Molecular Structures of Silylphosphine, Silylmethylphosphine, and Silyldimethylphosphine: an Electron Diffraction Study

By **C. Glidewell, (Miss) P. M. Pinder, A. G. Robiette,** and **G. M. Sheldrick,*** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The molecular structures of silylphosphine, silylmethylphosphine, and silyldimethylphosphine have been determined in the vapour phase by the sector-microphotometer method of electron diffraction. The Si–P bond lengths are, respectively 2·249(3), 2·248(3), and 2·245(3) Å. Substitution of SiH_3 for H in mono- and di-methylphosphine does not appear to influence the C–P bond length. The C–P–C and C–P–Si angles lie in the range 99—101°, similar to the C–P–C angles in the methyl phosphines, but in contrast to the structural variations found in the series $(H_3Si)_nNMe_{3-n}$. The bonding in the silyl phosphines is discussed.

In an electron diffraction study[1] of trisilylphosphine, $(SiH_3)_3P$, the Si–P–Si angle was found to be 96·5 (0·5°) and the Si–P bond length to be 2·248(0·003) Å. The values of these parameters do not appear in any way anomalous when compared with those of trimethylphosphine[2] [C–P–C angle 98·6 (0·3°), C–P bond length 1·845(0·003) Å]. The marked difference in stereochemistry between trisilylamine[3] [Si–N–Si angle 119·7 (0·1°)] and trimethylamine[4] [C–N–C angle 110·6 (0·6°)] is thus not repeated in the phosphines. Despite the lack of any unusual features in the molecular structure of trisilylphosphine, it has been suggested[5,6] (on the basis of chemical evidence, *viz.* the feeble basicities of silyl phosphines as compared with their methyl analogues) that the 3*d* orbitals of silicon may contribute substantially to the Si–P bond. If this is so, it is possible that changes in the substituents on phosphorus might give rise to changes in structural parameters, *e.g.* the Si–P bond length. Accordingly we have investigated the molecular structures of silylphosphine, SiH_3PH_2, silylmethylphosphine, SiH_3PHMe, and silyldimethylphosphine, SiH_3PMe_2.

EXPERIMENTAL

Each of the phosphines was prepared[7,8] by reaction of silyl bromide with the appropriate aluminium complex, $LiAl(PR'R'')_4$, (R', R'' = H or Me), and was purified by repeated fractional condensation *in vacuo*.

Intensities were recorded photographically on the Balzers' KD. G2 electron diffraction instrument at the University of Manchester Institute of Science and Technology,[9] and transferred to punched paper tapes using a Joyce–Loebl microdensitometer. Satisfactory plates were readily obtained for silylphosphine and silyldimethylphosphine. For silylmethylphosphine the data proved to be markedly inferior: subsequently, further plates were obtained for this compound, but their quality was not improved. We are unable to offer an explanation for these difficulties. The electron wavelength (0·05791 ± 0·00003 Å) was determined from the diffraction pattern of powdered thallium(I) chloride; this was confirmed by a direct measurement of the accelerating voltage. Data were obtained at nozzle-to-plate distances of 50 and 25 cm, giving a range of *ca.* 3 to 28 $Å^{-1}$ in the scattering variable *s*. The data reduction and full-matrix least-squares refinement programs have been described elsewhere.[1,10]

Molecular Models.—No attempts were made to distinguish between conformations which differ only in the rotation of CH_3 and SiH_3 groups about single bonds, since in these molecules the electron diffraction data are very insensitive to such changes. All CH_3 and SiH_3 groups were assumed to be axially symmetric with the axes lying along the C–P or Si–P bond. Other assumptions made were: SiH_3PH_2: the SiH_3 group staggers the P–H bonds and the angles H–P–H and H–P–Si are equal. There are then five independent geometrical parameters, chosen as the Si–H, P–H, and Si–P bond lengths and the H–Si–P and H–P–Si angles.

SiH_3PHMe: the SiH_3PCH_3 group has a plane of symmetry. The methyl H atom in this plane points away from the Si atom and similarly the in-plane silyl H atom

---

[1] B. Beagley, A. G. Robiette, and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1968, 3002.

[2] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, 1960, **32**, 512.

[3] B. Beagley and A. R. Conrad, *Trans. Faraday Soc.*, 1970, **66**, 2740.

[4] B. Beagley and T. G. Hewitt, *Trans. Faraday Soc.*, 1968, **64**, 2561.

