This article was downloaded by: [Universidad Autonoma de Barcelona] On: 28 October 2014, At: 07:00 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



# Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gpss20

Synthesis, Crystal Structure, and Flame Retardance of 2-(3-Silatranyl-Propylamino)-4-(2,4-Dichlorophenyl)-5,5-Dimethyl-1,3,2-Dioxaphosphinane-2-Sulfide

De-Jian Wang  $^{\rm a}$  , Qiong-Lin Mou  $^{\rm a}$  , Shi-Guan Wan  $^{\rm b}$  , Xin-Jian Song  $^{\rm a}$  & Da-Ting Tian  $^{\rm a}$ 

<sup>a</sup> Key Laboratory of Biological Resources Protection and Utilization of Hubei Province, School of Chemical and Environmental Engineering, Hubei University for Nationalities, Enshi, Hubei, People's Republic of China

<sup>b</sup> Guangdong Tyen Chemicals Co., Ltd., Foshan, Guangdong, People's Republic of China Accepted author version posted online: 23 Jan 2012.Published online: 07 Jun 2012.

To cite this article: De-Jian Wang , Qiong-Lin Mou , Shi-Guan Wan , Xin-Jian Song & Da-Ting Tian (2012) Synthesis, Crystal Structure, and Flame Retardance of 2-(3-Silatranyl-Propylamino)-4-(2,4-Dichlorophenyl)-5,5-Dimethyl-1,3,2-Dioxaphosphinane-2-Sulfide, Phosphorus, Sulfur, and Silicon and the Related Elements, 187:8, 944-951, DOI: <u>10.1080/10426507.2012.657311</u>

To link to this article: <u>http://dx.doi.org/10.1080/10426507.2012.657311</u>

# PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <a href="http://www.tandfonline.com/page/terms-and-conditions">http://www.tandfonline.com/page/terms-and-conditions</a>



Phosphorus, Sulfur, and Silicon, 187:944–951, 2012 Copyright © Taylor & Francis Group, LLC ISSN: 1042-6507 print / 1563-5325 online DOI: 10.1080/10426507.2012.657311

## SYNTHESIS, CRYSTAL STRUCTURE, AND FLAME RETARDANCE OF 2-(3-SILATRANYL-PROPYLAMINO)-4-(2,4-DICHLOROPHENYL)-5,5-DIMETHYL-1,3,2-DIOXAPHOSPHINANE-2-SULFIDE

# De-Jian Wang,<sup>1</sup> Qiong-Lin Mou,<sup>1</sup> Shi-Guan Wan,<sup>2</sup> Xin-Jian Song,<sup>1</sup> and Da-Ting Tian<sup>1</sup>

<sup>1</sup>Key Laboratory of Biological Resources Protection and Utilization of Hubei Province, School of Chemical and Environmental Engineering, Hubei University for Nationalities, Enshi, Hubei, People's Republic of China <sup>2</sup>Guangdong Tyen Chemicals Co., Ltd., Foshan, Guangdong, People's Republic of China

#### **GRAPHICAL ABSTRACT**



**Abstract** 2-(3-Silatranylpropylamino)-4-(2,4-dichlorophenyl)-5,5-dimethyl-1,3,2-dioxa phosphinane-2-sulfide **4** was synthesized by a nucleophilic substitution reaction of 2-chloro-1,3,2-dioxaphosphinane-2-sulfide **2** with  $\gamma$ -aminopropylsilatrane **3**, which was prepared by the cyclization reaction of triethanolamine and  $\gamma$ -aminopropyltriethoxysilane. The structure of the title compound was confirmed by IR, <sup>1</sup>H NMR, <sup>31</sup>P NMR, EI-MS, and elemental analysis as well as by single crystal X-ray diffraction and its thermal properties were studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). Thermal analysis and preliminary fire retardance testing suggest that compound **4** should function as a good flame retardant.

**Keywords** Crystal structure; flame retardance; (sulfur substituted)phosphonoaminopropyl silatrane; thermal property

Received 6 November 2011; accepted 10 January 2012.

The authors are thankfully acknowledge grants received from the National Nature Science Foundation of Hubei Province (No. 2011CDB087), the Key Project of Hubei Provincial Education Department (No. Q20111904), and the Project of Team Research for Excellent Mid-Aged & Young Teachers of Higher Education of Hubei Province, China (No. T201006).

