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### Radical Additions of Bis(trimethylsilyl)phosphite to Vinyltrimethylsilane and Vinyltriethoxysilane: Crystal Structure of 2-Trimethylsilylethane-phosphonic Acid

Amir H. Mahmoudkhani<sup>a</sup>, Vratislav Langer<sup>b</sup>, Oliver Lindqvist<sup>ab</sup>

<sup>a</sup> Göteborg University, Göteborg, Sweden <sup>b</sup> Chalmers University of Technology, Göteborg, Sweden

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## **RADICAL ADDITIONS OF BIS(TRIMETHYLSILYL)PHOSPHITE TO VINYLTRIMETHYLSILANE AND VINYLTRIETHOXY-SILANE: CRYSTAL STRUCTURE OF 2-TRIMETHYLSILYLETHANE-PHOSPHONIC ACID**

*Amir H. Mahmoudkhani,<sup>a</sup> Vratislav Langer,<sup>b</sup>  
and Oliver Lindqvist<sup>a,b</sup>*

*Göteborg University, Göteborg, Sweden<sup>a</sup> and Chalmers  
University of Technology, Göteborg, Sweden<sup>b</sup>*

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*Organosilicon-phosphonate compounds with the general formula  $(R)_n(RO)_{3-n}Si(CH_2)_mP(O)(OSiR'_3)_2$  are designed for application as novel materials for surface treatments and modifications. A solvothermal method based on the reaction of bis(trimethylsilyl)phosphite with vinyltrimethylsilane and vinyltriethoxysilane in the presence of a peroxide in benzene solvent was used to synthesize the silyl-substituted esters of organosilicon-phosphonate compounds. 2-Trimethylsilylethanephosphonic acid was prepared from its bis(trimethylsilyl) ester by alcoholysis. The crystal structure of the acid consists of two-dimensional arrays built up from the  $(P-O-H) \cdots O-P$  hydrogen bonds.*

**Keywords:** Crystal structure; hydrogen bonding; supramolecular array; surface treatment

The formation of carbon-phosphorus bonds by radical addition to olefins in the presence of a peroxide has been known for many years.<sup>1,2</sup> The synthesis of organosilicon-phosphonate compounds first described by Barnes and David in 1960,<sup>3</sup> in which dialkylphosphites were added to substituted vinyl-, allyl-, or cyclohexenylethylsilanes. Hydrolysis of the products with concentrated hydrochloric acid gave the corresponding phosphonic acid. A remarkable note to the above syntheses is the use of alkoxysilane derivatives, which permits the formation of gels during the course of hydrolysis via a conventional sol-gel process of alkoxysilane

Address correspondence to A. H. Mahmoudkhani, Department of Chemistry, Göteborg University, Göteborg, SE-41296, Sweden. E-mail: amir@inoc.gu.se

Phosphonic acids are versatile compounds for the preparation of self-assemblies of monolayers or layered solid materials. They react with many metal ions forming metal phosphonates, an important class of organic-inorganic hybrid materials with a wide range of application.<sup>11–13</sup> The properties of metal phosphonates can be modified by the alteration of organic phosphorus moiety. Recently, Van Alsten<sup>14</sup> introduced a methodology for improving surface properties based on the formation of metal phosphonate layers on the surface of metallic substrates. The layers formed on the surface act as a barrier to reduce corrosion and to increase durability of metallic objects. We also are interested in the chemical characteristics of the phosphites and phosphonates of alkaline-earth metal ions to obtain chemically modified surfaces and thin films for the protection of different objects such as limestones, sandstones, and metals against atmospheric influences, corrosion, and decay.<sup>15–18</sup> The natural affinity of calcium ions, as well as other metallic ions, with phosphonate group can be utilized for the formation of thin solid films and layers with requested properties. Our supramolecular approach for chemically modified surfaces using phosphonic acids is illustrated in Scheme 1.

