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AN ELECTRON DIFFRACTION DETERMINATION OF THE MOLECULAR STRUCTURES OF PERCHLORODISILOXANE AND METHOXYTRIFLUOROSILANE

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ABSTRACT

The molecular structures of $(Cl_3Si)_2O$ and F_3SiOCH_3 have been determined in the vapour phase by the sector microphotometer method of electron diffraction. For $(Cl_3Si)_2O$ a C_2 model with an "angle of twist" of 29° is preferred.

INTRODUCTION

Electron diffraction determinations have found angles at oxygen of 144±1° in disiloxane[1], $(H_3Si)_2O$, 156±2° in perfluorodisiloxane[2], $(F_3Si)_2O$, and 121±1° in methoxysilane[3], H_3SiOCH_3. Perchlorodisiloxane, $(Cl_3Si)_2O$, has been the subject of an electron diffraction study by the visual method[4], but the angle at oxygen was not determined. The small stereochemical effect of the oxygen "lone pairs" in compounds of this type has been interpreted[5] in terms of the delocalisation of these electrons into the vacant silicon *3d* orbitals. The presence of electronegative substituents on silicon might be expected to enhance this effect, widening the angle at oxygen and shortening the Si–O bond. As part of our systematic study of these stereochemical effects, we have determined the molecular dimensions of perchlorodisiloxane and methoxytrifluorosilane.

EXPERIMENTAL

Methoxytrifluorosilane was prepared by the fluorination of gaseous methoxytrichlorosilane with dry antimony trifluoride[6]. The crude product was purified by fractional condensation in vacuo, and the purity confirmed by IR spectroscopy and determination of the vapour density. Before the photographs were taken, the sample was pumped at −130° to remove traces of silicon tetrafluoride.

Perchlorodisiloxane was prepared by partial hydrolysis of silicon tetrachloride[7]; water was added dropwise to a well-stirred solution of silicon tetrachloride in diethyl ether at −78° ($H_2O : SiCl_4 : Et_2O = 1 : 4 : 4$), the volatiles distilled off and the fraction boiling at 130–135° collected (b.p. $(Cl_3Si)_2O$, 134°)[7]. The product was further purified by fractional condensation in vacuo, traces of silicon tetrachloride being removed by pumping on the sample at −78°. The purity was confirmed by IR spectroscopy and tensiometric measurements.

Intensities were recorded photographically on the Balzers' KD.G2 gas diffraction apparatus at University of Manchester Institute of Science and Technology[8], and transferred to punched paper tapes using an automated Joyce-Loebl microdensitometer. Calculations were performed using the Cambridge University "Titan" computer and our usual data reduction and least-squares refinement programs[9,10]. The weighting scheme, camera distances and s ranges employed are summarised in Tables 1 and 2. The wavelength of 0.05569±0.00005 Å was determined from the diffraction pattern of powdered thallium(I) chloride. The complex scattering factors of Cox and Bonham[11] were employed. All the distances are r_a[12], no corrections being applied for "shrinkage".

TABLE 1

ELEMENTS OF THE WEIGHT MATRIX

$w_{ii} = (s_i - s_{\min})/(s_1 - s_{\min})$	$s_{\min} \leqq s_i \leqq s_1$
$w_{ii} = 1$	$s_1 \leqq s_i \leqq s_2$
$w_{ii} = (s_{\max} - s_i)/(s_{\max} - s_2)$	$s_2 \leqq s_i \leqq s_{\max}$
$w_{ij} = 0$	$i \neq j \pm 1$
$w_{ij} = -0.5(w_{ii} + w_{jj})(p/h)_i$	$i = j \pm 1$