Address correspondence to Xin-Jian Song, Key Laboratory of Biological Resources Protection and Utilization of Hubei Province, School of Chemical and Environmental Engineering, Hubei University for Nationalities, Enshi, Hubei 445000, P. R. China. E-mail: whxjsong@yahoo.com.cn

#### INTRODUCTION

Flame retardants have been extensively used for polymer materials. There is a growing demand for new, environmental friendly flame retardants in modern society. Although halogenated flame retardants have been widely applied because of their excellent flame retarding effect, they are currently being phased out due to perceived environmental concerns such as the emission of toxic gases and corrosive smoke emission upon combustion.<sup>1,2</sup> Thus, more and more attention has been paid to such halogen-free flame retardants as intumescent flame retardants (IFR), especially nitrogen-phosphorus intumescent flame retardants owing to their high efficiency and low toxicity.<sup>3-6</sup> Silicon-containing compounds can significantly enhance the flame retardance of a polymer through both char formation in the condensed phase and the trapping of active radicals in the vapor phase.<sup>7-9</sup> In addition, sulfur is an important antiflaming element.<sup>10–13</sup> The inclusion of sulfur within the chemical structure may play a role in cooperativity with the elements of phosphorus, nitrogen, and silicon in the same flame retardant. However, there have been no reports on flame retardants simultaneously containing phosphorus, nitrogen, sulfur, and silicon. In view of these, and as a continuation of our search for good flame retardants and research on the stereochemistry of (sulfur substituted)phosphonoaminopropylsilatrane, 2-(3-silatranylpropylamino)-4-(2,4dichlorophenyl)-5,5-dimethyl-1,3,2-dioxaphosphinane-2-sulfide was investigated, focused on its preparation, crystal structure together with thermal stability, and flame retardance.

The synthetic route of the title compound 4 is outlined in Scheme 1.



Scheme 1 An outline of the synthetic route of the title compound 4.

## **RESULTS AND DISCUSSION**

#### Synthesis

The synthesis was initiated by allowing easily accessible 2,4-dichlorobenzaldehyde to react with isobutyraldehyde in the presence of potassium hydroxide to form diol **1** which readily reacted with phosphorus thiochloride to afford 2-chloro-1,3,2-dioxaphosphinane-2-sulfide **2**.<sup>14</sup> Nucleophilic substitution reaction of **2** with  $\gamma$ -aminopropylsilatrane **3** gave the target compound **4**. In this step, triethylamine needed to be added as an acid binding agent which resulted in a shorter reaction time and higher isolated yield. The structure of the title compound **4** was characterized by IR, <sup>1</sup>H NMR, <sup>31</sup>P NMR, EI-MS, and elemental analysis. These spectroscopic data are in good agreement with the assumed structure.

#### **Crystal Structure Analysis**

The selected bond lengths and angles are listed in Table 1 and the X-ray data are summarized in Table 2. The molecular structure, the packing diagram, and hydrogen-bond dimer of **4** are depicted in Figure 1, and Figures S 1 and S 2, respectively. Significant hydrogen bonding is demonstrated by the data presented in Table S 1. (Figures S 1 and S 2, and Table S 1 are included in the Supplemental Materials, available online.)

The crystal structure of **4** (Figure 1) reveals that the cyclic dioxaphosphinane ring in the molecule adopts a thermodynamically stable *cis* conformation, while the silatrane fragment forms a cage-like structure in which there exists an intramolecular Si  $\leftarrow$ N donoracceptor bond [Si1-N2 = 2.146(2) Å; see Table 1], which is remarkably longer than an usual Si-N bond (1.7-1.8 Å). In the crystal structure, centrosymmetrically related

