(Table V), we can find that the intramolecular hydrogen bond N—H···O is stronger than the intermolecular hydrogen bonds, and intermolecular hydrogen bond N—H···O′ is stronger than N—H···S′.

The spectroscopic data are in agreement with the crystal structure: the IR spectra of compound **a** exhibited the N—H stretching vibration absorption in 3212 and 3152 cm$^{-1}$, and compound **b** exhibited the N—H stretching vibration absorption in 3220 and 3167 cm$^{-1}$, respectively, which is in accord with the intramolecular and the intermolecular hydrogen bonds N—H···O and N—H···S. In $^{1}$H NMR spectra, the N—H proton peaks are observed in 11.43 ppm and 8.30 ppm; these two peaks shifted to low field, which is in accord with the intramolecular and intermolecular hydrogen bonds, respectively. The same cases also can be observed in compound **b**; the N—H proton peaks of compound **b** are observed in 11.38 ppm and 8.36 ppm. Moreover, owning to the formation of intermolecular hydrogen bonds C—H···F, the C—H proton peak shifted to low field in 1.67 ppm. Other protons on this methyl group gave tri-peaks in 1.37 ppm (J = 7.2); this confirms the existence of C—H···F intermolecular hydrogen bonds in compound **b**.

## EXPERIMENTAL

Melting points (m.p.) were determined with a digital electrothermal apparatus without calibration. IR spectra were recorded in KBr on a Nicilet NEXUS 670 FT-IR spectrophotometer, and $^{1}$H NMR spectra were recorded on a JNM-ECP400 instrument using TMS as the internal reference. Elemental analysis was determined on a PE-2400 CHN instrument. The X-ray diffraction were determined on CAD4 Enraf-Nonius X-ray instruments. The synthesis of **a**,**b** were according to our previous works[16]: we added powdered potassium thiocyanate (KSCN) (1.17 g, 12 mmol) to an ethyl acetate solution (15 mL) of ethyl chloroformate (1.09 g, 10 mmoles) and N,N,N′,N-tetramethylethane-1,2-diamine (TMEDA) (0.01 g, 0.1 mmoles). The reaction mixture was stirred at r.t. for 5 h. Then *m*-toluidine (1.07 g, 10 mmol) was slowly added to the reaction mixture with constant stirring. The reaction mixture was stirred at r.t. for 5 h again. After evaporating the solvent in vacuum, the precipitation was washed with 10 mL 75% ethanol three times and 15 mL $H_2O$ three times; recrystallization from DMF-EtOH-$H_2O$ gave compound **a**, yield 94%, m.p. 102–103°C, IR (KBr): $\nu = 3212$ (NH), 3152(NH), 1714 (C=O), 1603, 1538, 1474, (C=C) 1242 (C=S); $^1$HNMR ($CDCl_3$): $d_H = 11.43$ (s, 1H, NH), 8.30 (s, 1H, NH), 7.29 (m, 4H, ArH), 4.35 (q, 2H, $CH_2$), 2.40 (s, 3H, $CH_3$), 1.36, (t, 3H, $CH_3$); anal. calcd. for $C_{11}H_{14}N_2O_2S$: C, 55.44; H, 5.92; N, 11.76. Found: C, 55.41; H, 5.92; N, 11.78. Compound **b** was synthesized in a similar method, yield 90%, m.p. 187–188°C. IR (KBr): $\nu = 3220$ (NH), 3167 (NH), 1726 (C=O), 1565, 1534, 1510 (C=C), 125 (C=S). $^1$HNMR ($CDCl_3$): $d_H = 11.38$ (s, 1H, NH), 8.36 (s, 1H, NH), 6.99–7.67 (m, 4H, ArH), 4.36 (q, 2H, $CH_2$), 1.37 (t, J = 7.2, 2H, $CH_3$), 1.67 (s, 1H, $CH_3$). Anal. Calcd. for $C_{10}H_{11}N_2O_2SF$: C, 49.57; H, 4.58; N, 11.56. Found: C, 49.49; H, 4.58; N, 11.76.

The single crystal was obtained from the slow evaporation of EtOAc solution of compound **a**, **b** for one week, respectively. Intensity data were collected at 293(2) K on a CAD4 Enraf-Nonius diffractometer with graphite-monochromated Mo Ka ($\lambda = 0.71073$ Å) radiation, using the $\phi$-$\omega$ scan mode. Data collection and reduction were performed using MOLEN PC software. The structure was solved by direct methods using the SHELXS-97 program and successive difference Fourier syntheses to yield the positions of all non-hydrogen atoms, which were refined by full-matrix least-squares method on $F^2$ with temperature factors and anistropical thermal parameters using SHELXTL program.

## CONCLUSION

The synthesis and 1D catenulate supramolecular structure of two *N*-ethoxycarbonyl-*N'*-arylthioureas have been reported. The compounds **a** and **b** were synthesized in high yields. In the crystal of compounds **a** and **b**, there are inter- and intramolecular hydrogen bonds. The compounds were assembled to 1D catenulate supramolecular structure by the intermolecular hydrogen bonds. The $^1$H NMR and IR confirmed the existence of inter- and intramolecular hydrogen bonds.

Crystallographic data have been deposited to the Cambridge Crystallographic Data Center, CCDC 602850 for **a** and 602851 for **b**. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; web site: http://www.ccdc.ac.uk); web site upon request.

## REFERENCES

[1] D. Sriram, P. Yogeeswari, and K. Madhu, *Bioorg. Med. Chem. Lett.*, **16,** 876 (2006).

[2] S.-J. Xue, L.-P. Duan, S.-Y. Ke, and J.-M. Zhu, *Chin. J. Org. Chem.*, **24,** 686 (2004).

[3] J. T. Hackmann, US Patent 2923656, (1960);. *Chem. Abstr.*, **54,** 52028 (1960).

[4] A. Joos and W. Wirtz, Ger. Patent 2059872; (1972); *Chem. Abstr.*, **77,** 88114 (1972).

[5] V. K. Madan, A. D. Taneja, and V. P. Kudesia, *J. Indian Chem. Soc.*, **68,** 162 (1991).

[6] T.-B. Wei, J.-C. Cheng, and X.-C. Wang, *Chem. J. Chin. Univ.*, **13,** 12171 (1992).

[7] X. Shen, T. B. Wen, Q. T. Liu, X. Y. Huang, B. S. Kang, X. L. Wu, et al. *Polyhedron*, **16,** 2605 (1997).

[8] K. R. Koch, *Coord. Chem. Rev.*, **216,** 473 (2001).

[9] C. M. Juarez and A. J. B. Dutra, *Minerals Engineering*, **13,** 1083 (2000).

[10] F.-Y. Wu, Z.-C. Wen, and Y.-B. Jang, *Progress in Chemistry.*, **16,** 776 (2004).

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

[12] Y.-M. Zhang, W.-X. Xu, Y.-Q. Zhou, H. Yao, and T.-B. Wei, *Acta Chim. Sinica*, **64,** 79 (2006).

[13] Y.-M. Zhang, L.-Z. Yang, Q. Lin, and T.-B. Wei, *Transition Metal Chemistry*, **30,** 944 (2005).

[14] Y.-M. Zhang, L.-Z. Yang, Q. Lin, and T.-B. Wei, *J. Coord. Chem.*, **58,** 1675 (2005).

[15] S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, and K. Tanabe, *J. Am. Chem. Soc.*, **124,** 104 (2002).

[16] Q. Lin, Y.-M. Zhang, L.-M. Gao, T.-B. Wei, and H. Wang, *Phosphorus, Sulfur, and Silicon*, **179 (10)**, 2051 (2004).