TABLE 2

WEIGHTING FUNCTIONS, CORRELATION PARAMETERS AND SCALE FACTORS

Molecule	*Height (cm)*	*del s*	s_{min}	s_1	s_2	s_{max}	p/h	k
$(Cl_3Si)_2O$	50	0.200	2.00	5.60	12.00	16.00	0.473	1.02±0.03
F_3SiOCH_3	100	0.100	0.80	2.50	6.50	7.80	0.499	0.73±0.02
F_3SiOCH_3	50	0.200	2.80	5.20	11.00	15.00	0.497	0.87±0.01
F_3SiOCH_3	25	0.400	5.20	10.00	20.00	30.00	0.466	0.92±0.02

REFINEMENT OF THE $(Cl_3Si)_2O$ STRUCTURE

The same geometrical model was employed for $(Cl_3Si)_2O$ as for $(F_3Si)_2O$ (ref. 2). It was assumed that the molecule retained a two-fold axis of symmetry, that all Si–Cl bond lengths were equal, that all Cl–Si–Cl angles were equal, and that the axes of the Cl_3Si groups lay in the Si–O–Si plane. The six independent parameters required to define the molecular dimensions were chosen as the Si–O and Si–Cl distances, the Si–O–Si and Cl–Si–Cl angles, an angle of "twist" and an angle of "tilt". A zero angle of twist corresponds to the C_{2v} conformation with four long and two short non-bonded Si · · · Cl distances; the $SiCl_3$– groups may be rotated in opposite directions from this conformation by the angle of twist, so that C_2 molecular symmetry is retained. The angle of tilt is defined as the angle in the Si–O–Si plane between the axis of the Cl_3Si– group and the Si–O bond direction, such that a positive tilt is in the direction away from the other Cl_3Si– group.

From the experimental radial distribution curve, $P(r)/r$, (Fig. 1), it can be seen that the Si–O and Si–Cl bond lengths are determined by well resolved maxima, but three parameters (the angles Cl–Si–Cl, Si–O–Si and the angle of tilt) are primarily determined by the double maximum in the region 2.8–3.5 Å. This leads to a strong correlation between the Si–O–Si angle and the angle of tilt, as shown in the correlation matrix. The remaining maxima correspond to non-bonded Si · · · Cl and Cl · · · Cl distances. The C_2 model reproduces these features satisfactorily with a well-defined angle of twist, 28.9±1.5°. The amplitudes of the three Cl · · · Cl distances which would be influenced most by torsional motion have been fixed at the fairly large value of 0.20 Å; the remaining three Cl · · · Cl amplitudes were constrained to be equal, and refined to 0.15±0.03 Å. Attempts to refine most of the amplitudes led to values with large estimated standard deviations, as a result of the limited s range covered by the data; they were therefore constrained as shown

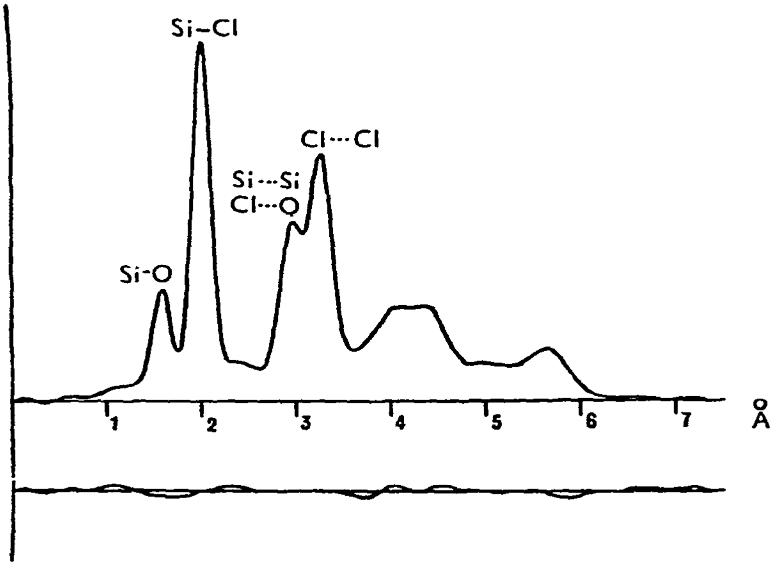

Fig. 1. Observed and difference radial distribution curve $P(r)/r$ for perchlorodisiloxane. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.0035\, s^2)/(Z_{Si}-f_{Si})(Z_O-f_O)$.

