Electron Diffraction Investigation on the Molecular Structures of Some Organosilicon Compounds. II

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The results of studies on the molecular structures of several organosilicon compounds as revealed by electron diffraction experiments are described in part I of this report. The results obtained are discussed below.

(1) Silicon-halogen Bond.—A number of compounds containing silicon-halogen bond have been investigated by electron diffraction and by microwave spectroscopy. The data on silicon-halogen bonds which have hitherto been determined are listed in Table 1 together with those of the present study. According to our finding, the distance between silicon and halogen

TABLE I

Compounds	By Electron Diffraction	By Microwave Spectroscopy	Reference
	(Si-F length (Å))		
SiF_4	1.54±0.02		3
$HSiF_3$		1.565±0.005	4
H_3SiF		1.593, 1.595±0.010	5, 4
$(CH_3)_3SiF$	1.57±0.02		6
	(Si-Cl length (Å))		
$SiCl_4$	2.01±0.02		7
$HSiCl_3$	2.01±0.03	2.021±0.002	8, 9
H_2SiCl_2	2.02±0.03		10
H_3SiCl	2.06±0.05	2.0479±0.0007, 2.048	10, 4, 9
$(CH_3)SiCl_3$	2.01±0.02	2.021	11, 9
$(CH_3)_2SiCl_2$	1.99±0.03		11
$(CH_3)_3SiCl$	2.09±0.03	2.03	12, 9
$(CH_3)_2SiClF$	2.03±0.03		6
F_3SiCl	2.01±0.02		10
	(Si-Br length (Å))		
$SiBr_4$	2.15±0.02		1
$HSiBr_3$	2.16±0.03		1
H_3SiBr		2.209±0.001	2
$(CH_3)SiBr_3$	2.17±0.03		Present work
$(CH_3)_2SiBr_2$	2.21±0.03		Present work
$(CH_3)_3SiBr$	2.21±0.03		Present work
F_2SiBr		2.16±0.02	5
F_3SiBr		2.147	5

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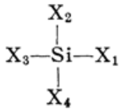
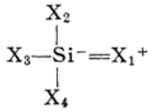
is not affected when hydrogen atoms of halogenosilane are replaced by methyl radicals. For example, The Si-Br lengths of $(CH_3)SiBr_3$ and $(CH_3)_3SiBr$ agree with these of $HSiBr_3$[1)] and H_3SiBr[2)]. On the other hand, these bond lengths vary when the number of halogen atoms attached to silicon is altered.

In general, silion-halogen distance of the derivatives of monohalogenosilane is longer by 0.03–0.06 Å than that of respective tetrahalogenosilane. The sum of Pauling-Huggins atomic radii[13)] is longer than the observed lengths, as is also the length calculated from Schomaker-Stevenson's rule[14)]. The double bond character of silicon-halogen bond and the change of character with the number of substituents provide an explanation of these facts[13)]. A reasonable representation of the ground electronic state of these molecule is a resonance hybrid of the forms a, b and c.



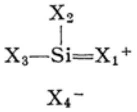
$$X_3{-}\overset{X_2}{\underset{X_4}{Si}}{-}X_1$$

(a)



$$X_3{-}\overset{X_2}{\underset{X_4}{Si^-}}{=}X_1^+$$

(b)



$$X_3{-}\overset{X_2}{Si}{=}X_1^+ \quad X_4^-$$

(c)

The structure b implies the double bond formation with the use of 3d orbital of silicon. When the number of halogen atoms attached to silicon is more than one, the contribution of the structure c becomes large. This may explain the change of the bond length with the number of substituents.

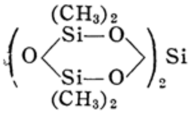
(2) **Silicon-carbon Bond.** — Available date on the bond length of Si–C are listed in Table II. These date agree with a value of 1.88 Å within an error of 0.03 Å. Bond and Brockway[15)], however, they have recently shown in their electron diffraction investigation using a sector on $Si(CH_3)_nH_{4-n}$ (n=1, 2 and 3) that Si–C length increased by about 0.01 Å with the introduction of each successive methyl radical. The bound length between silicon and aromatic carbon agress with that of