**SCHEME 1** Surface modification using phosphonic acids.

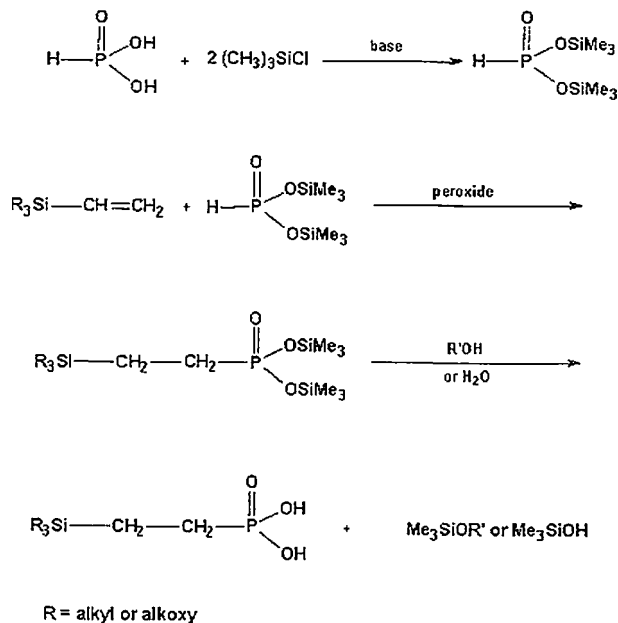
desired properties. This approach utilized a systematic exchange of the (P—)H atom with a (P—)R organic group, providing detailed information for a rational design of phosphorus-based materials for surface treatments. Organosilicon-phosphonate compounds with the general formula  $(R)_n(RO)_{3-n}Si(CH_2)_mP(O)(OR')_2$  (**I**) may be useful for such applications, if they can easily hydrolyze to form the corresponding phosphonic acids. In general, extreme conditions (such as concentrated hydrochloric acid and prolonged refluxing) are required for hydrolysis of the dialkyl esters of **I**, which can damage the substrate or not applicable for in situ treatment of large objects. The silyl esters of phosphorus are known to undergo hydrolysis extremely easy in the presence of moisture or alcohols.<sup>19</sup> Therefore compounds with the general formula  $(R)_n(RO)_{3-n}Si(CH_2)_mP(O)(OSiR'_3)_2$  can be good candidates for such applications since they may form glassy films. The rate of hydrolysis can be adjusted by the nature of alkyl or alkoxy groups on the individual silicon atoms.

In this study, we report the synthesis of bis(trimethylsilyl) esters of 2-trimethylsilylethanephosphonic acid and 2-(triethoxysilyl)ethanephosphonic acid by the radical addition of bis(trimethylsilyl)phosphite to vinyltrimethylsilane and vinyltriethoxysilane in the presence of *tert*-butyl peroxybenzoate. The crystal structure of 2-trimethylsilylethanephosphonic acid has also been determined by single-crystal x-ray diffraction technique.

## RESULTS AND DISCUSSION

The organosilicon-phosphonates compounds were synthesized using a solvothermal reaction of bis(trimethylsilyl)phosphites with vinyltrimethylsilane or vinyltriethoxysilane in the presence of peroxide in an autoclave with benzene as solvent. Yields of reactions were calculated based on the relative peak areas of the corresponding <sup>31</sup>P NMR signal for the respective compound and bis(trimethylsilyl)phosphite. We found that the solvothermal reaction in benzene provides higher yield than those reported by Barnes and David<sup>3</sup> or Hägele et al.<sup>4</sup> Furthermore, the yield of the reaction for vinyltriethoxysilane (~55%) is lower than that for vinyltrimethylsilane (~80%), which can be attributed to sol-gel polymerization, which occurs in the course of synthesis and isolation of products.

The reactions in the absence of solvent were also studied, but resulted in a 20–30% decrease of the yields for the above compounds. Bis(trimethylsilyl) esters easily hydrolyze to the corresponding acids. Hydrolysis of bis(trimethylsilyl), (2-triethoxysilane)-

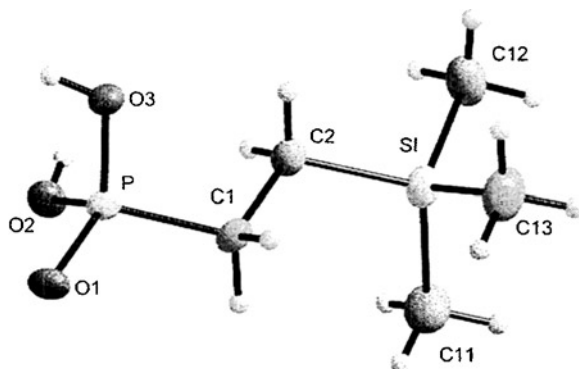


SCHEME 2

ethanephosphonate produced light-yellow gel materials being under further investigation. 2-Trimethyl-silylethanephosphonic acid was obtained quantitatively by alcoholysis of bis(trimethylsilyl),(2-trimethylsilane)ethanephosphonate with ethanol. The reaction steps are briefly summarized in Scheme 2.