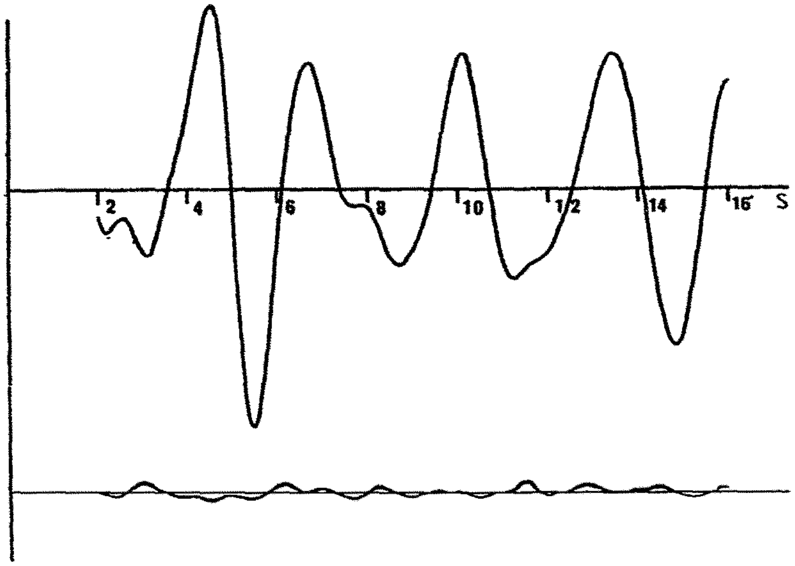

Fig. 2. Observed and weighted difference molecular intensity data for perchlorodisiloxane.

TABLE 3

MOLECULAR PARAMETERS FOR $(Cl_3Si)_2O$

(*a*) *Independent distances*

	Distance (*Å*)	*Amplitude* (*Å*)	*a* (*anharmonic constant*)
r 1 (Si–O)	1.592 ± 0.010	0.039 (fixed)	2.00
r 2 (Si–Cl)	2.011 ± 0.004	0.054 ± 0.007	2.00

(*b*) *Independent angles*

∠1 (Cl–Si–Cl)	109.3 ± 0.2°
∠2 (twist)	28.9 ± 1.5°
∠3 (tilt)	3 ± 3°
∠4 (Si–O–Si)	146 ± 4°

(*c*) *Dependent distances*

		Distance (*Å*)	*Amplitude* (*Å*)
d 1	(Si ··· Cl)	3.86 ± 0.03	0.19 (fixed)
d 2	(Si ··· Cl)	4.43 ± 0.05	0.16 ± 0.03
d 3	(Si ··· Cl)	4.16 ± 0.02	0.19 ± 0.06
d 4	(Cl ··· O)	3.01 ± 0.04	0.07 ± 0.03 (a)
d 5	(Cl ··· O)	2.90 ± 0.04	0.07 tied to (a)
d 6	(Cl ··· O)	2.95 ± 0.01	0.07 tied to (a)
d 7	(Cl ··· Cl)	4.01 ± 0.07	0.20 (fixed)
d 8	(Cl ··· Cl)	5.48 ± 0.07	0.15 ± 0.03 (b)
d 9	(Cl ··· Cl)	5.78 ± 0.03	0.15 tied to (b)
d 10	(Cl ··· Cl)	5.07 ± 0.04	0.20 (fixed)
d 11	(Cl ··· Cl)	4.41 ± 0.04	0.20 (fixed)
d 12	(Cl ··· Cl)	5.71 ± 0.02	0.15 tied to (b)
d 13	(Cl ··· Cl)	3.28 ± 0.01	0.08 ± 0.01
d 14	(Si ··· Si)	3.04 ± 0.03	0.09 (fixed)

in Table 3. The standard deviations given in Table 3 have been increased to allow for possible systematic errors, and for the effects of the strong correlation between the Si–O–Si angle and the angle of tilt; a small positive angle of tilt does not seem unreasonable. The resulting estimated standard deviations were approximately double the values obtained, by the usual least-squares procedure, for the random errors alone.

