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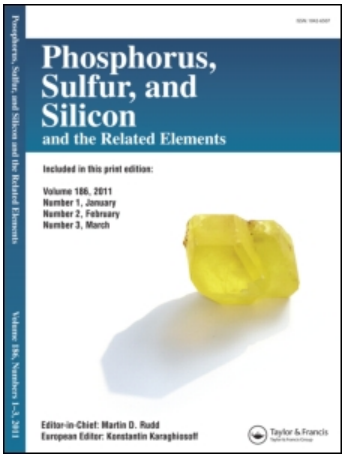

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One-Pot Synthesis and Crystal Structure of 4-Phenyl-3-[4-chlorophenoloxymethyl]-1*H*-1,2,4-triazole-5(4*H*)-thione

Tai-Bao Wei[a]; Jing Tang[a]; Hong Liu[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 Wei, Tai-Bao , Tang, Jing , Liu, Hong and Zhang, You-Ming(2007) 'One-Pot Synthesis and Crystal Structure of 4-Phenyl-3-[4-chlorophenoloxymethyl]-1*H*-1,2,4-triazole-5(4*H*)-thione', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 7, 1581 — 1587
To link to this Article: DOI: 10.1080/10426500701263547
URL: http://dx.doi.org/10.1080/10426500701263547

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Phosphorus, Sulfur, and Silicon, 182:1581–1587, 2007
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701263547

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One-Pot Synthesis and Crystal Structure of 4-Phenyl-3-[4-chlorophenoloxymethyl]-1*H*-1,*2*,4-triazole-5(4*H*)-thione

Tai-Bao Wei
Jing Tang
Hong Liu
You-Ming Zhang
College of Chemistry and Chemical Engineering, Gansu Key Laboratory of Polymer Materials, Northwest Normal University, Lanzhou, Gansu, P.R. China

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4-Phenyl-3-[4-chlorophenoloxymethyl]-1H-1,2,4-triazole-5-thione was synthesized with one-pot method. The structure of the title compound was conformed by IR, ^{1}H NMR, elemental analysis studies, and the crystal structure was determined by X-ray diffraction analysis. And, the intermolecular N—H···S and C—H···Cl hydrogen bonds link the molecules together as a tri-dimensional netlike supramolecular.

Keywords 4-Phenyl-3-[4-chlorophenoloxymethyl]-5-mercapto-1,2,4-triazole; crystal structure; one-pot synthesis

INTRODUCTION

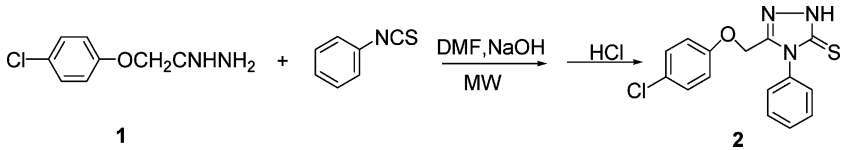
Substituted derivatives of triazole possess such comprehensive bioactivities as antimicrobial,[1–3] antiinflammatory,[4] analgesic,[5] antitumorial,[6] antihypertensive,[7] anticonvulsant,[8,9] and antiviral activities.[10] The broad biological activities that the 1,2,4-triazoles shown may be due to the presence of >N—C—S moiety.[11,12]

According to our previous work,[13–15] we are interested in the synthesis, biological activities, and crystal structure of triazole derivatives with the help of the microwave technology. As a part of our work, the 4-phenyl-3-[4-chlorophenoloxymethyl]-1H-1,2,4-triazole-5-thione is an important intermediate; however, to date, the traditional research on

Received November 11, 2006; accepted January 5, 2007
Financial support of this work by Natural Science Foundation (No. 20371040) of China, the Natural Science Foundation (No. 031-A21-004) of Gansu province, and the Foundation (No. 02-18) of Northwest Normal University are acknowledged.

Address correspondence to You-Ming Zhang, Department of Chemistry and Chemical Engineering, Gansu Key Lab of Polymer Materials, Northwest Normal University, Lanzhou, 730070, Gansu, China. E-mail: zhangnwnu@126.com.

synthesis of 1,2,4-triazole suffered from the disadvantages, such as long reaction time, low yield, and the inconvenience of handling. In view of these, we communicate our work for an efficient one-pot synthesis of substituted 1,2,4-triazoles and the crystal structure of the title compound.