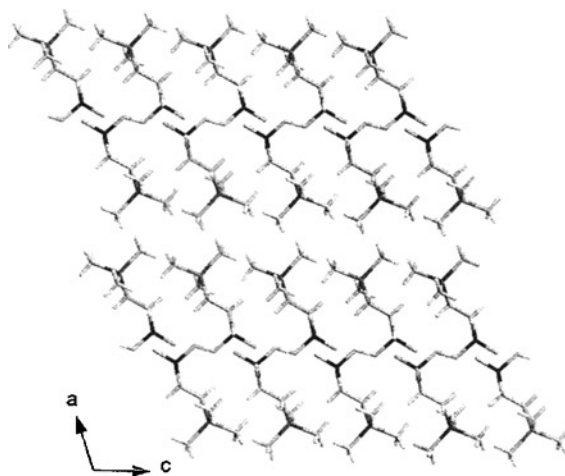
## 2-Trimethylsilylethanephosphonic Acid (SIP)

The compound **SIP**,  $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{P}(\text{O})(\text{OH})_2$ , crystallizes in monoclinic system with space group  $\text{P}2_1/\text{c}$  (No. 14). The asymmetric unit consists of one formula unit (see Figure 1). The material self-assembles into layers aligned parallel to the  $bc$  plane formed by hydrogen bonds of the  $\text{O}-\text{H} \cdots \text{O}$  type (see Figure 2). The first-level descriptors using PLUTO<sup>20</sup> based on the graphset theory<sup>21</sup> includes only C1,1(4) motifs, while the second-level comprises: R2,4(12) and R4,4(16) motifs. Both supramolecular ring motifs indicate tetramers that are linked together in different manner. A 12-membered ring motif, R2,4(12), is formed when two monomers act only as hydrogen bond acceptors and the other two act as donors. If all monomers act as hydrogen bond donor and acceptor, then a 16-membered ring, R4,4(16), is formed. The hydrogen bonding network

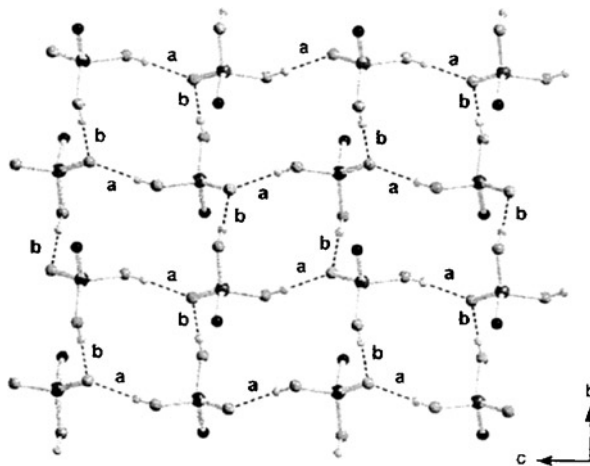


**FIGURE 1** Molecular structure and atom-numbering scheme for **SIP**. Thermal ellipsoids are shown at the 50% probability level.

and its motifs are shown in Figure 3. The two-dimensional hydrogen-bonded sheets are separated from each other by the trimethylsilylethyl moieties resembling the orientation of organic tails that are pointing out from the surfaces as indicated in Scheme 1. The structural correlation of phosphonic acids and their organic and inorganic salts and its consequences for the design of new solid materials are interesting and reported by us.<sup>22–25</sup>



**FIGURE 2** The packing diagram for **SIP**. Notice the organic tails are pointing out from the layers (parallel to the *bc* plane).



**FIGURE 3** The hydrogen-bonding pattern in the crystal structure of **SIP**. Supramolecular chain motifs, C1, 1(4), are formed by the (a) hydrogen bond parallel to *c* axis and also by the (b) hydrogen bonds parallel to *b* axis. The R2, 4(12) and R4, 4(16) ring motifs are built up from combinations of the (a) and (b) hydrogen bonds.