TABLE II

Compounds	Si-C Length (Å)	Reference
$Si(CH_3)_4$	1.888±0.02	16
$Si_2(CH_3)_6$	1.90 ±0.02	17
$HSi(CH_3)_3$	1.873±0.006	15
$H_2Si(CH_3)_2$	1.860±0.004	15
$H_3Si(CH_3)$	1.857±0·007	15
$(CH_3)_3SiF$	1.89 ±0.02	6
$(CH_3)_2SiClF$	1.89 ±0.02	6
$(CH_3)_3SiCl$	1.89 ±0.03, 1.87	12, 9
$(CH_3)SiCl_3$	1.876	9
$(CH_3)_3SiCH_2Cl$	1.88 ±0.04	18
$(CH_3)_3SiBr$	1.86 ±0.05	Present work
$((CH_3)_2SiO)_3$	1.86 ±0.04	19
$((CH_3)_3Si)_2O$	1.88 ±0.03	Present work
$Si(C_6H_5)_4$	1.87 ±0.03	Present work

TABLE III

MOLECULAR STRUCTURES OF SILOXANES

Compounds	Si-O (Å)	Si-C (Å)	∠Si-O-Si	∠O-Si-O	∠C-Si-C	Reference
$((CH_3)_3Si)_2O$	1.63±0.05	1.88±0.03	130±10°	—	114±4°	Present work
$((CH_3)_2SiO)_3$	1.66±0.04	1.86±0.04	125±5	115±5°	112±6	19
	1.64±0.03	1.88±0.03	130±4	109±4	109±4	21*
$((CH_3)_2SiO)_4$	1.63	1.88	140±5	109.5 (assumed)	109.5 (assumed)	Present work
$((CH_3)_2SiO)_4$	1.65	1.92	142.5	109	106	22*
$((CH_3)_3SiO)_4Si$	1.63	1.88	140±5	109.5 (assumed)	112±4	Present work
$(CH_3O)_4Si$	1.64±0.03	—	113±2(∠Si-O-C)			Present work

* Data from X-ray crystal analysis

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silicon and carbon in methyl radical within 0.03 Å. The bond angle of C–Si–C of trimethylsilyl group, $-Si(CH_3)_3$, is approximately tetrahedral, and somewhat larger values are obtained in certain compounds such as: $(CH_3)_3SiCl$ (113±2°), $(CH_3)_3SiBr$ (114±4°) and $Si(OSi(CH_3)_3)_4$ (112±4°).

(3) Silicon-oxygen Bond.—Silicon-oxygen bond is an important one which builds up the framework of both inorganic silicates and organosilicon polymers. The nolecular structures of organic compounds containing Si–O bond are summarized in Table 3. The Si–O lengths obtained for organosilicon compounds agree without exception with 1.64 Å. Smith⁽20⁾ deduced a value of 1.60±0.01 Å for Si–O length by reviewing the obtainable deta on various inorganic silicates and aluminosilicates. Introduction of methyl radical may increase Si–O length somewhat.

The valence angle of the oxygen atom in Si–O–C linkage, 112±3°, obtained for $(CH_3O)_4Si$ is in agreement with that in C–O–C linkage of methyl ether[23]. On the other hand, the angle Si–O–Si has a larger value, 130±10° in $((CH_3)_3Si)_2O$, 125±5° in $((CH_3)_2SiO)_3$, and 140±5° in $((CH_3)_2SiO)_4$ and $((CH_3)_3SiO)_4Si$. Since there may be a strain causing distortion in the ring structure of $((CH_3)_2SiO_3)$, a value of about 140° seems to be normal. The values of Si–O–Si angle reported for α–quartz and for α–cristobalite are 142°[24] and 150°[25] respectively. These values are consistent with those of organic siloxanes. It may be said, therefore, that Si–O–Si chain in organic siloxanes has a geometrical structure similar to that in inorganic silicates.

Smyth and Holland[26] studied the dielectric properties of hexamethyldisiloxane in detail over a wide range of temperature and discussed the properties of Si–O bond. They calculated a dipole moment of 0.66 D in the vapor phase, and of 0.46 D in the pure liquid. The atomic polarization was determined to be 7.9 cc. There were large discrepancies between the values of the group moment of $(CH_3)_3SiO$. Assuming Si–O–Si angle to be 130°, calculation from the observed moment gave 0.54 D (liquid) and 0.78 D (vapor), while a group moment 1.6–2.0 D was obtained from an approximate formula relating ionic character of the bond to electronegativity difference. These data were considered to be consistent with a valence angle of oxygen greater than 130°. However silicon has the ability to expand its 3d orbital and to form a partial double bond with more electronegative elements. Kurita and Kondo[27], assuming Si–O–Si angle to be 130°, showed that there was a fairly good agreement between a bond moment 1.55 D of Si–O calculated from the dipole moment data of hexamethyldisiloxane and a value of 1.1 D obtained by the Pauling's method[28], which permitted us to calculate the degrees of the double bond character and the ionic character of bonds in oxy-acid molecules.

