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The Siloxane Bond and Its Influence on the Structure and Physical Properties of Organosilicon Compounds

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The main characteristics of the structure of the siloxane bond are examined and the results of studies on the structures and properties of oxygen-containing silicon compounds by physical methods are reviewed.
The bibliography includes 405 references.

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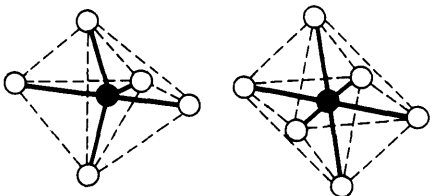
I. INTRODUCTION

Polymeric organic and inorganic silicon compounds have found recently a wide variety of numerous practical applications. The valuable properties of these compounds, the microstructure of which is based on alternating silicon and oxygen atoms, are due primarily to the nature of the siloxane bond $\geq$Si—O† in all silicon(IV) compounds. This bond is formed as a result of σ coupling of the hybridised s and p electrons of the silicon atom with the p electrons of oxygen; there is then the additional possibility of π interaction between the unshared p electrons of the oxygen atom and the $3d$ orbitals of silicon, which has been called p_π—d_π or $(p \rightarrow d)_\pi$ coupling.

The formation by s and p electrons of four tetrahedral σ bonds involving the silicon atom makes the latter similar to its immediate neighbour in the Periodic System—carbon. However, the possibility of $(p \rightarrow d)_\pi$ bonding introduces sharp differences between the structures and properties of the corresponding silicon and carbon compounds, Silicon, an element of the Third Period, has free $3d$ orbitals corresponding to the M shell and is therefore capable of functioning as an electron acceptor in the formation of a donor—acceptor d_π—p_π bond. However, research on organosilicon compounds in the course of more than 100 years has shown that at normal temperatures silicon does not form multiple p_π—p_π bonds.

Since, in contract to the p orbitals, not all the $3d$ orbitals have the same form and relative orientation in space, more than two d orbitals of the silicon atom cannot be used in its combination with the atoms of other elements, probably because of geometrical factors[2-4]. As a result, the maximum coordination number of silicon is six[4]. In hexacoordinate complexes the silicon atom has $3sp^3d^2$-hybridised orbitals and in pentacoordinate complexes it has $3sp^3d$-hybridised orbitals.

The angular functions of the d orbitals enable silicon to form a wide variety of σ and π bonds with other elements. However, according to quantum-chemical calculations the d orbitals in the free atoms of elements in the Third Period are too diffuse for the formation of σ bonds. Such bonds can be formed only when there are electronegative substituents at the silicon atom in the molecule, which can increase its effective positive charge. The $3d$ orbital is then compressed and becomes of comparable size to the $3s$ and $3p$ orbitals[2-4]. Of the five d orbitals only the d_γ orbitals ($3d_{z^2}$ and $3d_{x^2+y^2}$) can be used for the formation of σ bonds. Their hybridisation with the $3s$ and $3p$ orbitals can lead to several structures. The bipyramidal form (I), characteristic of the complexes of pentacovalent silicon, is stabilised by the hybridisation of the s and p orbitals with the d_{z^2} orbital[5]. The octahedral structure (II) is characteristic of the coordination compounds of hexacovalent silicon[5,6].



(I) (II)

The d_ϵ orbitals ($3d_{xz}$, $3d_{yz}$, and $3d_{xy}$) are involved in d_π—p_π bonding. In contrast to the p_π—p_π bond, this type of multiple bond does not prevent free rotation about the σ bond. A consequence of this is the relatively high freedom of rotation about the siloxane bond.

Numerous pieces of physical evidence for the occurrence of the $(p \rightarrow d)_\pi$ interaction between the silicon and oxygen atoms joined by the siloxane bond are considered below. The wide variety of the reactions involving the cleavage of the Si—O bond, related in one way or another to its $(p \rightarrow d)_\pi$ character, are of independent interest and are not considered in this review.

† The term "siloxane bond" was introduced into the nomenclature of organosilicon compounds by Stock[1] in 1917 to designate the linkage between the silicon and oxygen atoms. It is present in all silicon compounds of the type $\geq$Si—O—R, where R = —Si$\geq$H, a hydrocarbon group acyl group, metal, etc.

II. STRUCTURAL AND PHYSICAL CHARACTERISTICS OF THE SILOXANE BOND

1. Interatomic Distances and Valence Angles

The Si—O bond lengths and SiOR valence angles in organic siloxanes are listed in Table 1. According to the tabulated data, the Si—O bond length is 1.64 ± 0.03 Å in the vast majority of organic silicon derivatives. This value is much lower than the Si—O bond length calculated assuming the additivity of the atomic radii (1.83 Å; the atomic radii of silicon and oxygen are 1.17 and 0.66 Å respectively)[56].

Table 1.

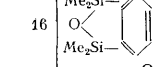
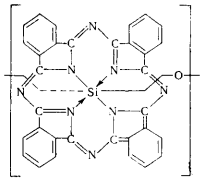
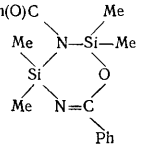
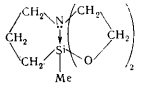
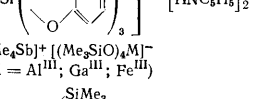
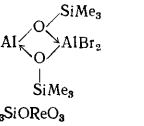
No.	Formula	Si-O bond length, Å	SiOR angle, deg	Method of determination	References
1	2	3	4	5	6
1	$(H_3Si)_2O$	1.633±0.001	144±1	—	7
		1.634±0.002	144.1±0.8	e	8
		—	~180	sp	9
		—	135—155	sp	10
		—	<180	sp	11
2	$(D_3Si)_2O$	—	~180	sp	9
3	$(Me_3Si)_2O$	—	140	sp	12
		—	137±7	sp	13
		1.65—1.66	130	x	14
		1.63±0.03	130±10	e	15
		1.63±0.05	130±10	e	16
		—	148	sp	17
4	$(Cl_3Si)_2O$	1.64±0.03	—	e	15, 16
		—	160—170	sp	18
5	$(F_3Si)_2O$	1.58±0.03	155.7	e	19
6	$Si(OSiMe_3)_4$	1.63	140±5	e	16, 20
7	$R(R_2SiO)_4SiR_3$ (R = Me, Et)	1.65—1.66	130	x	14
8	$H(Me_2SiO)_nOH$ ($n \geqslant 1000$)	1.64	130	x	21
9	Rubber based on polydimethylsiloxane raw rubber	—	140±10	x	22
10	$(Me_2SiO)_3$	1.66±0.04	125±5	e	23, 24
11	$O(Me_2SiO)_2Si(OSiMe_2)_2O$	1.64±0.03	130±5	x	25
12	$(Et_2SiO)_3$	1.65	125	x	14
13	$Me_2SiCH_2Si(RR')CH_2SiMe_2$ (R', R' = Me, Et, Ph)	—	125	sp	26
14	$Me_2Si(CH_2)_2Si(Me)R$ (R = Me, Pr, Bu, Ph)	—	120	sp	26
15	$Me_2SiCH_2—N(CH_2CH_2X)(CH_2SiMe_2)$ (X = NH_2, $NHCH_2CH_2NH_2$, OH)	—	110—115	sp	27
16		—	105	sp	26
17	$Me(Ph)SiCHCHSi(Ph)Me$ (R = H, Ph)	—	105	sp	26
18	$(Me_2SiO)_4$	1.66	140	x	14
		1.65	142.5	e	20
		1.63	140±5	e	28
19	$(Et_2SiO)_4$	1.66	140	x	14
20	$(Me_2SiO)_5$	1.66	145	x	14
21	$(Me_2SiO)_8$	—	—	x	29
22	$Me_8Si_8O_8$	1.63±0.04	136±2	x	30
23	$(Me_8Si_4O_3)_2$	1.65	148, 133	x	31
24	$(Me_4Si_2O)_2$	1.61	143.2	x	32
25	$(MeSiO_{1,5})_8$	1.61	145	x	33

Table 1 (contd.)