## CONCLUSION

A new class of organosilicon-phosphonate compounds with the general formula  $(R)_n(RO)_{3-n}Si(CH_2)_mP(O)(OSiR'_3)_2$  has been designed for surface treatment applications by the formation of protective thin films. Solvothermal reaction of bis(trimethylsilyl)phosphite with vinylsilanes in the presence of peroxide provides relatively higher yield than methods previously described. 2-Trimethylsilylethanephosphonic acid exhibits a layered structure, in which the  $(P-O)-H \cdots O-P$  hydrogen bonds form a two-dimensional network.

## EXPERIMENTAL

### General

All reactions involving the silyl esters were carried out under dry nitrogen atmosphere using standard Schlenk-line technique or in a glove box. Tetrahydrofuran (THF), diethylether and benzene were dried by distillation over sodium. Phosphorus acid ( $H_3PO_3$ ) was dried by azeotropic distillation with toluene for 6 h. Vinyltrimethylsilane was dried using  $P_2O_5$  and redistilled. Other chemicals were used as received.

**TABLE I** Crystallographic and Refinement Data

	<b>SIP</b>
Empirical formula	C <sub>5</sub> H <sub>15</sub> O <sub>3</sub> PSi
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c (No. 14)
a [Å]	14.4549(2)
b [Å]	7.3016(1)
c [Å]	9.7928(1)
β [°]	108.403(1)
V [Å <sup>3</sup> ]	980.71(3)
Z, ρ (calc.) [g · cm <sup>-3</sup> ]	4, 1.234
T [K]	183(2)
μ [mm <sup>-1</sup> ]	0.361
Refl. collec./unique	11288/3426
R(int.)	0.041
Data/restrain/parameter	3426/2/111
R1/wR2 (I > 2σ(I))	0.043/0.106
R1/wR2 for all data	0.068/0.120
Goodness-of-fit on F <sup>2</sup>	1.027
Larg. diff. peak/hole [e · Å <sup>-3</sup> ]	0.678/−0.567

[\*] R1 =  $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ , wR2 =  $\{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma w[(F_o^2)^2]\}^{1/2}$ .

**TABLE II** Selected Bond Distances [Å] and Angles [°] for **SIP**

P—O1	1.5047(10)
P—O2	1.5607(10)
P—O3	1.5507(10)
P—C1	1.7968(15)
Si—C2	1.8740(16)
O1—P—O2	106.72(6)
O1—P—O3	113.42(6)
O2—P—O3	110.40(6)
O1—P—C1	112.74(7)
O2—P—C1	109.40(7)
O3—P—C1	104.17(7)

**TABLE III** The Geometry<sup>a</sup> of Hydrogen Bonds for **SIP** [Å, °]

Notation	D—H···A	d(D—H)	d(H···A)	d(D···A)	<(DHA)
<b>1</b>					
<b>a</b>	O2—H2···O1 <sup>i</sup>	0.77(2)	1.84(1)	2.6045(15)	169(3)
<b>b</b>	O3—H3···O1 <sup>ii</sup>	0.80(2)	1.77(1)	2.5622(15)	175(3)

<sup>a</sup>Symmetry transformations used to generate equivalent atoms: (i) −x, y + 1/2, −z + 1/2; (ii) x, −y + 3/2, z − 1/2.

Solvothermal reactions were performed in a stainless steel autoclave with a quartz cell (with the capacity of 10 mL) at autogenous pressure. The IR spectrum was recorded on a Nicolet MAGNA-IR 560 spectrometer.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Varian XL-400 spectrometer operating at 400 MHz or 161.9 MHz, respectively. Chemical shifts were recorded relative to TMS or 85%  $\text{H}_3\text{PO}_4$  (external) and they are given in ppm.