SCHEME 1

The reaction sequence is shown in Scheme 1. 4-chlorophenoxyacetyl hydrazide **1** was prepared according to our previous work.[13] Under microwave irradiation, **1** reacted with phenylisothiocyanate in the mixed solution of DMF and 2 M NaOH gives the title compound. This method has the advantages of simple operation that shortened reaction times and gave high yield.

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RESULTS AND DISCUSSION

The crystal structure of title compound atom-labelling scheme was shown in Figure 1. The crystallographic data were summarized in

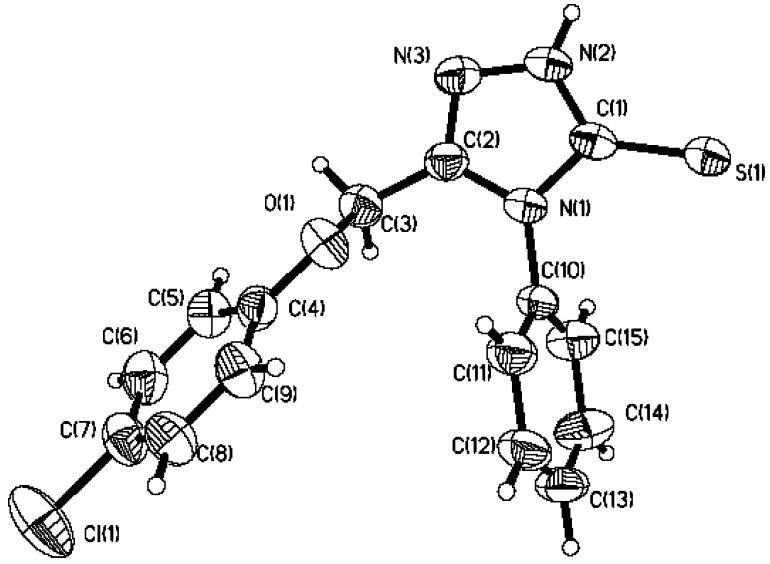

FIGURE 1 A plot of the title compound with displacement ellipsoid drawn at the 50% probability level.

TABLE I Crystal Data and Structure Refinement for $C_{15}H_{12}ClN_3OS$

Empirical formula	$C_{15}H_{12}ClN_3OS$	
Formula weight	317.79	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	*P*1	
Unit cell dimensions	$a = 7.221(3)$ Å	$\alpha = 101.140(9)^\circ$
	$b = 10.251(4)$ Å	$\beta = 102.734(7)^\circ$
	$c = 11.641(5)$ Å	$\gamma = 110.388(7)^\circ$
Volume	752.7(5) $Å^3$	
Z	2	
Density(calculated)	1.402 Mg/m^3	
Absorption coefficient	0.394 mm^{-1}	
F(000)	328	
Crystalsize	0.54 × 0.42 × 0.23 mm^3	
Theta range for data collection	2.45 to 27.01°	
Index ranges	–8< = h< = 8, –12< = k< = 12, –14< = l< = 14	
Reflections collected	5715	
Independent reflections	2884[R(int) = 0.0149]	
Data/restraints/parameters	2884/0/194	
Refinement method	SHELXL	
Final R indices[I>2sigma(I)]	R1 = 0.0390, wR2 = 0.0961	
R indices(all data)	R1 = 0.0545, wR2 = 0.1070	

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Table I. Part of the bond lengths and bond angles,selected torsion angles, and coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms in the structure of **2** were given in Table 2, Table 3, and Table 4, respectively.

As shown in Figure 1, the title compound contains a triazole ring and two benzene rings. Just as anticipation, the three rings are respectively in one plane and the triazole ring, the C4—C9 benzene ring and the C10—C15 benzene ring have mean deviations of 0.0027, 0.0018, and 0.0019 Å, respectively. The C10—C15 and C4—C9 planes form dihedral angles of 104.4° and 56.3°, respectively, with the the triazole ring. Finally, the dihedral angle between the benzene ring C4—C9 and C10—C15 is 72.1°.

There are two types hydrogen bonds in the crystal structure as shown in Figure 2. The first one is N(2A)—H(2A)···S(2B), and this type of hydrogen bonds link the molecules together like dimers. And the second one is C(9B)—H(9B)···Cl(1C). From Table 5, we can find that the hydrogen bond N(2A)—H(2A)···S(2B) is stronger than C(9B)—H(9B)···Cl(1C) because the hydrogen bond length of N(2A)—H(2A)···S(2B) is shorter than the latter. And, it also can be seen that the crystals were linked