No.	Formula	Si-O bond length, Å	SiOR angle, deg	Method of determination	References
1	2	3	4	5	6
26		1.66	—	x	34
		—	150	x	35
		—	180	x	36
27	$Si(OMe)_4$	1.65	—	e	37
		1.64±0.03	113±2	e	15, 16
28	$MeOSiH_3$	1.64±0.003	120.6±0.9	e	38
29	$PhOSiH_3$	1.648±0.007	121±1	e	39
30	$Me_2Si(OH)_2$	1.63	—	x	40
31	$Et_2Si(OH)_2$	1.63±0.02	—	x	41—43
32	Me_3SiOM (M = K, Rb, Cs)	1.60—1.61	123±2	x	44
33		1.670	—	x	45
34		1.663 1.669	—	x	46
35	$PhSi(OC_6H_4)_3N$	1.635 1.650	— —	x	47
36	$m\text{-}O_2NC_6H_4Si(OCH_2CH_2)_3N$	1.656, 1.661 and 1.650	122—123	x	48
37	$PhSi(OCH_2CH_2)_3N$	1.638, 1.664 and 1.665	—	x	8, 49
38		1.700 and 1.794	—	x	50
39		1.813, 1.765 and 1.775	—	x	51
40	$[Me_4Sb]^+[(Me_2SiO)_4M]^-$ (M = Al^{III}; Ga^{III}; Fe^{III})	1.56	147	x, PMR	52, 53
41		1.70	130	x	41, 54
42	$Me_3SiOReO_3$	1.69	164±5	x	55

*e = electron diffraction, sp = spectroscopic, x = X-ray diffraction.

In the dimeric molecule of dibromotrimethylsiloxyaluminium (compound 41 in Table 1), in trimethylsilylperrhenate (compound 42), and in tetra-alkylammonium (compound 38) and pyridinium (compound 39) siliconates the Si—O bond is longer than in the majority of organosilicon derivatives (1.7—1.8 Å), while in hexafluorodisiloxane (compound 5) and in tetramethylstiboniumtetrakis(trimethylsiloxy)-derivatives of metals (compounds 40) it is shorter (1.56 Å). In inorganic silicon derivatives (silicates) the Si—O distances vary over the range 1.54—1.78 Å.[7,57-61]. The Si—O bond is shortened in all silicon

compounds containing the Si—O—M group, where M is a metal atom with an effective positive charge (silicates, siliconates, and siloxanolates)[62]. In alkali metal trimethylsilanolates (compounds 32) the Si—O bond length is about 1.60 Å.

On the other hand, in the disiloxane linkage in silicate anions, the silicon atoms of which are joined in an anionic oxygen atom (Si—O⁻), the interatomic Si—O distance is longer than usual (1.75—1.85 Å).[59-62] The Si—O bond is lengthened (1.7—1.8 Å) also in organic silicon compounds where the oxygen atom is linked to an electron-accepting substituent (compounds 38—42 in Table 1).

The decrease of the Si—O bond length noted above cannot be accounted for solely by its appreciable ionic character, since the introduction of the appropriate correction for the difference between the electronegativities of the silicon and oxygen atoms leads to 1.77 Å.[62] The shorter length of the Si—O bond convincingly demonstrates its partial double bond character arising as the result of the $(p \rightarrow d)_\pi$ interaction. The degree of double bond character (bond order) depends on the nature of the substituents at the silicon and oxygen atoms. Electron-accepting substituents at the silicon atom, which decrease the energy of the 3*d* orbitals, or metal and oxygen atoms, which increase the effective negative charge of the silicon atom, increase the Si—O bond order. On the other hand, electron-donating substituents at the silicon atom or electron-accepting groups at the oxygen atom decrease the siloxane bond order.

Although no compound is known in which the silicon atom is joined to an oxygen atom by a double bond, presumably the order of the "short" Si—O bonds (1.56 ± 0.03 Å) approaches that of the double bonds Si=O as a result of the additional $(p \rightarrow d)_\pi$ interaction. In long Si—O bonds (1.7—1.8 Å) the degree of $(p \rightarrow d)_\pi$ coupling is reduced to a minimum and they can be regarded as virtually single bonds. On the other hand, in the majority of organosilicon compounds the Si—O bond (1.64 ± 0.03 Å) is 40—50% ionic[62,63] and its order is 1.2—1.5.[62]

The valence angle between the oxygen bonds increases in the sequence H_3COCH_3 (111.43°)[64] < H_3SiOCH_3 (120.6°)[38] < $H_3SiOSiH_3$ (144.0°).[8] This demonstrates an increase of the amount of *s* character of the oxygen σ orbitals. When oxygen combines with one and two silicon atoms (in methoxysilane and disoloxane), its hybridisation is the average between sp^3 and sp^2 and between sp^2 and *sp* respectively. The increase of the SiOSi angle, associated with the transition from the sp^3 hybridisation of the oxygen atom to sp^2 and to *sp*, in the limiting case, probably favours the formation of common mutually perpendicular π orbitals between the two lone pairs of the oxygen atom and the *d* orbitals of the two silicon atoms linked to them (Fig. 1).

The SiOC angles in methoxy- and phenoxy-silanes (compounds 28 and 29) are almost identical. In tetramethoxysilane (compound 27) the SiOC angle (113°) is smaller than in methoxysilane, which indicates a marked weakening of the interaction between the *p* electrons of each of the four oxygen atoms and the *d* orbitals of silicon as a result of the competing mutual influence of the methoxy-groups.

The SiOSi angle varies within very wide limits; from 105° (compounds 16 and 17) to 150—170° in hexahalogenosiloxanes (compounds 4 and 5) and from 125° to 180° in silicates[58,59,61]. The great flexibility of the SiOSi angle, which in the vast majority of silicon compounds is much greater than the tetrahedral valence angle of oxygen in the state of sp^3 hybridisation (109°), is not inconsistent with the presence of the $(p \rightarrow d)_\pi$ bond between oxygen and silicon, since the five orthogonal diffuse 3*d* orbitals of the latter make it possible to form π bonds for any steric orientation of oxygen.

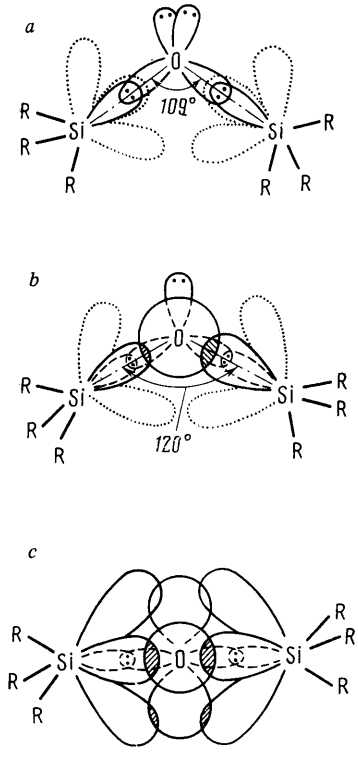
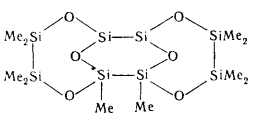


Figure 1. The overlapping of the electron orbitals of an sp^3-, sp^2-, and *sp*-hybridised oxygen atom (*a*, *b*, and *c* respectively) with the orbitals of the silicon atoms in the disiloxane group.

