Molecular Structure of Dimethyl(trifluorosilyl)arsine

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The molecular structure of dimethyl(trifluorosilyl)arsine has been determined by gas-phase electron diffraction. The following geometric parameters (r_a values) have been obtained: r(As–Si) 2.334(9), r(As–C) 1.979(5), r(Si–F) 1.569(2), and r(C–H) 1.096(12) Å; FSiF 107.3(5), CAsC 97.5(2.8), and SiAsC 93.5(9)°. The bond shortening due to SiH_3–SiF_3 substitution is discussed.

In an electron-diffraction study of trifluorosilylphosphine, $PH_2(SiF_3)$,[1] the Si–P bond length was found to be considerably shorter than for all silylphosphines with known structures.[2] Although the presence of multiple bonding in the Si–P bond has been suggested,[3] a similar situation has been excluded in the case of the Si–As bond. In order to investigate whether the short Si–P bond in $PH_2(SiF_3)$ is a result of $(p \rightarrow d)$ π bonding, we have studied the bond length in a comparable arsenic compound. The Si–As bond distance in trifluorosilylarsine can give some information about the inductive influence of the SiF_3 group. In this article we report the molecular structure of $AsMe_2(SiF_3)$.

TABLE 1

Experimental conditions

Camera distance	θ_c/°C		10^5 Camera pressure	Exposure time	λ [a]	s-Range [b]
mm	sample	nozzle	Torr	min	Å	$Å^{-1}$
500	−20	20	1	1.0—1.7	0.049 22(1)	1.4—17.0
250	20	20	1.5	2.5—4.0	0.049 22(2)	7.0—30.0

[a] Electron wavelength. [b] $s = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle.

EXPERIMENTAL

Dimethyl(trifluorosilyl)arsine was prepared [4] by reaction of $SiBrF_3$ with $AsMe(SnMe_3)$. The sample was purified by repeated fractional condensation *in vacuo* and its purity was checked by i.r. and n.m.r. spectra.

The diffraction photographs were recorded with a Balzers Gasdiffractograph KD-G2 [5] at 500- and 250-mm camera distances. An inlet system made of glass was used to avoid decomposition of the sample. The experimental conditions are summarized in Table 1.† Unfortunately, the photographs for the short camera distance were not exposed sufficiently because the gas flow through the nozzle was too low in spite of the higher sample temperature. After completion of the experiment, the nozzle opening was found to be partly blocked by a small piece of glass from breakage of part of the inlet system when changing the camera distance. One plate at this camera distance could be used but only to an s value of 30 $Å^{-1}$.

Structure Determination.—The usual techniques [6] were used for data reduction and for obtaining the modified molecular intensities. The experimental and theoretical intensity functions for the final model (Table 2) are shown in Figure 1 together with the difference curve. Scattering amplitudes and phase shifts of ref. 7 were used for calculating the theoretical intensities. Analysis of the radial distribution function (Figure 2) resulted in preliminary values for bond lengths, bond angles, and mean-square amplitudes. Approximate agreement between experimental and theoretical radial distribution functions in the range $r > 3.1$ Å could be obtained only when the SiF_3 group was staggered with respect to the PMe_2 group. This molecular model was refined by a least-squares procedure based on the molecular intensity function.

TABLE 2

Results of least-squares refinement. The error limits are three times the standard deviations

(*a*) Independent geometric parameters (r_a values) and scale factors (r in Å, angles in °)

r(As–Si)	2.334(9)	CAsC	97.5 (2.8)
r(As–C)	1.979(5)	SiAsC	93.5 (9)
r(Si–F)	1.569(2)	HCH	109.5 (ass.)
r(C–H)	1.096(12)	R_{500}	0.86 ± 0.04
FSiF	107.3 (5)	R_{250}	1.04 ± 0.06

(*b*) Principal dependent interatomic distances (r_a/Å)

$F \cdots F$	2.527(6)	$C \cdots F_1$	3.384(31)
$C \cdots C$	2.976(66)	$C \cdots F_2$	3.658(24)
$Si \cdots C$	3.151(24)	$C \cdots F_3$	4.572(37)
$As \cdots F$	3.256(12)		

(*c*) Mean-square amplitudes (l/Å)

As–Si	0.081(7)	$F \cdots C_{long}$	0.140(41)
As–C	0.079(10)	$C \cdots C$	0.080 (ass.)
Si–F	0.045(6)	$As \cdots H$	0.120 (ass.)
C–H	0.071(11)	$Si \cdots H$	0.200 (ass.)
$F \cdots F$	0.068(9)	$F \cdots H$	0.250 (ass.)
$As \cdots F$	0.115(11)	$C \cdots H$	0.150 (ass.)
$Si \cdots C$	0.083(23)	$H \cdots H$	0.200 (ass.)
$F \cdots C_{short}$	0.393(98)		

ass. = assumed

A diagonal weight matrix and a constant interval of $\Delta s = 0.2$ $Å^{-1}$ for the entire range of s were used. The following assumptions for the molecular model were made: (*i*) C_{3v} symmetry for the SiF_3 group; (*ii*) C_{3v} symmetry for Me groups; (*iii*) angle HCH = 109.5°; (*iv*) methyl groups are eclipsed to each other with one hydrogen atom of each

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† 1 Torr = (101 325/760) Pa and 1 Å = 100 pm.