[5] E. A. V. Ebsworth in 'Organometallic Compounds of the Group IV Elements,' ed., A. G. MacDiarmid, Dekker, New York, 1968, vol. 1, part 1.

[6] E. A. V. Ebsworth, C. Glidewell, and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1969, 352.

[7] A. D. Norman, *Chem. Comm.*, 1968, 812.

[8] C. Glidewell and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1969, 350.

[9] B. Beagley, A. H. Clark, and T. G. Hewitt, *J. Chem. Soc.* (*A*), 1968, 658.

[10] D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. J. Aylett, I. A. Ellis, and J. J. Monaghan, *J. Chem. Soc.* (*A*), 1969, 1224.

points away from the C atom. The angles H–P–Si, H–P–C, and C–P–Si are equal. The eight geometrical parameters are chosen as the Si–H, P–H, C–H, C–P, and Si–P bond lengths and the C–P–Si, H–Si–P, and H–C–P angles.

SiH_3PMe_2: the $P(CH_3)_2$ group has local C_{2v} symmetry with the in-plane methyl H atoms pointing away from the opposite C atoms. The SiH_3 group staggers the P–C bonds. There are eight independent geometrical parameters, chosen as the C–H, Si–H, C–P, and Si–P bond lengths and the H–C–P, H–Si–P, C–P–C, and C–P–Si angles.

In dimethylphosphine and trimethylphosphine the methyl groups were found to stagger the opposing C–P bonds: for methylphosphine the evidence also favoured a staggered conformation.[2,11]

Refinement. Most of the parameters involving hydrogen atoms were poorly determined, and further constraints in the refinements proved necessary in order to achieve physically acceptable results. The results of refinement under various constraints are presented in Table 1. Simultaneous refinement of the Si–H and P–H bonds in H_3SiPH_2 leads to unreasonably long Si–H and short P–H bonds. The relatively small effect on the other parameters of constraining the angles involving hydrogen can be seen in Table 1. In all three molecules, refinement of the Si–H bond length led to values in the range 1·51—1·52 Å, and to H–Si–P angles in the range 112—115°. The corresponding values in trisilylphosphine[1] are 1·485(10) Å and 110·9(1·4)°. Two recent studies have given Si–H bond lengths greater than 1·5 Å: in $(H_3Si)_2CH_2$ (ref. 12), Si–H = 1·515(4) Å, and in $(H_3Si)_3N$ (ref. 3), Si–H = 1·506(5) Å (in the latter case the fit was almost as good with Si–H fixed at 1·485 Å, and this value was preferred by the authors). Nevertheless, we felt that the silyl group parameters obtained in the present study were not reasonable, particularly when compared with those in trisilylphosphine. In all refinements quoted here, Si–H was fixed at 1·50 Å, and the angles H–Si–P and H–C–P were fixed at 111° [*cf.* angle H–C–P of 110·7 (0·5°) in trimethylphosphine [2]]. It was also necessary to fix the P–H bond length in silylmethylphosphine at 1·44 Å: this is close to the refined value of this parameter in phosphine, the methylphosphines,[11] and silylphosphine. The C–H bond lengths then refined to acceptable values.

TABLE 1

Effect of relaxing geometrical constraints. Estimated standard deviations (in parentheses) are taken directly from the least-squares refinements (employing off-diagonal weight matrices). Bond lengths in Å, angles in degrees. Preferred refinements are given in the first column

SiH_3PH_2					
Si–P	2·249(2)	2·249(2)	2·249(2)	2·249(2)	
Si–H	1·500(*)	1·500(*)	1·526(9)	1·525(10)	
P–H	1·438(12)	1·438(12)	1·398(15)	1·398(16)	
u(SiP)	0·048(4)	0·047(4)	0·046(4)	0·046(4)	
u(SiH)	0·083(6)	0·082(7)	0·052(20)	0·053(20)	
HSiP	111·0(*)	112·6(1·6)	111·0(*)	111·8(1·6)	
HPSi	91·1(1·7)	92·2(2·2)	93·3(2·1)	93·9(2·5)	
SiH_3PMe_2					
Si–P	2·245(2)	2·245(2)	2·247(2)	2·245(2)	2·246(2)
C–P	1·850(2)	1·851(2)	1·850(2)	1·851(2)	1·850(2)
Si–H	1·500(*)	1·515(8)	1·509(8)	1·515(8)	1·508(8)
C–H	1·083(6)	1·083(6)	1·078(6)	1·082(6)	1·078(6)
u(SiP)	0·046(4)	0·046(4)	0·047(4)	0·045(4)	0·047(4)
u(CP)	0·050(4)	0·048(4)	0·050(4)	0·049(4)	0·051(4)
u(SiH)	0·074(10)	0·075(10)	0·075(9)	0·076(10)	0·075(9)
SiPC	99·0(0·2)	98·8(0·3)	98·5(0·3)	99·8(0·3)	98·3(1·0)
CPC	100·9(1·0)	101·2(1·0)	101·5(1·0)	100·8(0·9)	101·6(1·5)
HSiP	111·0(*)	111·0(*)	111·0(*)	105·5(1·4)	111·6(3·8)
HCP	111·0(*)	111·0(*)	112·8(0·9)	111·0(*)	112·9(1·1)