With increase of the SiOSi angle, the SiO bond length diminishes and its order increases. A decrease of the SiO (Si) bond length by 0.02—0.03 Å corresponds to an increase of the SiOSi angle in silicates by 10°.[61]

The SiOSi angles in the planar six-membered rings of the silicate anions $[Si_3O_9]$ (Lazarev[61]) in cyclotrisiloxanes (compounds 10 and 12) and in octamethylspiropentasiloxane (compound 11) are 125—130°. In contrast to the planar cyclotrisiloxanes[14,23-25], cyclosiloxanes containing more than three siloxane units are non-planar[14,20,28,29]. In cyclosiloxanes consisting of more than three siloxane units (compounds 18—22), in silsesquioxanes (compound 25), and also in linear (compounds 8 and 9) and branched (compound 6) siloxanes the SiOSi angle is somewhat greater (130—145°). In the phthalocyaninesiloxane polymer (compound 26) the SiOSi angle is probably close to 180° owing to the steric hindrance due to the phthalocyanine groups[35,36]. In disiloxanes (compounds 1—5) the SiOSi angle varies in the range 135—156° according to electron diffraction data. We may note that indirect spectroscopic methods lead to unduly high values of these angles (155—180°, Table 1). The maximum SiOSi angle

(155.7°) has been observed, as expected, in hexafluorodisiloxane (compound 5), which contains the most electronegative substituents (fluorine atoms) at the silicon atoms.

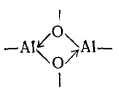


Two types of SiOSi angles were found in compound 23; 133° in the planar six-membered ring and 148° in the nonplanar seven-membered rings.

In contrast to the SiOSi angle, the OSiO angle in the majority of organosilicon compounds varies within narrow limits (110—120°).[14,20,21,23-25,28-33,40-43] In silanediols it amounts to 110° ± 2°.[40-43] In the five-membered ring of compounds 38 and 39, which have an ionic structure, the OSiO angle is 86—90°.[50,51] One oxygen atom of each five-membered ring occupies an equatorial position and the other is in an axial position, the axial SiO bonds (1.794 Å), being significantly longer than the equatorial bonds (1.700 Å).[50]

According to X-ray diffraction data, the geometrical shape of silatrane molecules (compounds 34—37), containing a pentacoordinate silicon atom, is that of a distorted trigonal bipyramid (with respect to the silicon atom) with equatorial oxygen atoms[49]. The SiOC angles in *m*-nitrophenyl-(2,2′,2″-nitrilotriethoxy)silane (compound 36) are 122—123°. The atrane half-rings in silatranes are completely identical, have a non-planar configuration, and are extremely mobile[49].

The SiOM angles (M = metal) in silicates and in organosilicon compounds are always greater than 120°. In the dimeric dibromotrimethylsiloxyaluminium molecule (compounds 41) the four-membered ring



is planar and the SiOAl angle is 130°. Tetramethylstibonium tetrakis(trimethylsiloxy)aluminate (compound 40), which forms orthorhombic crystals with two molecules per unit cell, has an ionic structure: the SiOAl angle is 147°.[52,53] In trimethylsilyl perrhenate (compound 42) the SiORe angle is 164°.[55]

As in t-butoxides, in tetrameric potassium, rubidium, and caesium trimethylsilanolates (compounds 32) the SiOM angle is 123° ± 2°.[44] According to cryoscopic and ebullioscopic data, alkali metal (Li, Na, or K) siloxanediolates are dimerised[65].

2. The Bond Energy

The siloxane bond is one of the most stable bonds formed by silicon and is inferior in this respect only to the Si—F bond. The Si—O bond strength calculated from heats of combustion has been estimated, the results ranging from 101 to 118 kcal mole^{-1} (Table 2). It is much lower than the value (242.4 kcal mole^{-1}) predicted by theory for the $Si^+ - O^-$ ionic bond[66]. The much higher energy of formation of the Si—O bond compared with the less polar C—O bond and the more polar Ge—O, Sn—O, and Pb—O bonds evidently indicates the occurrence of $(p \rightarrow d)\pi$ interaction between silicon and oxygen‡.

According to the data in Table 2, the Si—O (Si) bond energy is probably somewhat greater than the Si—O (C) bond energy.

Table 2. The siloxane bond energies.

No.	Formula	Si-O bond energy*, kcal mole^{-1}	References
1	$(Me_3Si)_2O$	117 112	12 68
2	$Me_3SiOSi(Me)_2OSiMe_3$	117 115	12 68
3	$Me_3Si[OSi(Me)_2]_2OSiMe_3$	117	12
4	$Me_3Si[OSi(Me)_2]_3OSiMe_3$	117 118	12 68
5	SiO_2	112	69
6	$(Me_2SiO)_4$	108	68
7	$(MeO)_4Si$	102	70, 71
8	$[(MeO)_3Si]_2O$	101	70, 71
9	$[(MeO)_2SiO]_3Si(OMe)_2$	102	70, 71
10	$[(MeO)_3Si]_2$	101	70, 71

* See Refs. 12 and 70—79 for the heats of combustion and formation of compounds containing the Si—O bond.

The heats of formation ΔH, entropies S, and heat capacities C_p of compounds containing the siloxane bond have been calculated very accurately according to an additive scheme[78]. For organosilicon compounds in the ideal gas state at 25° and 1 atm, ΔH_{Si-O} = −52 kcal, C_p = 9.6 cal g^{-1} deg^{-1}, and S = −1.24 eu.[78]

It has been shown for cyclodimethylsiloxanes and cyclomethyl(isopropoxy)siloxanes[79] that the Si—O bond energy in cyclosiloxanes depends on the number of siloxane units in the ring. The Si—O bond energies in cyclotetrasiloxanes and cyclopentasiloxanes, which have relatively unstrained rings, and in linear siloxanes are close to one another. The appreciable strain of the rings in cyclotrisiloxanes leads to an increase of the Si—O bond energy (to 9 kcal mole^{-1}).[79]§ The difference between the Si—O bond energies in cyclotrisiloxanes and cyclosiloxanes with large rings has been confirmed by the heats of their catalytic cleavage reactions. The heat of opening the D_3 ring is 3—4 kcal mole^{-1}.[81-83] Calorimetric measurements revealed a slight (to the extent of about 0.2 kcal mole^{-1}) strain of the rings in D_4 and D_5.[82] When the methyl groups in cyclodimethylsiloxanes are replaced by propyl or 3,3,3-trifluoropropyl groups, the heat of ring cleavage increases. The ring strain energy reaches 5.25 kcal

‡ The bond strength (and force constant) usually increase with increase of bond polarity. In the case of C—O the $(p \rightarrow d)\pi$ linkage cannot be formed (there is no 2*d* orbital). The Sn—O bond has a markedly ionic character and is more than 50% longer (2.30 Å) than the Si—O bond. Therefore the formation of $(p \rightarrow d)\pi$ linkages with participation of the 5*d* electrons of tin is greatly hindered[67].

§ The conclusion reached on the basis of measurements of diamagnetic susceptibility that the ring strain in D_3 and D_4 [80] is identical must be regarded as erroneous. (D = Me_2SiO).

mole^{-1} in F$_3$¶ and 1.3 and 0.75 kcal mole^{-1} in F$_4$ and F$_5$ respectively.[82]

In the compounds $R^1R^2Si\overset{\frown O \frown}{CH_2CH_2}SiR^3R^4$, where R^1, R^2, R^3, and R^4 = Me or Ph, the ring strain increases on replacement of methyl groups by phenyl groups. The heat of polymerisation of these compounds, which involves the dissociation of the Si—O bond, is 8—12 kcal mole^{-1}.[81]

Since the equilibrium ratio of the cyclosiloxane stereoisomers is in all cases without exception close to the statistical value[84-91], presumably the Si—O bond energy is the same in all the isomers of this cyclosiloxane. This hypothesis agrees well with the conclusion that the rates of polymerisation of F$_3$,[92] P$_3$, P$_2$D,[93] A$_2$D, A$_3$, A$_2$D$_2$, A$_3$D, and A$_4$[94,95] stereoisomers are similar†. Therefore the enthalpies of the A$_3$(ΔH_{cis} = 27 kcal mole^{-1} and ΔH_{trans} = 22 kcal mole^{-1}) and A$_4$ (ΔH_{cis} = 8 kcal mole^{-1} and for the remaining three isomers ΔH = 0) stereoisomers, obtained from the temperature variation of the equilibrium constants for their interconversion[90], appear to be unexpected. The difference between the enthalpies of the A$_3$ and A$_4$ stereoisomers is not consistent with their statistical distribution at equilibrium, established in the same study[90].