TABLE II Selected Bond Lengths (Å) and Bond Angles (°) for Compound 2

Bond lengths			
C1-N2	1.3316(26)	N2-N3	1.3693(25)
C1-N1	1.3726(24)	Cl1-C7	1.7398(23)
C1-S1	1.6739(22)	N1-C10	1.4411(23)
C2-N1	1.3767(25)	C4-O1	1.3757(23)
C2-N3	1.2942(26)	C3-O1	1.4212(25)
C2-C3	1.4829(28)		
Bond angles			
N1-C1-N2	103.07(0.17)	Cl1-C7-C6	119.78(0.18)
N1-C1-S1	128.48(0.15)	C8-C7-C6	121.21(0.21)
N2-C1-S1	128.45(0.15)	Cl1-C7-C8	119.00(0.19)
C1-N1-C2	107.71(0.16)	C4-O1-C3	116.91(0.16)
C1-N1-C10	125.88(0.16)	O1-C3-C2	107.79(0.17)
C2-N1-C10	126.37(0.16)	N3-N2-C1	114.29(0.17)
C3-C2-N3	123.98(0.19)	C2-N3-N2	103.52(0.17)
C3-C2-N1	124.59(0.17)	N3-C2-N1	111.41(0.18)

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to form a tri-dimensional netlike supramolecular through two times molecular packing (Figure 3).

EXPERIMENTAL

All commercially available products were used without further purification. Melting points were measured on a X-4 digital melting-point apparatus and are uncorrected. Microwave irradiation was carried out with a WP 750B commercial microwave oven at 2450MHz. IR spectra were measured as KBr pellets on a Digilab FTS-3000 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian

TABLE III The Selected Torsion Angles

N3-C2-C3-O1	-110.26(0.23)	N1-C2-C3-O1	71.73(0.25)
O1-C4-C5-C6	-179.32(0.19)	O1-C4-C9-C8	179.50(0.20)
N1-C10-C15-C14	179.70(0.20)	N1-C10-C11-C12	-179.93(0.19)
N2-C1-N1-C2	0.76(0.21)	S1-C1-N1-C2	-178.42(0.16)
N2-C1-N1-C10	178.41(0.18)	S1-C1-N1-C10	-0.77(0.30)
N3-C2-N1-C1	-0.72(0.23)	C3-C2-N1-C1	177.51(0.19)
N3-C2-N1-C10	-178.36(0.18)	C3-C2-N1-C10	-0.13(0.31)
C15-C10-N1-C1	-74.20(0.27)	C11-C10-N1-C1	105.73(0.23)
C15-C10-N1-C2	103.02(0.24)	C11-C10-N1-C2	-77.06(0.26)
N1-C1-N2-N3	-0.59(0.23)	S1-C1-N2-N3	178.59(0.16)
N1-C2-N3-N2	0.34(0.22)	C3-C2-N3-N2	-177.90(0.19)
C1-N2-N3-C2	0.17(0.24)	C5-C4-O1-C3	-21.10(0.28)

TABLE IV Final Atomic Coordinates ($\times 10^5$) for All Non-Hydrogen Atoms and Equivalent Thermal Parameters ($\times 10^5$ nm^2)

Atom	*x*	*y*	*z*	*U* (eq)
C1	26786(31)	46898(23)	11755(18)	4199(46)
C2	43242(32)	33520(21)	5651(17)	4182(45)
C3	58712(35)	27039(24)	5966(20)	4786(50)
Cl1	115433(11)	−5553(9)	31346(9)	9332(30)
N1	42562(25)	42697(18)	15732(14)	3971(38)
N2	19068(29)	39866(20)	−259(16)	4594(43)
N3	28978(28)	31549(20)	−4265(15)	4824(43)
O1	53873(23)	16264(16)	12193(14)	5154(38)
S1	19304(10)	58280(7)	19962(5)	5940(21)

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TABLE V Data of Hydrogen Bond for 2

D-H···A	D-H/nm	H···A/nm	D···A/nm	D-H···A/deg	Symmetry code
N(2A)-H(2A)···S(2B)	0.0828	0.2445	0.3272	177.61	−x, −y+1, −z
C(9B)-H(9B)···Cl(1C)	0.0930	0.2856	0.3756	163.2	—