The refinement converged to an index $R_G = (U'WU/I'WI)^{\frac{1}{2}} = 0.089$ and $R_D = (\sum w_{jj}U_j^2/\sum w_{jj}I_j^2)^{\frac{1}{2}} = 0.063$, where I is the vector of intensities, U the vector of residuals and W the weight matrix with elements w_{jk}.

TABLE 4

LEAST SQUARES CORRELATION MATRIX FOR $(Cl_3Si)_2O$ MULTIPLIED BY 1000

r 1	*r 2*	*∠1*	*∠2*	*∠3*	*∠4*	*u 2*	*u 4*	*u 5*	*u 6*	*u 10*	*u 15*	*k 1*
1000	−124	454	66	510	−624	−427	−9	88	−542	−154	−182	−247
−124	1000	−669	−29	220	−293	−38	−37	−2	−193	−41	−185	−100
454	−669	1000	116	−193	195	−3	116	33	209	82	222	162
66	−29	116	1000	24	6	−36	621	774	22	−287	106	−14
510	220	−193	24	1000	−938	−231	23	376	−824	−472	−27	−94
−624	−293	195	6	−938	1000	269	28	−263	799	318	116	121
−427	−38	−3	−36	−231	269	1000	173	67	380	228	460	755
−9	−37	116	621	23	28	173	1000	712	82	−148	246	258
88	−2	33	774	376	−263	67	712	1000	−200	−401	252	169
−542	−193	209	22	−824	799	380	82	−200	1000	419	439	362
−154	−41	82	−287	−472	318	228	−148	−401	419	1000	42	238
−182	−185	222	106	−27	116	460	246	252	439	42	1000	646
−247	−100	162	−14	−94	121	755	258	169	362	238	646	1000

REFINEMENT OF THE F_3SiOCH_3 STRUCTURE

Non-bonded distances through two or three angles contribute relatively little to the total molecular scattering for F_3SiOCH_3, so a simple conformation was assumed in which the above angles of "twist" and "tilt" are zero. The F_3Si– and H_3C– groups were assumed to lie on local three-fold axes of symmetry along the Si–O and C–O directions respectively, with the Si–F and C–H bonds staggered with respect to the O–C and O–Si bonds respectively. There were thus four short and two long F · · · H distances, so that the molecule retained a plane of symmetry. The independent geometrical parameters were chosen as the Si–F, Si–O, C–O and C–H distances and the Si–O–C and F–Si–F angles, the H–C–H angle being fixed at the tetrahedral value in most of the refinements.

In the radial distribution function, $P(r)/r$, (Fig. 3), the C–O, Si–O and Si–F distances contribute to a single peak, making it difficult to refine these three distances and their associated amplitudes simultaneously. In most of the refinements, the Si–O distance was fixed at the value (1.58 Å) found in $(F_3Si)_2O$ (the difference between the values in H_3SiOCH_3 (1.640) and $(H_3Si)_2O$ (1.634) is barely significant); the Si–F amplitudes were constrained to be equal, and the C–O amplitude was fixed at 0.050 Å. A similar problem arises because the Si · · · C, F · · · O and F · · · F contributions overlap to form a composite peak in $P(r)/r$; it was found necessary to constrain the O · · · F and F · · · F amplitudes to be equal, and to fix the Si · · · C amplitude at 0.130 Å. All the amplitudes involving hydrogen were fixed at typical values.