3. Dipole Moments

The dipole moments μ of linear[96-110] and cyclic[97,100,111-114] siloxanes, silanols[103,115-117], alkoxysilanes, acyloxysilanes[118-131], and silatranes[132-135] have been largely compiled in the handbook of Osipov et al.[136] The experimental dipole moments of the linear siloxanes $Me_3SiO(D)_nMe_3$ and cyclosiloxanes D_n with a large number n of siloxane units in the ring agree well with the values calculated by the empirical formula[97] $\mu = 0.7\sqrt{n}$.

The dipole moment of D$_3$, which has a planar strained ring, is zero[100]. The configuration of the F$_3$ stereoisomer has been established on the basis of the dipole moments (expressed in D). The compound with μ = 4.7 D is the *cis*-isomer and that with μ = 2.98 D is the *trans*-isomer[87].

The dipole moments of disiloxanes are comparatively small (0.24—1.03).[96-105] The SiOSi angle calculated from the dipole moments of disiloxanes is much greater than the tetrahedral value: 160 ± 15° [97] (131° [102]) in hexamethyldisiloxane and about 180° [96] in disiloxane (this value is evidently too high).

As already stated, an increase of the SiOSi angle indicates an increase of the Si—O bond order. The dipole moment of the Si—O bond, calculated from the dipole moments of disiloxanes[96,97,100] and branched[13], linear[137], and cyclic siloxanes[100] and alkoxysilanes[118], is 1.2—1.65 D. Judging from the dipole moment, the polarity† of the Si—O bond is much lower than might have been expected bearing in mind the large difference between the electronegativities of silicon (1.89) [63] and oxygen (3.50).[63]

The group dipole moment increases in the series $\mu_{H_3SiO} < \mu_{Me_3SiO} < \mu_{Ph_3SiO}$. The value of μ_{H_3SiO} in disiloxane is 0.28—0.40 D [96] and μ_{Me_3SiO} amounts to 0.95—1.05 D in alkoxytrimethylsilanes[13,101,102] and 1.3 D in hexamethyldisiloxane[101]; μ_{Ph_3SiO} in hexaphenyldisiloxane is 1.2—1.7 D.[104] The smaller group dipole moment of Me$_3$SiO in alkoxytrimethylsilanes compared with hexamethyldisiloxane is due to the different polarities of the Si—O bond and the different types of $(p \rightarrow d)_\pi$ interactions between the oxygen and silicon atoms.

The dipole moments of methoxymethylsilanes in the series $Me_{4-n}Si(OMe)_n$ are greater than for hexamethyldisiloxane and increase with increase of n:[13]

$$\mu_{(Me_3Si)_2O} < \mu_{Me_3SiOMe} < \mu_{Me_2Si(OMe)_2} < \mu_{MeSi(OMe)_3} < \mu_{Si(OMe)_4}.$$

The dipole moments of tetra-alkoxysilanes Si(OR)$_4$ with branched alkyl groups are smaller than those of tetra-alkoxysilanes with normal alkyl groups and with increase of the degree of branching μ falls. The dipole moments of mixed alkoxysilanes having the general formula $(MeO)_nSi(t\text{-}Bu)_{4-n}$ vary linearly with n.[127]

The dipole moments of methoxymethylsilanes[13,118] and tetra-n-alkoxysilanes[118,129] agree satisfactorily with the values calculated for the tetrahedral model of these compounds, which postulates free rotation about the Si—O bond. In the presence of two or more phenoxy-groups at the silicon atom[128] or of branched alkoxy-groups in trialkoxyphenylsilanes[124], the rotation about the Si—O bond is greatly restricted. Free rotation about the siloxane bond in tetra-n-alkoxysilanes and ethoxypropylsilanes is somewhat hindered[127,128]. The rotation about the Si—O bond is probably only relatively free even in methoxysilanes[128]. A small energy barrier to rotation exists in all alkoxysilanes, but it is not large enough for the estimation of the restriction of free rotation from the dipole moments.

The dipole moments of silanediols show that the internal rotation of the two hydroxy-groups is hindered and that the molecular configuration with an SiOSi angle of 102° is preferred[116].

The high dipole moments of silatranes, which greatly exceed the values calculated without taking into account the donor—acceptor interaction between the silicon and nitrogen atoms[132,135], demonstrate the existence of a transannular N → Si bond.

The dielectric constants ϵ of linear siloxanes are somewhat higher than those of cyclic compounds[139]. The dipole moments of hexa-alkyldisiloxanes are close to that of benzene (2.28). With increase of molecular weight, $\epsilon_{20°}$ increases from 2.18 for hexamethyldisiloxane to 2.79 for $Me_3SiO[SiO(Me)_2]_{300}SiMe_3$ and from 2.39 for D$_4$ to 2.74 for D$_8$.[139] Polydimethylsiloxanes with viscosities ranging from 30 000 to 1 000 000 cS have almost identical dielectric constants (ϵ = 2.63 – 2.77).[139] The dielectric constants of polydimethylsiloxanes decrease with increase of temperature and remain virtually constant when the frequency is raised to 10^8 Hz.[139] When the methyl groups at the silicon atoms in cyclodimethylsiloxanes are replaced by polar groups [$F_3CCH_2CH_2$ or $NC(CH_2)_n$ with n = 1 –3], ϵ increases by a factor of 2—4.[87,114] Nevertheless, the dielectric constants of even the most polar cyclosiloxanes, containing CH_2CN groups at the silicon atoms, do not exceed 10,[112] while ϵ_{MeCN} = 37.5.

III. SPECTROSCOPIC CHARACTERISTICS OF THE SILOXANE BOND

1. Vibrational Spectra. The Force Constants and Bond Order

The number of publications devoted to the vibrational spectra of silicon compounds containing siloxane bonds is extremely large. The results of spectroscopic

¶ F = $CF_3CH_2CH_2(Me)SiO$, P = $CH_3CH_2CH_2MeSiO$, and A = PhMeSiO.

† The Si—O bond refraction (1.751 ml mole^{-1}) [138] is much greater than that of the C—O bond in ethers (1.51 ml mole^{-1}).

studies have been summarised in a series of reviews and monographs[57,61,140-149], the most thorough consideration having been given to silicates[61,146]. In this section only the most general features of the vibrational spectra of organosilicon compounds containing Si—O bonds are briefly considered.

Owing to the appreciable ionic character of the siloxane bond, the intensities of the bands and lines due to its vibrations are several times greater than those corresponding to the C—O bond[144,150]. As a result of the strengthening of the Si—O bond due to the $(p \rightarrow d)\pi$ interaction[6-15], the C—O—C and Si—O—Si groups absorb in virtually the same region, despite the greater mass of the atoms in the latter[144,151].

Although the problem of the spectroscopic characteristics of the siloxane bond has attracted the attention of investigators for a long time, it has not so far been possible to calculate theoretically the vibrational spectra of even the simplest compounds containing this bond[61,152,153]. This situation makes it difficult to interpret the spectra and leads to errors (sometimes fairly considerable) in the calculation of the dynamic interaction coefficients K_q, the force constants K_c‡, and the bond orders. Bearing also in mind that there are different approaches to the calculation of the latter parameter[110,154,155], the literature values of the Si—O bond order should be used with some caution.