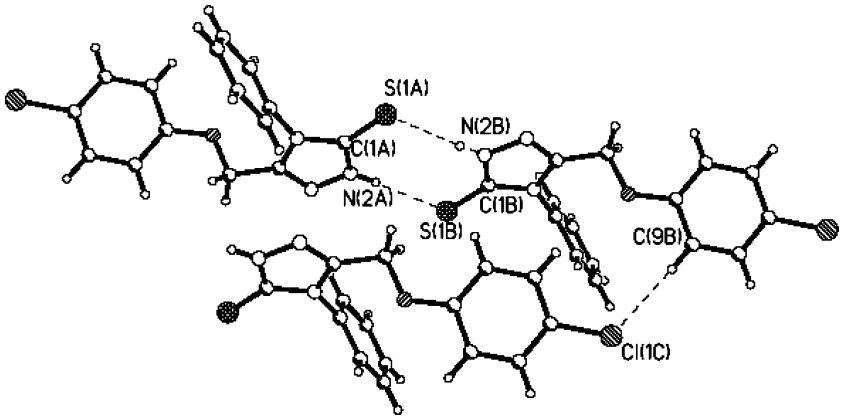

FIGURE 2 Two types of hydrogen bonds in the crystal structure.

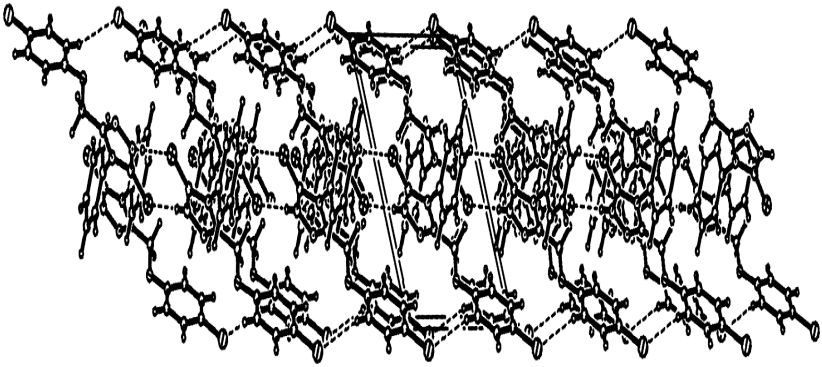

FIGURE 3 Intermolecular N—H···S and C—H···Cl hydrogen bonds link the molecules together as a tri-dimensional netlike supramolecular.

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Mercury plus-400 MHz spectrometer with TMS as internal standard. X-ray intensity data was collected on Siemens P4 diffractometer with *Mo Ka* radiation.

Synthesis of 4-Phenyl-3-[4-chlorophenoloxymethyl]-1H-1,2,4-triazole-5-thione 2

4-Chlorophenoxyacetyl hydrazide (5 mmol, 0.93g) **1** and phenylisothiocyanate (5 mmol, 0.68 g) were dissolved in 5 mL DMF, then 10 mL 2M NaOH was added, and the mixture was reacted under the microwave irradiation (400W) for 5 min. After cooling, the solution was acidified by 12 mL 2M HCl. The crude product was precipitated, filtered, and washed with distilled water. Pure compounds were obtained by recrystallization from the mixed solution of DMF and H_2O (DMF : H_2O = 1:3). Crystal was also gained from the solution of DMF and H_2O.

2: Yield 83%, m.p. 214–216°. IR: 3433 (NH), 1620 cm^{-1} (C = N). ^1H NMR (400 MHz, DMSO-d_6): δ 14.115(s, 1H, NH), 4.993(s, 2H, CH_2), 7.536–6.850 (m, 9H, Ar-H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 168.689, 155.939, 147.823, 133.366, 129.594, 129.304, 129.266, 128.054, 125.463, 116.737, 60.419. Anal. Calcd for $C_{15}H_{13}ON_3S$: C 56.69; H 3.81; N 13.22. Found C 56.52; H 4.01; N 13.49.

It was interesting for us to find out, from the data shown above, an unusual NMR shift of the N—H (14.1 ppm) appeared in the title compound. We all know that the chemical shift like this for N—H hydrogens is not always large, and the reason for this may be the N-H formed the strong hydrogen bond, N—H···S.

CONCLUSION

The synthesis and 3 D catenulate supramolecular structure of the title compound have been reported. The compound **2** is synthesized with the method of one-pot synthesis, and this method has the advantages of simple operation that shortened reaction times and gave high yield. Interesting, there is an unusual NMR shift of the N—H is found. Finally, in the crystal of compounds **2**, there are two types of hydrogen bonds in the crystal structure; and, with the help of them, the compound was assembled to 3D catenulate supramolecular structure by these two types of intermolecular hydrogen bonds.

SUPPLEMENTARY MATERIAL

Crystallographic data have been deposited to the Cambridge Crystallographic Data Center, CCDC 617525 for **2**. 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, or http://www.ccdc.ac.uk), upon request.

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