Under these conditions the refinement converged to the parameter values given in Table 5, the reliability indices being $R_G = 0.097$ and $R_D = 0.059$. These parameters were used to calculate the difference curves given in Figs. 3 and 4.

TABLE 5

MOLECULAR PARAMETERS FOR F_3SiOCH_3

(a) *Independent distances*

		Distance (Å)	*Amplitude (Å)*	*a (anharmonic constant)*
r 1	(Si–O)	1.580 (fixed)	0.055±0.003 (a)	2.00
r 2	(C–O)	1.392±0.015	0.050 (fixed)	2.00
r 3	(Si–F)	1.559±0.006	0.055 tied to (a)	2.00
r 4	(C–H)	1.109±0.025	0.075 (fixed)	2.00

(b) *Independent angles*

∠1	(Si–O–C)	131.4±3.2°
∠2	(F–Si–F)	108.2±1.6°
∠3	(H–C–H)	109.5° (fixed)

(c) *Dependent distances*

		Distance (Å)	*Amplitude (Å)*
d 1	(Si · · · C)	2.71±0.04	0.130 (fixed)
d 2	(O · · · F)	2.58±0.03	0.086±0.020 (b)
d 3	(O · · · H)	2.05±0.03	0.125 (fixed)
d 4	(Si · · · H)	3.59±0.03	0.150 (fixed)
d 5	(Si · · · H)	3.02±0.04	0.150 (fixed)
d 6	(C . . . F)	3.32±0.03	0.162±0.020
d 7	(C · · · F)	3.95±0.02	0.087±0.020
d 8	(F · · · H)	4.58±0.05	0.180 (fixed)
d 9	(F · · · H)	3.05±0.05	0.180 (fixed)
d 10	(F · · · H)	3.74±0.04	0.180 (fixed)
d 11	(F · · · H)	4.27±0.04	0.180 (fixed)
d 12	(F · · · H)	4.36±0.03	0.180 (fixed)
d 13	(F · · · F)	2.53±0.03	0.086 tied to (b)
d 14	(H · · · H)	1.81±0.06	0.120 (fixed)

(d) *Dependent angles*

∠4	(F–Si–O)	110.7±1.3°
∠5	(H–C–O)	109.5° (fixed)

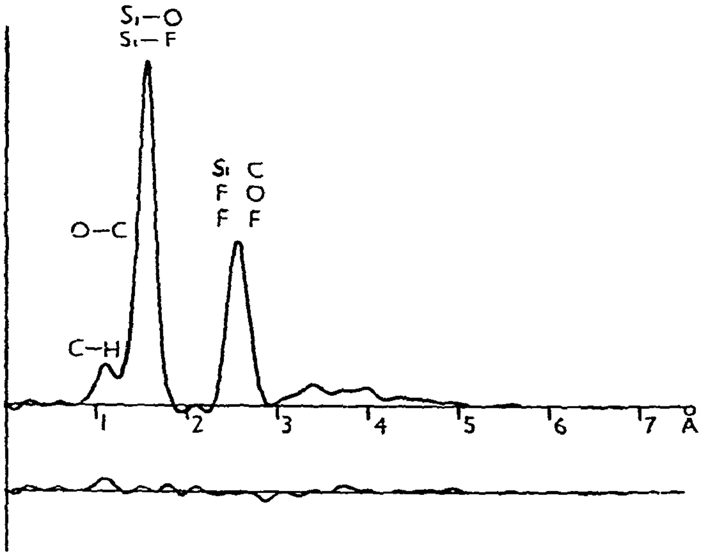

Fig. 3. Observed and difference radial distribution curve $P(r)/r$ for methoxytrifluorosilane. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.0020\, s^2)/(Z_{Si}-f_{Si})(Z_F-f_F)$.