Bond	Dist.	Bond	Dist.
S(1)-P(1)	1.9298(9)	O(2)-C(9)	1.448(3)
P(1) - O(1)	1.5987(15)	O(3)-C(15)	1.408(4)
P(1) = O(2)	1.5810(17)	O(4)-C(17)	1.416(3)
P(1) - N(1)	1.601(2)	O(5) - C(19)	1.426(3)
Si(1)-O(3)	1.6538(19)	N(1)-C(12)	1.460(3)
Si(1) = O(4)	1.6618(16)	N(2)-C(18)	1.464(3)
Si(1)-O(5)	1.6656(17)	N(2)-C(20)	1.468(3)
N(2) - Si(1)	2.146(2)	N(2)-C(16)	1.471(3)
O(1) - C(7)	1.461(2)		
Angle	(°)	Angle	(°)
O(2)-P(1)-O(1)	101.62(9)	O(5)-Si(1)-C(14)	97.35(10)
O(2) = P(1) = N(1)	104.14(10)	C(7) - O(1) - P(1)	115.41(12)
O(1) - P(1) - N(1)	106.49(9)	C(9) = O(2) = P(1)	116.23(16)
O(2) - P(1) - S(1)	114.73(7)	C(15) - O(3) - Si(1)	122.55(17)
O(1) - P(1) - S(1)	113.39(6)	C(17) - O(4) - Si(1)	122.66(15)
N(1) - P(1) - S(1)	115.12(8)	C(19) - O(5) - Si(1)	121.60(15)
O(3) - Si(1) - O(4)	117.66(10)	C(12) - N(1) - P(1)	126.34(19)
O(3) - Si(1) - O(5)	119.43(11)	C(18)-N(2)-C(20)	113.5(2)
O(4) - Si(1) - O(5)	117.48(9)	C(18)-N(2)-C(16)	114.5(2)
O(3) - Si(1) - C(14)	97.22(13)	C(20)-N(2)-C(16)	113.6(2)
O(4) - Si(1) - C(14)	98.84(10)		

Table 1 Selected bond lengths (Å) and bond angles (°) for compound 4

Empirical formula	C <sub>20</sub> H <sub>31</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>5</sub> PSSi	
Formula weight	541.49	
CCDC deposit no.	848545	
Crystal system	Orthorhombic	
Space group	Pbcn	
a (Å)	13.3238(7)	
$b(\text{\AA})$	18.9520(10)	
c (Å)	20.3489(11)	
$\alpha$ (°)	90	
$\beta$ (°)	90	
$\gamma$ (°)	90	
Volume (Å <sup>3</sup> )	5138.4(5)	
Z	8	
Density (calcd.) (Mg·m <sup><math>-3</math></sup> )	1.400	
Absorption coefficient (mm <sup>-1</sup> )	0.476	
F(000)	2272	
$\theta$ range for data collection (°)	1.87 to 28.00	
Index ranges	$-13 \le h \le 17, -24 \le k \le 24, -24 \le l \le 26$	
Reflections collected	30151	
Independent reflections	$6131 [R_{int} = 0.0367]$	
Absorption Correction	None	
Refinement method	Full-matrix least-squares on $F^2$	
Data/restraints/parameters	6131/0/292	
Goodness-of-fit on $F^2$	1.046	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0488, wR_2 = 0.1315$	
<i>R</i> indices (all data)	$R_1 = 0.0715, wR_2 = 0.1477$	
Large diff. peak and hole $(e \cdot Å^{-3})$	0.643 and -0.269	

 Table 2 Crystallographic data and parameters for compound 4

molecules are linked by pairs of N–H…S hydrogen bonds into dimers, generating rings with graph-set motif  $R_2^2(8)$  (Figure S 2 and Table S 1).

#### **Thermal Properties**

From the TG-DSC thermograms (Figure 2), it appeared that the decomposition of the sample begins at 280 °C and occurs in two stages. The first decomposition step occurs between 280 and 350 °C and is accompanied by a loss of 57.3% of the initial sample mass. The second step of decomposition occurs between 350 and 600 °C. When reaching 500 °C, 32.05% char residue could be observed, illustrating a good char-formation ability and thermal stability of this fire retardant. From the corresponding DSC profile, one endothermic peak in the first decomposition stage are noted, as is very beneficial in intumescent flame retardant system according to the condensed phase flame-retardant process, because the endothermic decomposition of flame retardant removes heat and cools the polymer materials.

#### Flame Retardance

The flame retardance in epoxy E-44 of compound **4** was preliminarily evaluated employing horizontal burning test.<sup>15</sup> The samples (110 mm  $\times$  6 mm  $\times$  3.5 mm) were prepared by mixing the fire retardant, epoxy resin (E-44) and curing agent (polyamide resin



Figure 1 Molecular structure of compound 4 with the atomic labeling.



Figure 2 TG-DSC thermograms of compound 4.

#### SYNTHESIS, CRYSTAL STRUCTURE, AND FLAME RETARDANCE

Compd.	Reach the first line (25 mm away from ignition)	Reach the second line (100 mm away from ignition)	Burning length (mm)
blank	yes	yes	burn out
4	no	no	12

Table 3 Results of horizontal burning test of compound 4 (GB2408-80)

650) in a 1:5:4 w/w ratio. Two marked lines were drawn on each sample at a distance of 25 mm and 100 mm from the end to be ignited. The horizontal burning test was conducted according to GB2408-80 horizontal standard. Five specimens were tested for repeatability. The results are outlined in Table 3. Besides, the samples foam and expand when burning without melting and dropping and with low smoking. It is evident from the results that the title compound has good flame resistance.