The fundamental vibrations of the Si—O—Si disiloxane group lie in the following ranges: 450 — 630 cm^{-1} (symmetric vibrations, ν_s) and 930—1170 cm^{-1} (antisymmetric vibrations, ν_{as}). Intense bands in the infrared spectra§ and weak lines in the Raman spectra correspond to the ν_{as} wavenumbers with the opposite relation for the ν_s wavenumbers[140,162,179]. The assignment of the bands and lines corresponding to other vibrations of the siloxane bond is possible only in the simplest cases and is not often encountered in the literature. For example, it has been suggested that the 35 cm^{-1} wavenumber in the infrared spectrum of D_3 corresponds to the $\delta_\perp$ (SiOSi) out-of-plane deformation vibrations[180]. In the far infrared spectra of the higher cyclosiloxanes D_n the $\delta_\perp$ band is displaced towards higher wavenumbers: 50—70 cm^{-1} (n = 4), 80 cm^{-1} (n = 5), 80 and 100 cm^{-1} (n = 6), and 100 and 120 cm^{-1} (n = 7). The $\delta_\perp$ band of hexamethyldisiloxane has been found at 130 cm^{-1} [180] (at 69—86 cm^{-1} in the Raman spectrum) [181]¶.

In the vast majority of spectroscopic studies only antisymmetric Si—O bond vibrations are quoted and discussed. The infrared spectra of disiloxanes, cyclosiloxanes (Table 3), linear[151,182,188,212,214] and branched[211,213,215] siloxanes, silsesquioxanes[201], carbacyclosiloxanes[216], and cyclosiloxazanes[217] contain at least one intense ν_{as} band, the position of which depends more on the structure of the siloxane than on the nature of the substituents at the silicon atom. In the spectra of cyclosiloxanes with a strained ring the band is displaced towards lower wavenumbers. The minimum ν_{as} (Si—O) wavenumber (930 cm^{-1}) has been observed in the infrared spectra of carbacyclosiloxanes with the most strained five-membered ring[216]. In the spectra of cyclotrisiloxanes and six- and seven-membered carbacyclosiloxanes the band is in the region 990—1030 cm^{-1}, [216] and in the spectra of relatively unstrained cyclotetrasiloxanes and eight-membered carbacyclosiloxanes it is displaced towards still shorter wavelengths (1060—1090 cm^{-1}). Estimates of the force constants and bond orders have confirmed that the siloxane bonds in strained rings are appreciably weakened[149,195]. The vibrational spectra of cyclosiloxanes demonstrate the additivity of the intensities, which is probably due to the compensation of the $(p \rightarrow d)\pi$ interaction of the adjacent siloxane bonds[120].

Table 3. The characteristic absorption bands of the Si—O bond in the infrared spectra of siloxanes.

Formula	ν_s, cm^{-1}	ν_{as}, cm^{-1}	References *py* *
1	2	3	4
$(H_3Si)_2O$	—	1100	171, 185
$(D_3Si)_2O$(gas)	—	1094	171
$[Me_3SiH]_2O$	550	1058	57, 142, 171
$(Me_3Si)_2O$	516	1053	57, 162, 171, 172, 175, 181, 187—191
$[(CD_3)_3Si]_2O$	461	1060	181
$[(C_nH_{2n+1})_3Si]_2O$ $n=2-4$	—	1069	142, 186, 191, 192
$[Ph(Me)_2Si]_2O$	560	1063	57, 142, 171, 190
$(Ph_3Si)_2O$	—	1075	171, 191, 193
$[CH_2{=}CH(Me)_2Si]_2O$	522	1056	142, 194
$[ClCH_2(Me)_2Si]_2O$	521	1069	57
$[Cl_2CH(Me)_2Si]_2O$	578	1085	57, 142
$[F(Me)_2Si]_2O$	550	1084	142, 194
$[Cl(Me)_2Si]_2O$	578	1070	57, 142, 171, 195
$[I(Me)_2Si]_2O$	551	1068	142, 194
$[Cl_2(Me)Si]_2O$	638	1075	57
$(Cl_3Si)_2O$	718	1170	166, 185, 196
$(Br_3Si)_2O$	693	1094	197
$[HO(Me)_2Si]_2O$	555	1073	57, 171, 172, 195
$[OH(Ph)_2Si]_2O$	—	1078	171
$[MO(Me)_2Si]_2O$			198
M-Li	565, 537	1055, 1022	198
M-Na	551	1040, 1000	198
M-K	539	998	198
$[(MeO)_3Si]_2O$	577	808, 838	199, 200
$Me_3Si[OSi(Me)_2]_nOSiMe_3$		1090	
$n=1$	—	1050, 1083	150, 151, 188
$n=2$	—	1039, 1076	151
$n=3$	—	1034, 1066	151
$n=4$	—	1057, 1085	151
$n=300-7000$	—	1020, 1090	182
$[H(Et)SiO]_3$	—	1023	205, 206
$(Me_2SiO)_3$	607	1020	150, 180, 183, 201—204
$[Me(C_nH_{2n+1})SiO]_3$ (n=6—10)	—	1015—1025	207
$[Me(Ph)SiO]_3$	532	1018	193
$(Ph_2SiO)_3$	—	1015, 1032	201
$[Et(EtO)SiO]_3$	—	1023	206, 208
$(H_2SiO)_4$	593	1114	209
$[H(Me)SiO]_4$	578	1090	209
$[H(Et)SiO]_4$	—	1085	205
$(Me_2SiO)_4$	555	1078	150, 201, 209, 210
$[Me(Ph)SiO]_4$	510, 530	1085	193
$(Ph_2SiO)_4$	—	1070	201
$[H(Et)SiO]_5$	—	1089	205
$(Me_2SiO)_5$	488, 553	1083	150, 201, 210
$[H(Et)SiO]_6$	—	1086	205
$(Me_2SiO)_6$	496, 552, 591, 638	1070, 1090	150, 201, 210
$(Me_2SiO)_7$	—	1060, 1090	150, 201

*The numbers of the references quoting the tabulated absorption band wavenumbers are underlined.

The nature of the substituents at the silicon atoms has little influence on the position of the ν_{as} band of the SiO(Si) bond in the spectra of cyclosiloxanes. Only when the methyl groups in D_4 are substituted by hydrogen atoms is it displaced towards shorter wavelengths[209,211] (Table 3),

‡ The values of K_q', and K_c have been quoted in a number of publications[18,142,143,150,154-178].

§ In the infrared spectra of linear and cyclic siloxanes more than 50% of the intensity corresponds to the contribution by the antisymmetric vibrations of the Si—O bonds[182]. The intensity of the ν_{as} vibrations of the Si—O bonds in linear disiloxanes is approximately 10 times greater than the ν_s intensity[183].

¶ Infrared spectra of disiloxanes in the range from 30 to 100 cm^{-1} have been published also by Robinson and Lafferty[184].

while in linear siloxanes such a shift is not observed[142, 211-213]. In the infrared spectra of linear[140,151,182,188,212,214] and branched[213,215] siloxanes and also cyclosiloxanes containing more than four siloxane units (Table 3) the ν_{as}[Si—O(Si)] band is split into two (or more) components. In the spectra of cyclodimethylsiloxanes, starting with D_4, the shift of the absorption maxima towards higher wavenumbers with increase in ring size is relatively small (20—30 cm^{-1}). The spectra of linear polydimethylsiloxanes $Me_3Si[OSiMe_2]_nOSiMe_3$ showed two bands with maxima in the wavenumber ranges 1034—1057 cm^{-1} and 1066—1085 cm^{-1} (n = 1—4) [151] and at 1020 and 1090 cm^{-1} (n = 300—7000) [182] (Table 3). The ν_{as}(Si—O) absorption maxima in the spectra of branched siloxanes have been recorded at 1040 and 1110 cm^{-1}.[211,213,215] In the infrared spectra of the majority of cyclosiloxazanes two bands due to the ν_{as} vibrations of the Si—O bond are also observed. In the spectra of compounds with a six-membered ring these bands are displaced towards longer wavelengths, which probably indicates the strain of the siloxazane ring[217].

