MOLECULAR STRUCTURE OF BIS(TRIMETHYLSILYL) HYPOPHOSPHITE (Me<sub>3</sub>SiO)<sub>2</sub>P-H

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The organosilyl esters of hypophosphorous acid have only recently been known [1]. The presence of a tricoordinate phosphorus atom, a mobile trialkylsilyl group, and a P-H bond causes high reactivity of these compounds and predetermines a diversity of their transformations. Different phosphorus-containing compounds are formed, for example in the reactions of bis(trimethylsilyl) hypophosphite with unsaturated [2] and carbonyl [3, 4] compounds. This was the reason for studying the structure of the molecule of  $(Me_3SiO)_2P-H$  in the gaseous phase.

Bis(trimethylsilyl) hypophosphite was synthesized by reacting sodium hypophosphite with trimethylchlorosilane and diethylamine in absolute toluene at -10°C [5], and had the following physical constants: bp 53.5-54°C (15 mm Hg),  $\delta p$  141 ppm, Jp-H 175 Hz. In the IR spectrum, the 2165 cm<sup>-1</sup> band is assigned to v(P-H) vibration.

The electronograms of the (Me<sub>3</sub>SiO)<sub>2</sub>P-H vapors were obtained at two nozzle-photographic plate distances (186 and 366 mm), at room temperature. The geometrical model of the molecule







UDC 539.27

Fig. 1. Model and Newman projections of models I and II of bis(trimethylsilyl) hypophosphite molecule.

Fig. 2. Radial distribution curves of models I and II of bis(trimethylsilyl) hypophosphite molecule (continuous line - theoretical; dots - experimental).

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Branch, Academy of Sciences of the USSR. Translated from Zhurnal Strukturnoi Khimii, Vol. 26, No. 2, pp. 175-177. March-April, 1985. Original article submitted June 10, 1983.

TABLE 1. Geometrical Parameters of Bis(trimethylmethyl-silyl) Hypophosphite\*

Param- eter	Model I	Model II	
Valence distances (ra), Å			
P-0 Si-0. Si-C C-H P-H	(1,637(2) 1,657(2) 1,905(1) 1,130 † 1,400 †	1,637(2) 1,657(2) 1,905(1) 1,130 † 1,400 †	
Valence angles (deg)			
$\begin{array}{c} PO_{3}Si_{4}\\ PO_{8}Si_{9}\\ OSiC\\ OPO.\\ SiCH\\ HPO\\ \phi_{1}\\ \phi_{2}\\ \phi_{3}\\ \phi_{4}\\ \phi_{5} \end{array}$	$\begin{array}{c} 135,0(1,4)\\ 145,2(2,2)\\ 110,5(0,5)\\ 99,3(1,0)\\ 117,3(1,5)\\ 100 \\ 175,5(1,6)\\ 168,4(2,2)\\ 37,6(2,5)\\ 20,0(3,7)\\ 60 \\ \end{array}$	$\begin{array}{c} 441,5(1,1)\\ 133,2(1,5)\\ 109,1(0,4)\\ 100,5(1,2)\\ 111,5(1,5)\\ 100 \\ 1\\ 31,0(4,2)\\ 11,0(1,9)\\ .75,9(3,0)\\ 80,4(2,0)\\ 60 \\ \end{array}$	
CSiC R, %	108,4 <b>∓</b> 16,7	111,4 <b>∓</b> 14,7	

\*Standard deviations are given in parentheses. +Fixed values. ‡Calculated values.

TABLE 2. Vibration Amplitudes of Bis-(trimethylsilyl) Hypophosphite

Parameter	Model I	Model II
P0 } si0 } siC CH PH	$\begin{array}{c} 0,059(2)\\ 0,059(2)\\ 0,047(2)\\ 0,088 \\ *\\ 0,100 \\ * \end{array}$	0,056(2) 0,056(2) 0,045(2) 0,088 * 0,100 *
$\left. \begin{array}{c} P \dots Si_4 \\ P \dots Si_9 \end{array} \right\}$	3,044 0,073(18) 3,143 0,078(18)	3,110 0,059(13) 3,024 0,067(13)
$ \begin{array}{c} P & \dots & C_{5} \\ P & \dots & C_{6} \\ P & \dots & C_{7} \\ P & \dots & C_{10} \\ P & \dots & C_{11} \\ P & \dots & C_{12} \end{array} $	$\begin{array}{cccc} 3,659 & 0,160(22) \\ 4,525 & 0,091(22) \\ 4,014 & 0,100(22) \\ 3,793 & 0,100(22) \\ 4,481 & 0,100(22) \\ 4,255 & 0,071(22) \end{array}$	$\begin{array}{c} 4,009 & 0,145(16) \\ 4,528 & 0,091(16) \\ 3,786 & 0,084(16) \\ 3,940 & 0,084(16) \\ 4,502 & 0,071(16) \\ 3,956 & 0,144(16) \end{array}$
$ \left. \begin{array}{c} O_3 \dots Si_9 \\ O_8 \dots Si_4 \\ O_3 \dots C_5, \ 6, \ 7 \end{array} \right\} $	3,843 0,114(12) 3,624 0,120(12) 2,931 0,080(12)	3,770 0,125(9) 3,520 0,119(9) 2,906 0,079(9)
$ \begin{array}{c} O_{\mathfrak{s}} \dots & O_{\mathfrak{s}} \\ O_{\mathfrak{s}} \dots & C_{11} \\ O_{\mathfrak{s}} \dots & C_{12} \end{array} $	2,496 0,093(16) 4,643 0,119(16) 5,387 0,119(16)	$\begin{array}{c} 2,517 & 0,067(9) \\ 4,890 & 0,074(9) \\ 3,860 & 0,074(9) \end{array}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 4,497  0,136(29) \\ 5,141  0,111(29) \\ 6,254  0,111(29) \\ 3,992  0,141(29) \\ 4,332  0,111(29) \\ 5,045  0,171(29) \\ 6,264  0,151(29) \end{array}$	$\begin{array}{cccc} 4,260 & 0,144(28) \\ 3,930 & 0,087(28) \\ 6,130 & 0,183(28) \\ 4,459 & 0,100(28) \\ 5,927 & 0,093(28) \\ 5,084 & 0,087(28) \\ 3,739 & 0,107(28) \end{array}$