#### CONCLUSION

In summary, the present article describes the synthesis, crystal structure, thermal stability as well as flame retardance of 2-(3-silatranylpropylamino)-4-(2,4-dichlorophenyl)-5,5-dimethyl-1,3,2-dioxaphosphinane-2-sulfide as the first example of intumescent flame retardants simultaneously incorporating phosphorus, nitrogen, sulfur, and silicon. Thermal analysis and preliminary fire retardance testing in epoxy E-44 suggest that the title compound should function as a good flame retardant, as may be attributed to the synergetic effect of phosphorus, sulfur, silicon, and nitrogen elements. In spite of only a single example and the preliminary results of fire testing presented by this work, we believe that such a type of novel flame-retardant additives show the potential of application in epoxy resin and other polymer materials, ready to be further investigated.

#### **EXPERIMENTAL**

Melting points were measured with an X-4 digital melting-point apparatus and uncorrected. <sup>1</sup>H NMR spectra were obtained using a Varian Mercury Plus-400 Spectrometer with TMS as internal standard and DMSO- $d_6$  as the solvent. IR spectra were recorded using a Nicolet NEXUS 470 FT-IR spectrophotometer with KBr pellets in the range of 4000– 400 cm<sup>-1</sup>. MS spectra were performed by a Finnigan Trace MS 2000 organic mass spectrometer using the electron ionization (EI) method. Elemental analysis was measured by a Perkin-Elmer CHN 2400 elemental analyzer. X-ray diffraction data were collected using a Bruker Smart APEX-CCD diffractometer equipped with a graphite-monochromatized Mo  $K\alpha$  ( $\lambda = 0.71073$  Å) radiation. DSC experiments were carried out with a CDR-1 thermal analyzer at a heating rate of 10 K/min under a nitrogen flow. 1-(2,4-Dichlorophenyl)-2,2dimethylpropane-1,3-diol **1** was prepared according to a previously reported method.<sup>16,17</sup>

#### Synthesis of the Title Compound 4

To a stirred solution of 1 (10 mmol, 1.75 g) and phosphorus thiochloride (10 mmol) in dry tetrahydrofuran (8 mL), a solution of triethylamine (11 mmol) in dry tetrahydrofuran (8 mL) was dropwise added over 1 h at ice-bath temperature, then at room temperture with stirring for 14 h. After filtration, the solvent was removed under reduced pressure, and

the residual mixture was recrystallized from cyclohexane to afford white crystals 2. mp: 122–123 °C; Yield: 65%.

Triethanolamine (10 mmol, 1.49 g) and aminopropyltriethoxysilane (10 mmol, 2.21 g) were placed into a 100-mL, round-bottomed, three-necked flask fitted with a thermometer and a reflux condenser. The mixture was stirred at reflux for 3 h. The ethanol produced was removed by distillation at reduced pressure to afford  $\gamma$ -aminopropylsilatrane **3** in 83% yield as white solid. mp: 87–88 °C (Lit.<sup>18</sup> 87.2–87.9 °C).

To a mixture of  $\gamma$ -aminopropylsilatrane **3** (5 mmol, 1.16 g), triethylamine (6 mmol), and anhydrous 1,2-dichloroethane (15 mL), a solution of **2** (5 mmol, 1.73 g) in anhydrous 1,2-dichloroethane (5 mL) was added dropwise. The reaction mixture was stirred for 3 h at room temperature. The solvent was removed under reduced pressure and the residue was washed twice with a little water and was recrystallized from ethanol-water to give 2-(3-silatranylpropylamino)-4-(2,4-dichlorophenyl)-5,5-dimethyl-1,3,2-dioxaphosphinane-2-sulfide **4** in 76% yield as yellowish crystals. mp: 187–188 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  7.45-7.70 (m, 3H, Ar-H), 6.06 (t, *J* = 10 Hz, 1H, NH), 5.80 (s, 1H, OCH), 3.33-3.94 (m, 8H, OCH<sub>2</sub>), 2.51-2.94 (m, 8H, NCH<sub>2</sub>), 1.49-1.55 (m, 2H, C-CH<sub>2</sub>), 1.48 (s, 3H, CH<sub>3</sub>), 1.02 (s, 3H, CH<sub>3</sub>), 0.16 (t, *J* = 8 Hz, 2H, SiCH<sub>2</sub>); <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  70.1; IR (KBr,  $\nu$  in cm<sup>-1</sup>): 3229 (N–H), 1096 and 1005 (P–O–C), 1027 (Si–O–C), 751 (P=S); EI-MS (%): *m*/z 329 (0.6), 299 (1.5), 270 (6.7), 174 (100), 129 (7.8), 91 (2.6). Anal. Calcd. for C<sub>20</sub>H<sub>31</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>5</sub>PSSi: C 44.36, H 5.77, P 5.72; Found: C 44.51, H 5.68, P 5.85.