## Syntheses

### A) *Bis(trimethylsilyl)phosphite*

There are two methods for the preparation of bis(trimethylsilyl)-phosphite in the literature.<sup>26,27</sup> The compound was prepared with based on the method described by Sekine et al.<sup>26</sup> with some modifications. A solution of phosphorus acid (0.2 mmol) in THF (200 mL) was added slowly during 2 h to a solution of trimethylsilylchloride (0.38 mmol) in ether (200 mL) at room temperature under dry nitrogen atmosphere. Then triethylamine (0.38 mmol) was added dropwise. The mixture was refluxed for about 2 h. The white precipitate formed was filtered off under nitrogen atmosphere and washed with THF (100 mL). Distillation of filtrate under vacuum gave the pure product,  $(\text{Me}_3\text{SiO})_2\text{P}(\text{O})\text{H}$  (Yield 94%), b.p.  $79^\circ\text{C}$  at 11 mmHg. NMR ( $\text{CDCl}_3$ ),  $\delta$  ( $^{31}\text{P}$ ) =  $-13.31$ ,  $\delta$  ( $^1\text{H}$ ): 0.21 (s, 18H,  $\text{CH}_3$ ), 6.84 (d, 1H,  $J_{\text{P-H}} = 698.7$  Hz); IR (NaCl): 2963, 2425, 1419, 1261, 1049, 1013, 856, 762, 697.

### B) *2-Trimethylsilylethanephosphonic Acid, Bis(trimethylsilyl) Ester*

Bis(trimethylsilyl)phosphite (5 mmol) and vinyltrimethylsilane (5 mmol) were added to dry benzene (5 mL) in a quartz cell of the autoclave. *tert*-Butyl peroxybenzoate (1 drop) was added to the solution. The autoclave was sealed and kept in an oven at  $150^\circ\text{C}$  for about 5 h. Then, the solvent was removed under vacuum. The product and the residue of the starting materials were separated using fractional distillation under vacuum, b.p.  $118\text{--}120^\circ\text{C}$  at 10 mmHg. Yield  $\sim 70\%$ . NMR ( $\text{CDCl}_3$ );  $\delta$  ( $^{31}\text{P}$ ): 28.71;  $\delta$  ( $^1\text{H}$ ): 0.20 (s, 9H), 0.22 (s, 18H), 0.66 (m, 2H), 1.64 (m, 2H).  $\nu(\text{P=O})$ :  $1253\text{ cm}^{-1}$ .

### C) *2-Trimethylsilylethylphosphonic Acid (SIP)*

The compound was prepared by the alcoholysis of bis(trimethylsilyl) 2-trimethylsilylethylphosphonate under refluxing with ethanol for 6 h. The solvent was removed under vacuum and the product was extracted with dioxane. The solvent was then evaporated under vacuum to give a

pure white solid material, m.p. 144–146°C. Yield 84%. NMR (CDCl<sub>3</sub>);  $\delta$  (<sup>31</sup>P): 16.11;  $\delta$  (<sup>1</sup>H): 0.21 (s, 9H), 0.62 (m, 2H), 1.46 (m, 2H); IR,  $\nu$ (P=O): 1268 cm<sup>-1</sup>. Single crystals of the product were obtained from its melt, when it was kept in an oil bath by slow cooling under the vacuum. The material was, in addition, structurally characterized by x-ray diffraction technique.

#### ***D) 2-Triethoxysilylethanephosphonic Acid, Bis(trimethylsilyl) Ester***

An experimental procedure as given in the B section, was adopted except that vinyltriethoxysilane was used as the starting material. Attempts to purify the desired product (yield ~50%) using fractional distillation failed due to the sol-gel polymerization and thermal decomposition (at above 100°C), which occurs upon heating the mixture during the fractional distillation under vacuum. NMR (CDCl<sub>3</sub>);  $\delta$  (<sup>31</sup>P): 28.01.

### **Crystal Structure Determination**

Data were collected using a Siemens SMART CCD diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å, graphite monochromator). Full sphere of reciprocal lattice was scanned by 0.3° steps in  $\omega$  with a crystal-to-detector distance of 3.97 cm. Preliminary orientation matrix was obtained from the first frames using SMART.<sup>28</sup> The collected frames were integrated using the preliminary orientation matrices which were updated every 100 frames. Final cell parameters were obtained by refinement on the positions of reflections with  $I > 10\sigma(I)$  after integration of all the frames using SAINT.<sup>28</sup> The data were empirically corrected for absorption and other effects using SADABS.<sup>29</sup> The structures were solved by direct methods and refined by full-matrix least squares on all F<sup>2</sup> data using SHELXTL.<sup>30</sup> The non-H atoms were refined anisotropically. The (O—)H hydrogen atoms were located from difference Fourier map and refined isotropically with restrained bond distance of 0.80 Å. Other H atoms were constrained to idealized positions using appropriate riding models and refined isotropically. Molecular graphics were obtained using Diamond.<sup>31</sup> Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Center as supplementary publication no. CCDC-102189. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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