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group pointing away from the mirror plane; (*v*) no internal rotation for the SiF_3 group or the **Me groups**; and (*vi*) mean-square amplitudes for some similar interatomic distances were grouped together and some were assumed (see Table 2). With these assumptions, seven geometric parameters, nine mean-square amplitudes, and the scale factors for both camera distances, R_{500} and R_{250}, were refined simultaneously.

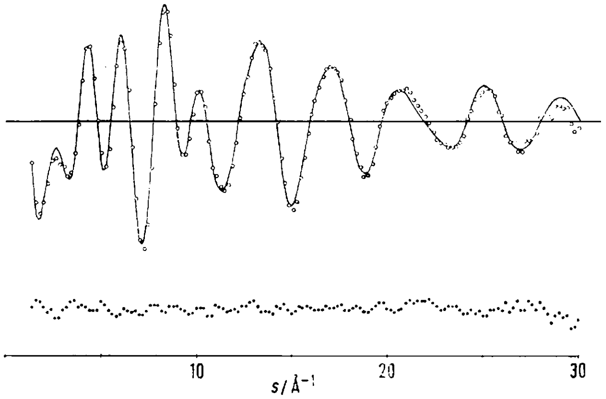

FIGURE 1 Modified molecular intensity functions: (○), experimental; (——), theoretical; (●), difference

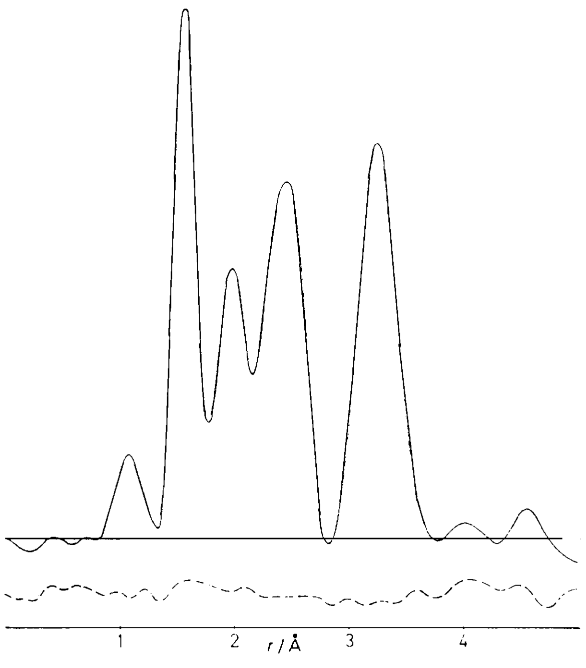

FIGURE 2 Radial distribution functions: (——), experimental; (— — —), difference between experimental and theoretical

Only three correlation coefficients c_{ij} were >0.75, *i.e.* $c[r(\text{As–Si}),\ l\ (\text{F}\cdots\text{F})] = 0.77$, $c[(\text{SiAsC}),\ l\ (\text{As}\cdots\text{F})] = 0.81$, and $c[l(\text{Si–F}),\ R_{250}] = 0.89$. The results of this least-squares analysis are given in Table 2. The large values for the mean-square amplitudes of the As–Si and As–C distances are not believed to indicate errors in the data, since for the Si–F amplitude a ' reasonable ' value is obtained [l(Si–F) = 0.043(2) Å for SiF_4] [8]. These large amplitudes are possibly a consequence of uncertainties in the phase shift of arsenic.

DISCUSSION

The structure parameters of $AsMe_2(SiF_3)$ are given in Table 2. Only the somewhat unexpected Si–As bond length needs to be discussed in some detail. The results for the Si–F and As–C bond distances and the bond angles at silicon and arsenic correspond to the respective values in similar compounds, such as $NMe_2(SiF_3)$ [r(Si–F) 1.567(6) Å, FSiF 105.0(9)],[9] $PH_2(SiF_3)$ [r(Si–F) 1.571(2) Å, FSiF 106.9(2)°],[1] and $AsMe_3$ [r(As–C) 1.98(2) Å, CAsC 96(5)°].[10]

The large mean-square amplitudes for the short non-bonded fluorine–carbon distances [$l(\text{F}\cdots\text{C})_{\text{short}}$ 0.393(98) Å] indicate that the torsional motion of the SiF_3 group around the As–Si bond is important, *i.e.* the potential barrier to internal rotation is low. Since the contribution of these F···C distances to the total molecular intensities is quite small (<5%), no attempt was made to determine this potential barrier from the electron-diffraction data. The neglect of internal rotation is the cause of part of the difference between the experimental and theoretical radial distribution functions in the range $r > 3.1$ Å.