#### **Crystallographic Measurement**

The colorless crystals of compound **4** were obtained by vapor diffusion of THF in dimethylformamide at room temperature. A single crystal with dimensions of  $0.24 \times 0.24 \times 0.20 \text{ mm}^3$  was selected and mounted on a BRUKER SMART APEX-CCD diffractometer. The intensity data were collected by using a  $\psi$ - $\omega$  scan mode at 298(2) K. Absorption correction was not applied. The structure was solved by direct methods with SHELXS-97<sup>19</sup> and expanded using Fourier difference techniques. Structural refinement was carried out by full-matrix least-squares techniques on  $F^2$  using the SHELXL-97 package.

#### SUPPLEMENTARY MATERIAL

Crystallographic data for compound **4** have been deposited in the Cambridge Crystallographic Data Center (Deposition No. CCDC-848545). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

#### REFERENCES

- Huang, H. H.; Tian, M.; Liu, L.; He, Z. H.; Chen, Z. Q.; Zhang, L. Q. J. Appl. Polym. Sci. 2006, 99, 3203-3209.
- 2. Chen, J.; Liu, S. M.; Zhao, J. Q. Polym. Degrad. Stab. 2011, 96, 1508-1515.
- 3. Lu, S. Y.; Hamerton, I. Prog. Polym. Sci. 2002, 27, 1661-1712.
- 4. Lv, P.; Wang, Z.; Hu, Y.; Yu, M. Plast. Rubber Compos. 2008, 37, 311-318.
- 5. Li, L. Y.; Chen, G. H.; Liu, W.; Li, J. F.; Zhang, S. Polym. Degrad. Stab. 2009, 94, 996-1000.

- Wang, X.; Hu, Y. A.; Song, L.; Xuan, S. Y.; Xing, W. Y.; Bai, Z. M.; Lu, H. D. Ind. Eng. Chem. Res. 2011, 50, 713-720.
- 7. Li, Q.; Zhong, H. F.; Wei, P.; Jiang, P. K. J. Appl. Polym. Sci. 2005, 98, 2487-2492.
- 8. Wang, H. F.; Li B. Polym. Advan. Technol. 2010, 21, 691-697.
- 9. Li, Q.; Jiang, P. K.; Wei, P. J. Polym. Sci., Part B: Polym. Phys. 2005, 43, 2548-2556.
- 10. Kandola, B. K.; Horrocks, A. R. Polym. Degrad. Stab. 1996, 54, 289-303.
- 11. Deng, Y.; Wang, Y. Z.; Ban, D. M.; Liu, X. H.; Zhou, Q. J. Anal. Appl. Pyrol. 2006, 76, 198-202.
- Ren, Y. L.; Cheng, B. W.; Zhang, J. S.; Zang, H. J.; Kang, W. M.; Ding, C. K. Acta Chim Sinica. 2007, 65, 2034-2038.
- 13. Ren, Y. L.; Cheng, B. W.; Xu, L.; Jiang, A. B.; Lu, Y. C. J. Appl. Polym. Sci. 2010, 115, 1489-1494.
- 14. Shao, R. L.; Yang, G. F.; Miao, W. S.; Li, G. R. Chem. J. Chin. Univ. 1995, 16, 391-394.
- 15. Ma, Z. L.; Zhao, M.; Hu, H. F.; Ding, H. T.; Zhang, J. J. Appl. Polym. Sci. 2002, 83, 3128-3132.
- 16. ten Hoeve, W.; Wynberg, H. J. Org. Chem. 1985, 50, 4508-4514.
- Shi, D. Q.; Liu, Y.; Feras, A. D.; Tan, X. S.; Chen, J. X. Phosphorus Sulfur Silicon Relat. Elem. 2005, 180, 1937-1946.
- 18. Samour, C. M. US Patent 3118921, 1964-01-21.
- 19. Sheldrick, G. M. Acta Cryst. 2008, A64, 112-122.