* Parameter not refined.

RESULTS

The principal structural parameters obtained are given in Table 2. For silylmethylphosphine the two sets of data (see Experimental section) gave results which did not differ significantly: the results given represent refinements in which both sets of data were employed simultaneously. Plots of the combined intensity data and their weighted differences are shown for all three molecules in Figure 1. The radial-distribution curves *P(r)/r* resulting from the Fourier inversion of these data are displayed in Figure 2. The high noise level in the intensity curve and *P(r)/r* curve can be clearly seen for silylmethylphosphine; the poor data for this molecule are also reflected in the high *R* factor in Table 2. Values of the vibrational amplitudes refined are reasonably satisfactory, except that the Si–H amplitude in silylmethylphosphine is somewhat low (with a large standard deviation).

TABLE 2

Structural parameters (estimated standard deviations in parentheses)

	SiH_3PH_2	SiH_3PHCH_3	$SiH_3P(CH_3)_2$
Bond lengths (Å)			
Si–P	2·249(3)	2·248(3)	2·245(3)
C–P		1·857(4)	1·850(3)
Si–H	1·50 [a]	1·50 [a]	1·50 [a]
P–H	1·438(20)	1·44 [a]	
C–H		1·081(11)	1·083(8)
Angles (°)			
C–P–C			100·8(1·2)
C–P–Si		101·2(0·7)	99·0(0·5)
H–P–Si	91(3)	101·2 [b]	
Refined amplitudes			
Si–P	0·047(5)	0·045(5)	0·046(5)
C–P		0·042(7)	0·050(5)
Si–H	0·083(10) [c]	0·06(2) [d]	0·074(12) [e]
Si · · · C		0·12(2)	0·129(9) [f]
P · · · H	0·16(3)	0·10(2)	0·112(10)
Si · · · (P)H	0·14(4)	0·10 [g]	
Generalised *R* factor			
(see ref. 1)	0·16	0·23	0·14

[a] Indicates parameter not refined. [b] Angle H–P–Si assumed equal to angle C–P–Si in model; see text. [c] Si–H Amplitude used also for P–H amplitude. [d] Si–H Amplitude used also for P–H and C–H amplitudes. [e] C–H Amplitude fixed at 0·075 Å. [f] Si · · · C Amplitude used also for C · · · C amplitude. [g] P · · · H Amplitude used also for Si · · · (P)H and C · · · P(H) amplitudes.

DISCUSSION

The parameters which are best determined in this work are those which define the geometry of the heavy atoms, *i.e.* the Si–P and C–P bond lengths, and Si–P–C and C–P–C angles. We compare in Table 3 structural

---

[11] L. S. Bartell, *J. Chem. Phys.*, 1960, **32**, 832.

[12] A. Almenningen, H. M. Seip, and R. Seip, *Acta Chem. Scand.*, 1970, **24**, 1697.

parameters of phosphines substituted with silyl and/or methyl groups.