The position of the ν_s(SiO) band in the spectra of silsesquioxanes with organic substituents is the same as in the SiO_2 spectrum (an intense broad band in the region of 500 cm^{-1}).[218] In the spectra of the octamers $(RSiO_{1.5})_8$, 3—4 maxima are observed and in the spectra of the hexamers $(RSiO_{1.5})_6$ between 6 and 8 maxima at 360—660 cm^{-1}.[141,219]

In contrast to cyclosiloxanes, the positions of the ν_s(SiO) and ν_{as}(SiO) bands in the spectra of disiloxanes depend to a large extent on the nature of the substituents at the silicon atoms. With increase of the electronegativity of the substituents (in particular following the substitution of the methyl groups in hexamethyldisiloxane by hydrogen or halogen atoms and phenyl or hydroxy-groups) the ν_s(SiOSi) and ν_{as}(SiOSi) bands are displaced towards higher wavenumbers (Table 3). Thus, on passing from hexamethyldisiloxane to disiloxane and to hexachlorodisiloxane, the ν_{as}(SiOSi) change from 1060 to 1100 and 1170 cm^{-1} respectively[185]. The force constants of the Si—O bond calculated from the spectroscopic characteristics of these three compounds are 6.96×10^{-6}, 8.17×10^{-6}, and 9.18×10^{-6} cm^{-2} and the bond orders are 1.13, 1.33, and 1.49 respectively[165]. The main cause of the strengthening of the siloxane bond with increased electronegativity of the substituents at the silicon atoms is believed to be the enhancement of the $(p \rightarrow d)\pi$ interaction due to the increase of the positive charge at the silicon atom[142,149,158,160,164-166,175,185,220].

In the spectra of alkali metals tetramethyldisiloxane-1,3-diolates $(MOMe_2Si)_2O$ (M = Li, Na, or K) the ν_{as}(SiOM) bands are displaced towards higher wavenumbers relative to the ν_{as}(SiOH) band in the spectrum of $(HOMe_2Si)_2O$ (910 cm^{-1}): 980 cm^{-1} (for M = Li), 963 cm^{-1} (for M = Na), and 941 cm^{-1} (for M = K),[198] while the ν_{as}(SiOSi) bands undergo the opposite shift towards lower wavenumbers (Table 3). This shows that, together with the increase of the force constant of the SiO(M) bond on passing from M = H to M = K, the Si—O(Si) bonds are weakened[198].

The Si—O(C) bond in alkoxysilanes is much weaker than the Si—O(Si) bond in siloxanes. The ν_s(SiOC) wavenumber occurs in a shorter wavelength region (700—850 cm^{-1}) than the ν_s(SiOSi) wavenumber[143,148,149,158,162,173,185,192,221].

As a result, the splitting of the Si—O stretching vibration bands into ν_s and ν_{as} in the spectra of alkoxysilanes is much less marked (about 200 cm^{-1}) than for siloxanes (about 500 cm^{-1}). This is associated both with the breakdown of the symmetry in the electronic configuration of oxygen and with the change of the angle between its valence bonds[162].

On passing from hexamethyldisiloxane to methoxytrimethylsilane, the coefficient of dynamic interaction diminishes from 6.96×10^{-6} to 6.17×10^{-6} cm^{-2}.[158,165] The order of the siloxane bond in tetramethoxysilane is unity, because its force constant in this case virtually coincides with the calculated constant for a "single" Si—O bond[177]. The order of the siloxane bond in alkoxyalkylsilane molecules is also close to unity[143,155,165]. On passing from n = 1 to n = 4, there is a linear growth of the intensity of the ν_{as}(SiOC) band in the spectra of the compounds $Me_{4-n}Si(OEt)_n$.[221]

When the methyl groups in methoxytrimethylsilane are substituted successively by chlorine atoms, the ν_{as}(SiOC) band shifts towards shorter wavelengths (from 720 cm^{-1} for Me_3SiOMe to 810 cm^{-1} for Cl_3SiOMe),[158,222,223] while the force constant increases correspondingly from 6.17×10^6 cm^{-2} to 8.23×10^6 cm^{-2}.[158]

This change is proportional to the increase of the force constant on passing from $(Me_3Si)_2O$ to $(Cl_3Si)_2O$. The shift of the ν_{as}(SiOC) band towards higher wavenumbers† is observed also when hydrogen atoms are replaced by chlorine in tetraethoxysilane[227].

Thus, as in disiloxanes, highly electronegative substituents at the silicon atom in alkoxysilanes also cause an appreciable increase in the Si—O bond order. The effect of the $(p \rightarrow d)\pi$ interaction plays a decisive role in this phenomenon[142,149,153,158,160,162,165,224,225]. The occurrence of this effect in methylmethoxysilanes probably has a significant influence also on the nature of the Si—C bonds, namely it leads to their weakening and a decrease of their covalent character[179].

Apart from the corresponding ν_s(Si—O) and ν_{as}(Si—O) lines the tetramethoxysilane spectrum shows an intense polarised line at 640 cm^{-1}, probably due to the fully symmetrical stretching vibrations of the SiO_4 tetrahedron[199,200].

An intense absorption in the region of 1000—1200 cm^{-1}, due to the stretching vibrations of the C—O bonds, is observed in the spectra of all alkoxysilanes and alkoxysiloxanes[153,156,158,167,174,177-179,191,208,221-223,226-244]. This absorption region is extremely stable and depends little on the nature of the substituents at the silicon atoms[153,221,222,227,245].

In the infrared spectra of the silatranes $RSi(OCH_2CH_2)_3N$, containing a pentacoordinate silicon atom, the absorption band due to the C—O bond is in the region of 1100 cm^{-1}.[246] In the spectra of vinyloxy-, phenoxy-, and acetoxy-silanes, where the C—O bond order is enhanced, this band is located at 1180, 1250—1280, and 1200—1270 cm^{-1} respectively[249-251].

Comparison of the vibrational spectra of siloxanes, silanols, and siloxanols containing analogous substituents at the silicon atom shows that the siloxane bond in the SiO(H) group is only a little weaker than in the SiO(Si)

† A slight shift of the ν_{as}(Si—OC) band is observed also when a halogen atom, an alkyl group, a phenyl group, and an alkoxy- or acetoxy-group are introduced in the p-position of the trimethylphenoxysilane ring, which indicates some change in electron density at the silicon and oxygen atoms, but these shifts are too small to yield a correlation[247]. The position of the ν_{as}(Si—OC) band depends little on the nature and position of the substituent in the benzene ring of phenoxychlorosilanes[168,248].

group[158,163,171,172,175]. For example, the force constant of Si—O bond in Me_3SiOH and Me_3SiOD is $K^* = 6.92 \times 10^6$ cm^{-2}, while in $(Me_3Si)_2O$ it is $K^* = 6.96 \times 10^6$ cm^{-2}.[158,163] When silanols are associated via hydrogen bonding, the Si—O(H) bonds are strengthened still more[149,252,253]. Association of silanol molecules shifts also the split ν_{as}[SiO(H)] bands. Thus the infrared spectrum of triethylsilanol shows maxima at 841 and 828 cm^{-1}.[254]

Very intense ν(SiO) absorption bands are observed in the infrared spectra of alkali metals trimethylsilanolates in the range 900—1000 cm^{-1}.[57,158,198] As was to be expected, high force constants indicate an appreciable strengthening of the Si—O(M) bond (M = alkali metal) relative to the Si—O(H) [163,198] or Si—O(Si) [57] bonds. Thus the order of the siloxane bond in Me_3SiONa is 25% higher than in Me_3SiOH and 40% higher than in Me_3SiOMe.[163]

The absorption band characteristic of the SiO—M bond in the infrared spectra of the products of the interaction of $(EtO)_4Si$ with lithium, sodium, potassium, and magnesium, and other metal acetates in an aqueous alcoholic medium shifts towards a longer wavelength with increase of the atomic weight of the metal[255]. The assignment of the ν(SiO) and ν(MO) bond vibrations in the spectra of siloxane derivatives of the elements with organic substituents is usually difficult. So far only ν[SiO(M)] absorption bands have been identified (M is a Group III—VI or VIII element) and these occur as a rule in the range 800—1100 cm^{-1}.[231,256-290]

In the infrared spectra of organosilicon peroxides $R_3SiOOSiR_3$ (R = Me or Et) and also $Me_3SiOOCMe_3$ the bands in the range 750—770 cm^{-1} have been assigned to the symmetric vibrations of the Si—O bond and those at 146 and 175—185 cm^{-1} to the deformation vibrations of this bond[291-293].