Table 3 compares experimental Si–E bond lengths (E = O, N, P, or As) in silyl and trifluorosilyl compounds with the respective values calculated by the Schomaker–Stevenson equation.[11] Although the Schomaker–Stevenson approximation for estimating single bond lengths is insufficient due to various reasons, a semiquantitative discussion is possible on this basis. Since the structure of $AsMe_2(SiH_3)$ is not known, data for $As(SiH_3)_3$ are used for comparison. This seems to be justified since the Si–P bond lengths in $P(SiH_3)_3$ and $PMe_2(SiH_3)$ are equal within the error limits. The comparison of the Si–E bond lengths shows that in all cases the bond is shortened by substitution of SiH_3 by SiF_3 groups. In the case of

TABLE 3

Comparison of Si–E bond lengths (Å) (E = O, N, P, or As)

Compound	Ref.	r(Si–E)	Δ [a]	r_{SS} [b]	r_{SS} − r(Si–E)
$OMe(SiH_3)$	*c*	1.640 (3)	0.06	1.69	0.05
$OMe(SiF_3)$	*d*	1.580		1.69	0.11
$NMe_2(SiH_3)$	*e*	1.715 (4)	0.06	1.77	0.05
$NMe_2(SiF_3)$	9	1.654 (15)		1.77	0.12
$P(SiH_3)_3$	*f*	2.248 (3)		2.24	−0.01
$PH_2(SiH_3)$	2	2.249 (3)	0.04	2.24	−0.01
$PH_2(SiF_3)$	1	2.207 (3)		2.24	+0.03
$As(SiH_3)_3$	*g*	2.355 (1)	0.02	2.35	−0.01
$AsMe_2(SiF_3)$		2.334 (9)		2.35	+0.02

[a] $\Delta = r(\text{SiH}_3\text{–E}) - r(\text{SiF}_3\text{–E})$. [b] Schomaker–Stevenson distance given by $r_{AB} = r_A + r_B - 0.09|x_A - x_B|$ (r_A and r_B covalent radii, x_A and x_B electronegativities). [c] C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley, and J. M. Freeman, *J. Mol. Structure*, 1970, **5**, 417. [d] W. Airey, C. Glidewell, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Structure*, 1971, **8**, 413. [e] C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Structure*, 1970, **6**, 231. [f] B. Beagley, A. G. Robiette, and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1968, 3002. [g] B. Beagley, A. G. Robiette, and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1968, 3006.

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O and N, the decrease in the bond length is *ca.* 0.06 Å, whereas this effect is found to be smaller in phosphorus and arsenic compounds (0.04 and 0.02 Å respectively). If we assume that no $(p\rightarrow d)$ π bonding occurs in silylarsines, we must conclude on the basis of the reported data for $PH_2(SiF_3)$, that multiple bonding is not important also in the Si–P bond. Since the differences between the Schomaker–Stevenson values and the experimental bond distances are practically identical for P and As, it seems plausible to explain the bond strengthening only by an inductive effect of the SiF_3 group and not by π interaction. Glidewell *et al.*[2] pointed out that the low basicity of silyl-substituted phosphines (as compared to the alkyl analogues) does not necessarily arise from the interaction of the phosphorus lone pair with the Si 3*d* orbitals. Similarly, participation of the 3*d* orbitals in the Si–P bond is not the only explanation[12] for an increased ionization potential of the P lone pair.[13]

A comparison of the SiH_3–SiF_3 substitution effect with that of CH_3–CF_3 is of interest in the present discussion. Whereas the C–E bond is shortened in oxygen and nitrogen compounds on substitution of CH_3 by CF_3 groups, the same substitution causes an increase in this bond length in phosphorus and arsenic compounds. These bond changes are correlated with the electronegativity of the E atom:[14] substitution of CH_3 by CF_3 in EMe_n ($n = 2$ or 3, depending on E) results in a decrease of the C–E bond length if the electronegativity of E is larger than 2.5 (electronegativity of carbon), and the C–E bond length increases if the electronegativity of E is smaller than 2.5. If a similar correlation is applied to the SiH_3–SiF_3 systems, whereby in all cases the electronegativity of E is larger than that of Si, a shortening of the Si–E bond due to the inductive influence of the SiF_3 group should be observed. The experimental values are indeed in agreement with the expected bond shortening. Nevertheless, we consider this interpretation as a ‘ bond hypothesis ’, suggesting that the SiF_3 group has a similar inductive influence to the CF_3 group.

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