(4) Cyclic Compound Containing Silicon Atoms as Ring Members.—Dimethylcyclopolysiloxane, dimethylcyclopolysilazane and dimethylcyclopolysilthiane can be prepared by treating dimethyldichlorosilane with water, ammonia and hydrogen sulfide respectively.

As regards the trimer of cyclosiloxane, electron diffraction data[19] indicated that the six-membered ring is planar. The trimer can be prepared by the cracking of dimethylpolysiloxanes, while the hydrolysis product of dimethyldichlorosilane contains only a small amount of the trimer[29]. Scott[30] investigated the redistribution equilibrium between dimethylcyclopolysiloxanes and linear polysiloxanes catalyzed by sulfuric acid. He concluded that the ring having the smallest number of members of cyclic polysiloxane, as in the trimer in this case, had a slight strain, while the ring structures of the tetramer or the polymer of larger size were probably free from strain. He attributed this strain to the deformation of normally large Si–O–Si angle in forming a small membered ring. Actually the difference between the molecular structure of the trimer and that of the tetramer exists in the Si–O–Si angle, which is 125° for the trimer and 140° for the tetramer. It is likely that a strain free Si–O–Si angle takes a probable value of about 140° and is easily deformable by intra- and intermolecular forces.

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As regards the silthiane compounds, dimethylsubstituted polymers having a ring larger than that of the trimer have not yet been isolated. When the cyclic trimer is heated at about 200° under atomospheric pressure, the dimer is distilled. In this case, the valence angle of sulfur atom should have been deformed from about 110° in the trimer to about 75° in the dimer. The ring structure of the dimer is similar to that of silicon disulfide, in which successive SiS_4 tetrahedrons are joined with a common edge leading to a fibrous frame extending in one dimension. This structure of silicon disulfide have been interpreted as an ionic packing of Si^{4+} and S^{2-} whose ionic radii ratio has a certain critical value, at which the change in coordination number four to three may be expected to occur. The Si–S bond of tetramethylcyclodisilthiane is supposed to have as large ionic character as that of silicon disulfide.

Brewer and Haber[31] studied the rearrangement equilibrium between linear and cyclic dimethylpolysilazanes at high temperature under high pressure. They found that the tendency of ring formation is greater in the silazane than in the corresponding siloxane systems. The rings of both the trimer and the tetramer of dimethylcyclopolysilazane have puckered structures. The difference between the valence angles of the nitrogen atom in the trimer and the tetramer may be due to the steric repulsion of methyl radicals.

In Table IV, comparison is made of the observed bond lengths of silicon and other electronegative elements with the sums of Pauling-Huggins radii and with the values calculated from Schomaker-Stevenson's rule.

TABLE IV

Bond	Obs.	Bond Length (Å) Calcd. after Pauling-Huggins	 Calcd. after Schomaker-Stevenson	Electronegativity Difference
Si–C	1.88	1.94	1.88	0.7
Si–N	1.73[32], 1.78	1.87	1.80	1.2
Si–O	1.63	1.83	1.76	1.7
Si–F	1.54–1.60[3,4]	1.81	1.69	2.2
Si–S	2.15–2.18	2.21	2.15	0.7
Si–Cl	2.00–2.02	2.16	2.15	1.2
Si–Br	2.17–2.21	2.31	2.22	1.0

In general, with increasing electronegativity difference, the difference increases between the calculated bond lengths and observed ones. Among these values, the contraction is remarkable for the most polar Si–O and Si–F bonds. This may indicate the presence of either one or both of the following causes; 1) larger ionic character of the bond than is suggested by the electronegativity difference, 2) partial double bond character arising from resonance. Craig et al.[33] discussed this problem in detail, and were led to the conclusion that presumably $d\pi-p\pi$ bonding is a common one giving rise to a strong bond and that the polar character in σ-bonds can give extra stability by increasing the $d\pi-p\pi$ overlap.

Summary

The vapors of methyl or ethyl substituted silicon compounds containing Si–Cl, Si–Br, Si–O, Si–N and Si–S bonds were studied by electron diffraction method and their molecular structures were determined. Bond lengths obtained are summarized in Table IV. The Si–Br length in methylbromosilane series changes with the number of substitutions of Br, but the length is in accord with the data of corresponding bromosilanes. The valence angles of oxygen in linear and cyclic siloxanes were estimated to be about 140° and this value is nearly the same as that in α-quartz. The valence angles of silicon in cyclic compounds are almost tetrahedral and those of oxygen, nitrogen and sulfur vary with the size of the ring.

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