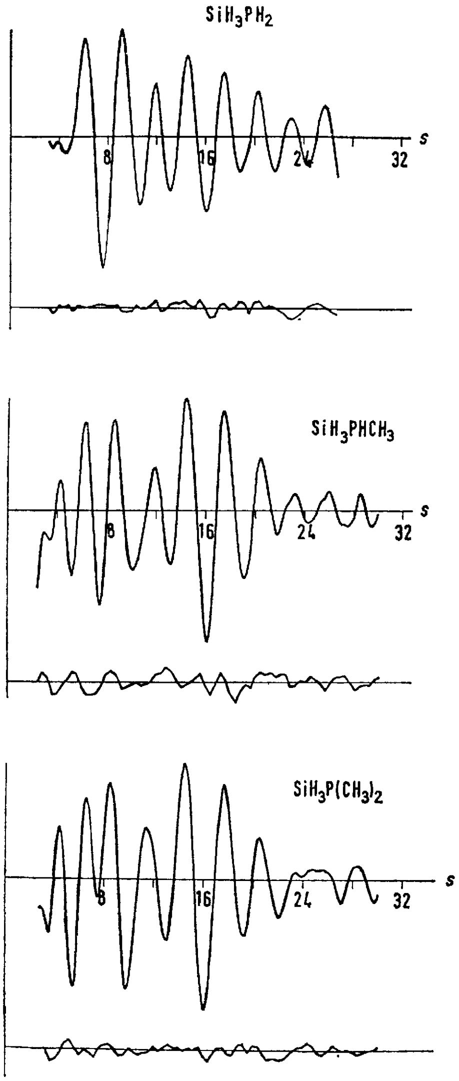

FIGURE 1 Observed and weighted-difference combined molecular-intensity data for the silylmethylphosphines

In the methylphosphines there is a small but definite trend in the C–P bond lengths. It appears that this is found also in the two silylmethylphosphines studied here, although taken in isolation the difference between their C–P bond lengths is not very significant. The C–P–C angles in $(CH_3)_2PH$ and $(CH_3)_2PSiH_3$ differ only by the sum of their standard deviations. We conclude that substitution of SiH_3 for H in CH_3PH_2 and $(CH_3)_2PH$ does not alter appreciably the geometry of the rest of the molecule. The Si–P–C angles lie in the general range of C–P–C angles in these molecules. There is no significant difference between the Si–P bond lengths in any of the silyl-substituted phosphines so far studied.

There appear to be no anomalous features in the stereochemistry of silylphosphines. Present theoretical understanding of *d*-orbital participation in the bonding of second-row elements is not so far advanced that we can readily predict what effect a substantial contribution from the 3*d* orbitals of silicon and/or phosphorus would have on the geometry of a substituted phosphine. We may however contrast the behaviour of the silylphosphines with that of the silylamines. Substitution of SiH_3 for H in methylamines causes large changes in the angles at nitrogen (Table 4), the co-ordination about nitrogen being planar in more than one case; such planar co-ordination has been frequently cited as evidence for $p_\pi \rightarrow d_\pi$ bonding in silicon–nitrogen compounds.[3,5,13] There are also changes in the Si–N bond length with increasing SiH_3 substitution. Chemically, there is a very marked decrease in base strength along the series $(CH_3)_3N$, $(CH_3)_2NSiH_3$, $CH_3N(SiH_3)_2$, $N(SiH_3)_3$, which has also been taken [5] to indicate the presence of $p_\pi \rightarrow d_\pi$ bonding. Since none of the geometrical effects found in the silylamines is present in the silylphosphines, it is necessary to consider briefly the variation of acidic and basic properties of silyl- and methyl-phosphines.

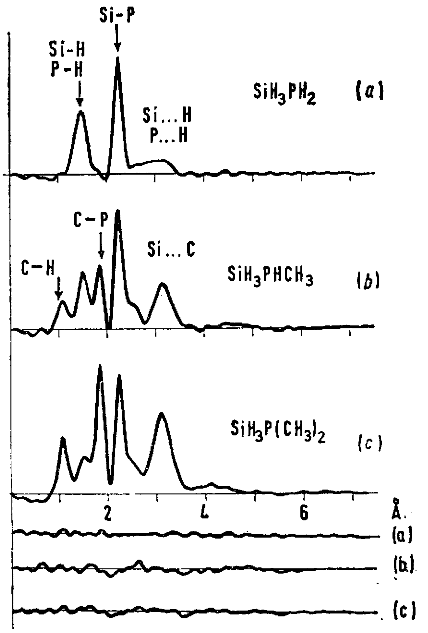

FIGURE 2 Observed and difference radial-distribution curves $P(r)/r$. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0{\cdot}003\,s^2)/(Z_{Si} - f_{Si})(Z_P - f_P)$

TABLE 3

Principal structural parameters of silyl and methyl phosphines (bond lengths in Å, angles in degrees)

	C–P	Si–P	C–P–C	Si–P–C
CH_3PH_2 [a]	1·856(3)			
$(CH_3)_2PH$ [a]	1·851(3)		99·2(0·6)	
$(CH_3)_3P$ [b]	1·845(3)		98·6(0·3)	
$(SiH_3)_3P$ [c]		2·248(3)		
SiH_3PH_2 [d]		2·249(3)		
SiH_3PHCH_3 [d]	1·857(4)	2·248(3)		101·2(0·7)
$SiH_3P(CH_3)_2$ [d]	1·850(3)	2·245(3)	100·8(1·2)	99·0(0·5)

[a] Ref. 11. [b] Ref. 2. [c] Ref. 1. [d] This work.