2. NMR Spectra

Only the ^{29}Si isotope, which has a magnetic moment ($I = 1/2$), can be used for a direct investigation of the siloxane bond by NMR. Studies on the ^{29}Si chemical shifts, which require a special technique owing to the relatively low natural abundance of this isotope (4.7%) and the low sensitivity of ^{29}Si NMR spectroscopy[294], have so far been extremely limited in scope[295-307]. The chemical shifts in the ^{29}Si and ^{13}C NMR spectra of related silicon and carbon compounds vary in the opposite sequences. The $\delta(^{29}Si)$ chemical shifts vary within wide limits depending on the number of siloxane bonds and the nature of the substituents at the silicon atom. Selected data are presented in Table 4.

The shifts $\delta(^{29}Si)$ for silicon atoms forming a single bond with oxygen are positive (the region of the lowest fields relative to Me_4Si), increasing with increase of the electronegativity of the substituents linked to the oxygen atom. For trimethylsilyl esters of organic and inorganic acids, an almost linear relation is observed between $\delta(^{29}Si)$ and the pK_a of the corresponding acids[299,305]. For silicon linked to two and more oxygen atoms, the $\delta(^{29}Si)$ are negative—with the exception of the acyloxysilanes[303]. The absolute values of the chemical shifts increase steadily with increase of the number of siloxane bonds at the silicon atoms [$\delta(^{29}Si)$ = −113.0—109.0 for quartz].[303] Presumably the increase of the chemical shift in the above sequence is due to the overall transfer of π-electron density at the oxygen atoms to silicon via the $(p \rightarrow d)_\pi$ coupling mechanism[302]. For polydimethylsiloxanes and cyclodimethylsiloxanes D_n (n = 4—6), the $\delta(^{29}Si)$ are in the range between −23.0 and −19.7 p.p.m.; for D_3, the signal is displaced towards lower fields (−9.9 p.p.m.).[302] Thus the ^{29}Si NMR method, like other physical procedures, reveals a significant difference between the state of the silicon atoms forming part of the strained planar cyclotrisiloxane molecule and the silicon atoms in any other unstrained structures. For linear oligomers MD_nM (M = Me_3Si, D = Me_2SiO, n = 0–6), the $\delta(^{29}Si)$ corresponding to the silicon atoms in the M and D fragments change slightly on passing from n = 0 and 1 to n = 3 and then remain constant[302].

Table 4. The chemical shifts in the ^{29}Si NMR spectra of compounds containing the siloxane bond.

Compound	δ, p.p.m.	References
$(Me_3Si)_2O$	6.3	298, 302
$(Et_3Si)_2O$	9.1	301
$(Me_3Si^*O)_2Si^{**}Me_2$	6.1 (*)	302
	−22.1 (**)	
$(Me_3Si^*O)_3Si^{**}Me_2$	6.7 (*)	302
$(Me_3Si^*O)_4Si^{**}$	−65.0 (**)	
	8.0 (*)	302
	−105.2 (**)	
SiO_2	−113—109	302
$(Me_2SiO)_n$ n=3	−9.2	302
n=4	−20.0	302
n=5	−22.8	302
n=6	−23.0	302
$Me_3Si^*O[Si^{**}(Me)_2O]Si^*Me_3$ n=1	6.1 (*)	302
	−22.1 (**)	
n=2	6.7 (*)	302
	−22.3 (**)	
n=3	6.5 (*)	302
	−22.4 (**)	
Me_3SiOMe	17.2	302, 306
$Me_2Si(OMe)_2$	−2.5	302, 306
$MeSi(OMe)_3$	−41.4	302, 306
$(MeO)_4Si$	−79.2	302, 306
$(Me_3SiO)_3B$	12.3	305
$(Me_3SiO)_3PO$	20.0	305
$Me_3SiOCOMe$	22.0	305, 306
$Me_3SiOCOCF_3$	33.2	305
$(Me_3SiO)_2SO_2$	33.7	305
$Me_3SiOSO_2CF_3$	44.6	305
$Me_2Si(OCOMe)_2$	7.0	303
$Me_2Si(OCOCF_3)_2$	−14.0	303
$Ph_2Si(OH)_2$	−31.7	303

Data for the spin—spin interaction constants J between a hydrogen atom and a silicon atom, also involved in bonding with oxygen atoms are relatively few; $J(^{29}Si—H)$,[308-318] $J(^{29}Si—C—H)$,[312,319,320] and $J(^{29}Si—O—C—H)$[312,319] have been determined. The attempt to trace a correlation between the $J(^{29}SiH)$ and the number of substituents X in the molecules of the $X_{4-n}SiH_n$ series in accordance with the equation

$$J(X_{4-n}SiH_n) = J(SiH_4) + (4-n)\,[J(SiH_3X) - J(SiH_4)]$$

was unsuccessful[311,313]. The greatest deviations from the linear relation were observed for compounds with the most electronegative substituents (X = OR, F, or Cl) like, incidentally, the deviations from the analogous $J(^{13}CH)$ relation for the corresponding carbon compounds[321-323]. The deviations have been explained by the appreciable polarisation of the carbon or silicon atom in these compounds[311,313].

The general equation, which is more suitable for the calculation of $J(^{29}SiH)$ and $J(^{13}CH)$ for compounds of the type HMXYZ (M = C or Si) takes into account the pair interactions of the substituents:

$$J(HMXYZ) = J(MH_4) + A(\alpha_x+\alpha_y+\alpha_z)+B(\alpha_x^2+\alpha_y^2+\alpha_z^2)+C(\alpha_x\alpha_y+\alpha_y\alpha_z+\alpha_z\alpha_x).$$

The maximum deviations of the calculated J from the experimental values do not exceed 6—9 Hz. For M = Si, we have A = 18.26 Hz eV^{-2}, B = 1.78 Hz eV^{-2}, and C = −2.98 Hz eV^{-2}. The parameters α, which constitute a measure of the effective electronegativities of the corresponding substituents, can be determined by means of the above equation from the J for the compounds MH_3X, MH_2X_2, etc. For silicon derivatives, α_X = −1.49 eV when X = OMe, and α_X = −1.76 eV when X = $OSiH_3$.[310] The values of α_X for the series of compounds with M = Si are always smaller than for the corresponding compounds with M = C. This may be due to the higher polarisability of the silicon atom in relation to carbon and at any rate provides no grounds for the interpretation of the experimental findings by taking into account the possibility of π bonding in the silicon compound.