Further refinements were performed to obtain estimates of the errors introduced by the various constraints; in particular, refinements were performed for Si–O distances of 1.56, 1.57, $\cdots$, 1.61 Å. The C–O bond length was found to be remarkably insensitive to the value assumed for the Si–O bond length, changing by only 0.002 Å over the above range. The Si–O–C angle varied from 133 to 128°. Higher values of the Si–O bond length led to rather low values of the F–Si–F angle, e.g.: Si–O = 1.60 Å, angle F–Si–F = 107.2° (cf. 108.8±0.5° in $(F_3Si)_2O$), $u(F \cdots F) = u(F \cdots O) = 0.071$ Å, u(Si–O) = 0.052 and Si–F = 1.555 Å. These results lead us to give some preference to the Si–O length of 1.58 Å. The estimated standard

TABLE 6

LEAST SQUARES CORRELATION MATRIX FOR F_3SiOCH_3 MULTIPLIED BY 1000

r 2	*r 3*	*r 4*	*∠1*	*∠2*	*u 1*	*u 6*	*u 10*	*u 11*	*k 1*	*k 2*	*k 3*
1000	441	303	−431	−211	−177	−353	−109	−41	−158	−350	−458
441	1000	290	−521	−560	−81	−552	−45	−47	−135	−237	−231
303	290	1000	−120	−162	46	−184	30	28	−70	−38	−7
−431	−521	−120	1000	777	172	672	193	61	150	312	306
−211	−560	−162	777	1000	115	897	51	87	139	235	185
−177	−81	46	172	115	1000	280	155	52	152	361	714
−353	−552	−184	672	897	280	1000	56	103	202	374	418
−109	−45	30	193	51	155	56	1000	−132	3	133	214
−41	−47	28	61	87	52	103	−132	1000	14	54	74
−158	−135	−70	150	139	152	202	3	14	1000	202	180
−350	−237	−38	312	235	361	374	133	54	202	1000	421
−458	−231	−7	306	185	714	418	214	74	180	421	1000