Ignoring solvation effects, the problem of acid–base behaviour reduces to the relative stability of positively

[13] C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Structure*, 1969, **4**, 215.

TABLE 4

Effect of silyl substitution in methylamines (bond lengths in Å, angles in degrees)

	C–N	Si–N	C–N–C	C–N–Si	Si–N–Si	Reference
$(CH_3)_3N$	1·454(2)		110·6(0·6)			4
$(CH_3)_2NH$	1·455(2)		111·8(0·6)			4
$(CH_3)_2NSiH_3$	1·462(4)	1·715(4)	111·1(1·2)	120·0(0·4)		*a*
CH_3NH_2	1·465(2)					*b*
$CH_3N(SiH_3)_2$	1·465(5)	1·726(3)		117·3(0·2)	125·4(0·4)	13
$(SiH_3)_2NH$		1·725(3)			127·7(0·1)	10
$(SiH_3)_3N$		1·734(2)			119·7(0·1)	3

[a] C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Structure*, 1970, **6**, 231. [b] H. K. Higginbotham and L. S. Bartell, *J. Chem. Phys.*, 1965, **42**, 1131.

and negatively charged species [say $(SiH_3)_2PH_2^+$ and $(CH_3)_2PH_2^+$ on the one hand, $(SiH_3)_2P^-$ on the other] as compared with the parent silyl- or methyl-phosphines. A Lewis acid-base adduct, *e.g.* $(CH_3)_3P,BF_3$ may also be regarded as carrying a partial positive charge on phosphorus. It is well known[14] that in molecular orbital formulations of chemical bonding, the largest bonding contributions are obtained when the relevant atomic orbitals are close together in energy (other things, *e.g.* the overlap and resonance integrals, being equal). We assume that the bonding in these molecules occurs primarily through the *p* orbitals on phosphorus and silicon or carbon. In the absence of other information, the binding energies of these *p* orbitals may be approximated by their valence-shell ionisation potentials, which are:[15] P, 10·48; Si, 8·15; C, 11·26 eV. If a phosphine behaves as a base, so that a partial positive charge is placed on the phosphorus atom, the binding energy of the phosphorus *p* orbitals will be increased (for example, the ionisation potential of P^+ is 19·65 eV).[16] Whatever the magnitude of this effect, it is clear that the energy matching of phosphorus 3*p* orbitals with silicon 3*p* orbitals will be less favourable, *i.e.* the formation of a cationic species is likely to be less favourable for a silylphosphine than it is for a methylphosphine. For the formation of an anionic species the converse is true; the binding energy of the phosphorus 3*p* orbitals will be somewhat decreased, a situation which will be more favourable for energy matching with the silicon 3*p* orbitals. If this qualitative argument were to be extended to any sort of semi-quantitative basis (*e.g.* extended Hückel MO calculations), some information on the molecular geometry of such species as $(SiH_3)_2P^-$ would be required. Such calculations seem to us to be of dubious significance at the present time, but we believe that the qualitative arguments offer a convincing explanation of the variation in chemical properties in these molecules. We can see no reason to suppose, either on structural or on chemical grounds, that the *d* orbitals in silylphosphines are, in Coulson's sense,[17] chemically significant.

We thank Professor D. W. J. Cruickshank and Dr. B. Beagley for the provision of experimental facilities, the Cambridge University Computer Laboratory for the provision of computing facilities, and the S.R.C. for a maintenance grant (to P. M. P.).

[1/1552 *Received, 25th August,* 1971]

[14] C. A. Coulson, 'Valence,' Oxford University Press, 1961, 2nd edn., pp. 74—76.

[15] V. I. Vedeneyev, L. V. Furvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, 'Bond Energies, Ionisation Potentials and Electron Affinities,' Edward Arnold, London, 1966.

[16] C. E. Moore, 'Atomic Energy Levels,' N.B.S. Circular 467, 1949.

[17] C. A. Coulson, *Nature*, 1969, **221**, 1106.