\*Fixed values; amplitudes which were. more specifically defined by the group method are enclosed in braces.

(Fig. 1) is determined by C-H, Si-O, Si-C, P-H, and P-O internuclear distances, O-P-O, P-O-Si, O-Si-C, H-P-O, and H-C-Si valence angles, and also by rotation angles around the P-O ( $[\phi_1$  and  $\varphi_2$  ) and Si-O ( $\varphi_3$  and  $\varphi_4$ ) bonds. The angles  $\varphi_1 = \varphi_2 = 0^\circ$  correspond to a model in which the OPO and POSi planes are orthogonal, while at  $\phi_3 = \phi_4 = 0^\circ$  the P-O and C-Si bonds are screened. Clockwise rotation around the P-O and Si-O bonds, in the direction from the oxygen atom to phosphorus and from the silicon atom to oxygen, respectively, was taken as the positive direction.

The search for the optimal model was carried out at different torsion angles. In more precise specification of geometrical parameters, several limitations were accepted: 1) the OSiMe<sub>3</sub> and SiMe groups have a local  $C_{3V}$  symmetry; 2) the C-H bonds are the same and fixed in alternative positions with respect to the Si-O bonds; 3) the C-H internuclear distances were not more precisely specified and were taken as equal to 1.13 Å from the experimental radial distribution curve (Fig. 2). Preliminary calculations showed that the difference in the Si-O and P-O bond lengths is 0.02 Å. This relationship was further used in the more precise specification of the parameters of the molecule.

Table 1 shows the geometrical parameters of the two models, the theoretical radial distribution curves, and the intensities at which f(r) and sM(s) satisfactorily agree with the experimental values, and Table 2 gives the corresponding vibration amplitudes. First, we should note that the P-O-Si valence angles differ in the two models. Attempts to more precisely define the models with the same P-O-Si angles were unsuccessful; in all cases we obtained unsatisfactory agreement between the theoretical and experimental f(r) and sM(s)curves. Table 1 shows that the torsion angles  $arphi_3$  and  $arphi_4$  markedly differ from the ideal values (60°). Calculations with  $\varphi_3 = \varphi_4 = 60^\circ$  were also unsuccessful.

If we do not take into account the mutual disposition of the unshared electron pair (UEP) and the SiMe3 group, then the models found are fairly similar (see Tables 1 and 2). Strictly speaking, such a result should have been expected, since the contribution to the general scattering from the internuclear distances H(1)...X (where X = Si, C, H) is not high. If we take into account the position of the UEP of the phosphorus atom, we can note the following:

In model I, the two SiMe<sub>3</sub> groups are present in approximately gauche-position with respect to the UEP of the phosphorus atom. This is indicated by the dihedral angles H(1)POSi, equal to 172 and 156° (see Fig. 1). In model II, one SiMe<sub>2</sub> group is present in the trans-position with respect to the UEP of the phosphorus atom. This is indicated by the dihedral angles O(8)PO(3)Si(4) and H(1)PO(3)Si(4). However, the second SiMe<sub>3</sub> group is present in a screened position with respect to the H(1) atom (see Fig. 1).

No data are available in the literature on the conformational composition of bis(trimethylsilyl) hypophosphite. Our results do not exclude the possibility that in the gaseous phase there are molecules with a cis-gauche- and trans-trans disposition of the SiMe<sub>3</sub> groups with respect to the UEP of phosphorus. It should be noted that no satisfactory agreement was obtained with the experimental data for any of the models with  $arphi_1=-arphi_2$ including those also for the model with  $q_1 \approx 0$  and  $q_2 \approx 180^\circ$ , i.e., a model in which one of the SiMe<sub>3</sub> groups is located in a gauche position with respect to the UEP of phosphorus, and the other in the trans-position. In other words, models with the trans-disposition of the SiMe, group, for which there are no intramolecular steric interactions, did not satisfy the experimental data. The values of the P-O-Si valence angles obtained (about 134 and 143°) indicate a change in the hybridization of the oxygen atom, as has already been established, for example in disiloxane [6], perchloro-, and perfluorodisiloxanes [7, 8]. A change in the valence angle at the oxygen atom in disiloxane compounds is usually explained by delocalization of the UEP of the oxygen atoms to the vacant d-orbitals of silicon. In our case, increase in the P-O-Si angles is due to the simultaneous influence of the silicon and phosphorus atoms on the value of this angle.

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