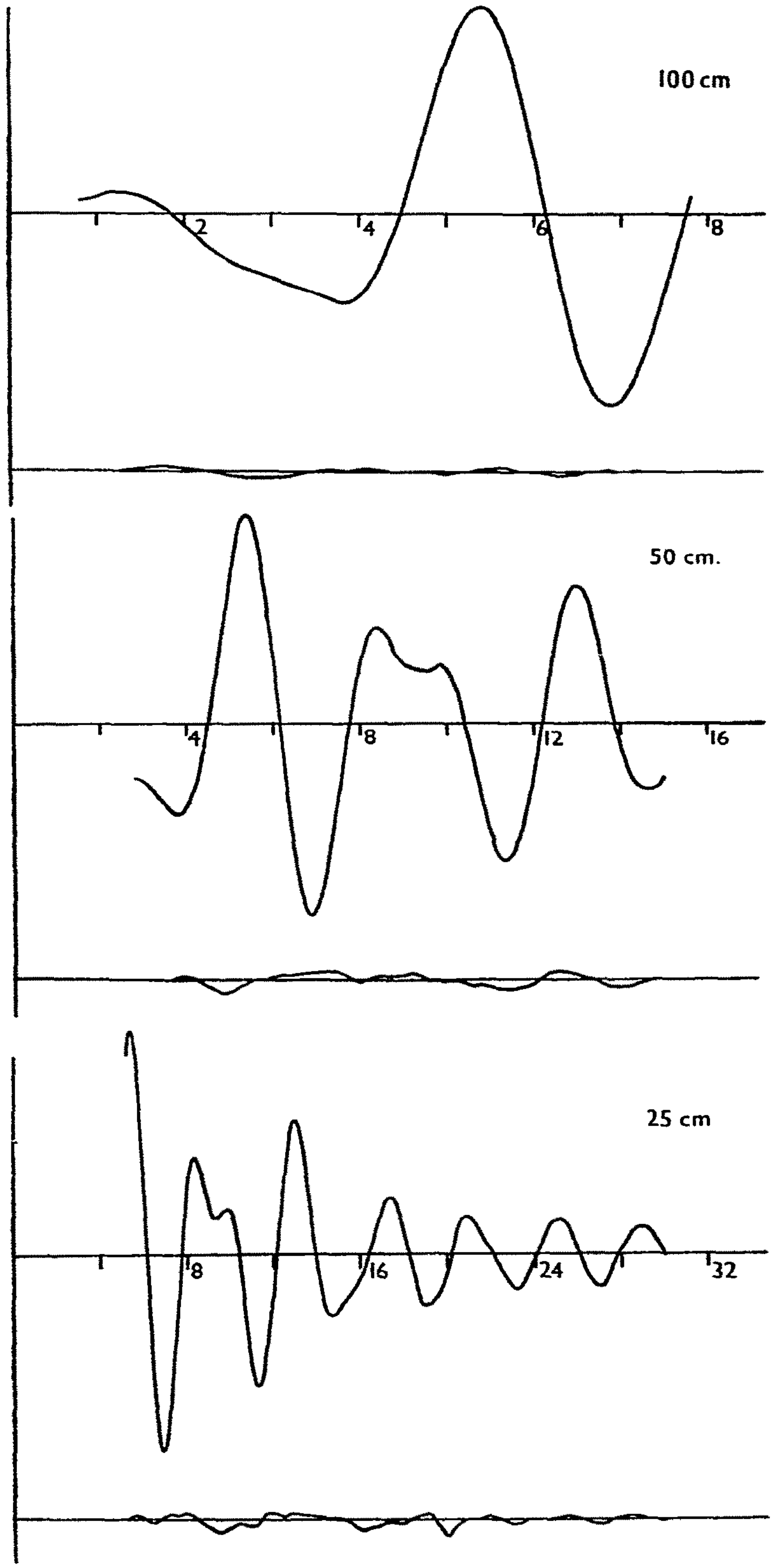

Fig. 4. Observed and weighted difference molecular intensity data for methoxytrifluorosilane.

deviations given in Table 5 include the least-squares estimates of random errors plus estimates of possible errors introduced by the various constraints.

DISCUSSION

A number of Si–O bond lengths and valence angles at oxygen are summarised in Table 7. The apparent angles determined by electron diffraction are likely to be too small because no allowance has been made for shrinkage[13,14]. The shrinkage correction may well be substantial here, since there is the possibility of low frequency large amplitude deformations at oxygen. The frequency of the Si–O–Si deformation in $(H_3Si)_2O$ has been reported[15] as 68 cm^{-1}. The Si–O–Si angle in $(Cl_3Si)_2O$ is not significantly different from the value in $(H_3Si)_2O$; both are smaller than that in $(F_3Si)_2O$. The Si–O–C angle in F_3SiOCH_3 is somewhat greater than that in H_3SiOCH_3. These results are not inconsistent with the concept of delocalisation of electrons of π-symmetry into the vacant silicon 3*d* orbitals, since the 3*d* orbitals will tend to contract and become lower in energy as the effective nuclear charge on silicon is increased by σ-withdrawing substituents.

TABLE 7

Si–O BOND LENGTHS AND VALENCE ANGLES AT OXYGEN

Molecule	r_a(*Si–O*)	r_a(*C–O*)	*Angle M–O–M'*	*Reference*
$(H_3C)_2O$	—	1.416±0.003	111.5±1.5	16
$(H_3Si)_2O$	1.634±0.002	—	144.1±0.9	1
$(Cl_3Si)_2O$	1.592±0.010	—	146 ±4	this work
$(F_3Si)_2O$	1.580±0.025	—	155.7±2.0	2
H_3SiOCH_3	1.640±0.003	1.418±0.009	120.6±0.9	3
F_3SiOCH_3	1.58 (assumed)	1.392±0.015	131.4±3.2	this work

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