Numerous compounds containing the siloxane bond have been investigated by ^{1}H NMR. Some of the results obtained have been described in other sections and have been examined in another review[324]. Many factors which are difficult to take into account and which influence the proton chemical shift hinder the analysis on the basis of ^{1}H NMR data of the changes in electron density at the silicon and oxygen atoms joined directly. Nevertheless ^{1}H NMR spectroscopy can be used successfully to refine ideas on the nature of the siloxane bond. Systematic studies by ^{1}H NMR on siloxanes[302,325-330], heterosiloxanes[274,276,279,280,331,332], and alkoxysilanes[312,319,333-337] confirm the significant role of π bonding in the structure of these molecules. It has been shown for oligomeric siloxanes of the type $Me_2(X)SiO[Si(Me)_2O]_nSi(X)Me_2$, where X = Me, H, Cl, or $ClCH_2$ and n = 0—6, that the influence of the substituent X can be transmitted through the chain via two or even three siloxane bonds[326]. Relations of the type

$$\tau_i(OCH_2) \text{ or } \tau_i(OCCH_3) = a + b\Sigma\sigma_i^*,$$

(σ^* are the inductive Taft constants for the substituents R), in which the parameter b diminishes with increase of the number n, have been found for the ethoxysilanes $R_{4-n}Si(OEt)_n$.[334] A similar tendency, characterising the decreased ability of the silicon atom to transmit the inductive effect of the substituents to the adjoining bonds with increase of the number of Si—O bonds in the molecule, has also been observed by kinetic methods[338] and by infrared spectroscopy[339] for compounds of different classes. Thus the phenomenon is probably general.

3. Electronic Spectra

Liquid polydimethylsiloxanes are transparent in the visible and near ultraviolet regions. In the range 246—270 nm a number of absorption bands have been observed in the ultraviolet spectra of linear and cyclic polydimethyl- or polymethylphenyl-siloxanes[340].

The attachment of an oxygen atom to a silicon atom linked to a vinyl[341], phenyl[342], or pentafluorophenyl[342] group does not have a significant influence on the absorption of these groups. The λ_{max} for the vinyl group in the ultraviolet spectra of linear and cyclic siloxanes are in the same range (178—180 nm) as for trialkylvinylsilanes and are independent of the number of oxygen atoms joined to the Si—CH=CH_2 group[341].

A bathochromic shift of the absorption band due to the phenyl group relative to the analogous carbon derivatives has been observed in the ultraviolet spectra of methylphenoxysilanes[225]. The position of the absorption maximum of the phenyl group in methylphenoxysilanes $Me_nSi(OPh)_{4-n}$ (n = 1—4) is independent of the number of phenoxy-groups[225,343,344].

The ultraviolet spectra of alkoxy- and trialkylsiloxybenzenes[225,343-345] or their complexes with tetracyanoethylene[345] and the results of quantum-chemical calculations[345] on the structure of phenoxy-derivatives of silicon indicate the occurrence of the $(p \rightarrow d)_\pi$ interaction between the oxygen and silicon atoms.

IV. PHYSICAL PROPERTIES AND MOLECULAR STRUCTURES OF POLYSILOXANES

Owing to the weak intermolecular interaction, the surface tension of polydiorganosiloxanes (particularly polydimethylsiloxanes) is much lower than that of the usual organic liquids with the same densities and boiling points[346,347]. In the series of linear polydimethylsiloxanes it increases from 15 dynes cm^{-1} for hexamethyldisiloxane to 22 dynes cm^{-1} for the polydimethylsiloxane oil with a viscosity of 10^5 cP.[139,347,348] The surface tensions of cyclodimethylsiloxanes D_n (n = 3—7) increase with increase of ring size from 17.3 to 18.3 dynes cm^{-1} at 25°C.[349] The surface tensions of mixtures of polyorganosiloxanes are additive[346].

A relatively high compressibility, which decreases with increase of molecular weight approaching an asymptotic value, is characteristic of the lower polydimethylsiloxanes[350]. With increase of pressure, the compressibility of polydimethylsiloxanes increases more slowly than that of hydrocarbons. At pressures of about 1000 kgf cm^{-2} the compressibility of polydimethylsiloxanes is higher than that of dodecane but at 40 000 kgf cm^{-2} it is lower[350]. At a pressure of 35 000 kgf cm^{-2} high-molecular-weight polydimethylsiloxane does not crystallise[351]. When the methyl groups in the polydimethylsiloxane are replaced by higher alkyl groups, the compressibility gradually falls with increase of the size of the substituent, increasing after substitution by hydrogen atoms[139].

The boiling points as well as the heats of evaporation of the linear polydimethylsiloxane $M_3D_nM_3$, where n = 1—6, and cyclodimethylsiloxanes D_m (m = 3—8) are lower than those of the alkanes having the same molecular weight[139,348]. With increase of n by unity, the heat of evaporation of polydimethylsiloxane increases by only 960 cal mole^{-1}.

With increase of molecular weight, the boiling points of polydimethylsiloxanes increase more slowly than in the case of n-alkanes.

The heat capacities of dimethylsiloxane polymers with a viscosity of 0.65—1000 cS (0.32 – 0.35 cal g^{-1} deg^{-1}) are somewhat lower than those of the corresponding hydrocarbons[139].

The viscosities of low-molecular-weight linear and cyclic polydiorganosiloxanes are somewhat lower than those of hydrocarbons with comparable molecular weights[348,349]. The activation energies for the viscous flow of siloxanes are also lower than for hydrocarbons. The activation energy amounts to 3.8 kcal mole^{-1} for

polydimethylsiloxanes[352], to 5.41 kcal mole^{-1} for siloxane polymers with tetramethylene units in the main chain[353],

$$Me_3SiO[Si(Me)_2(CH_2)_4Si(Me)_2O]_nSiMe_3-$$

and to 6—7 kcal mole^{-1} for saturated hydrocarbons[353]. The average length of the flow segment of high-molecular-weight polydimethylsiloxane corresponds to 7.2 siloxane units[352], while the length of the similar segment for long hydrocarbon chains corresponds to 20—25 units[354].

When the methyl groups in polydimethylsiloxane are replaced by the polar chloromethyl[355], phenyl[108], or chlorophenyl[356] groups, the activation energy for the viscous flow increases, amounting to 4.3 kcal mole^{-1} for polymethylpropylsiloxane, 7.9 kcal mole^{-1} for polymethyl-3,3,3-trifluoropropylsiloxane, and 11.9 kcal mole^{-1} for polymethylphenylsiloxane[357].

With increase of pressure, the viscosity of polydiorganosiloxanes increases more than that of hydrocarbons[358]. With increase of shear rate, the viscosity of polysiloxanes diminishes and at high shear rates the temperature variation of the viscosity becomes insignificant[359].

The low temperature coefficients of the viscosity of polydimethylsiloxanes[108,350,352,353,359] and the decrease of their viscosity with increase of shear rate show that siloxane molecules have a coiled conformation. Indeed the structure of the coiled siloxane molecule with the alkyl groups "sticking out" is responsible for the insignificant molecular interaction, as a result of which the viscosity is also relatively low. With increase of temperature, the molecules uncoil and the intermolecular interaction becomes more intense, which leads to an increased viscosity, partially compensating its usual decrease with temperature. As a result, the temperature coefficient of the viscosity of polymethylsiloxane is much lower than for hydrocarbons.

The coiling of the siloxane chain is probably the cause of the greater deviation of the heats of mixing of polydimethylsiloxanes with benzene from the theoretical values[360].

Indeed the siloxane chain in the polydimethylsiloxane film on the surface of water at 20°C is coiled into a helix containing six monomeric units per turn[347]. With increase of temperature, the length of the turn of the helix increases. Substitution of methyl groups by phenyl groups reduces the tendency of the siloxane chain to coil up[108,347]. This tendency is manifested to an even greater extent when methyl groups are replaced by ethyl groups[347].

The helical shape of the siloxane molecule (Fig. 2) has also been established by electron diffraction[361] and X-ray diffraction[21] methods. An X-ray diffraction study of extended polydimethylsiloxane raw rubber[21] and the finished rubber obtained from it[22] showed that there are six siloxane bonds in the monoclinic cell with the parameters (Å) $a = 13.0$, $b = 8.3$, $c = 7.75$, and $\beta = 120°$. In the polydimethylsiloxane molecule the *trans*-configuration is preferred to the *gauche*-configuration[362,363].

The coiling of the siloxane molecule into a helix has been explained[362,364] by the tendency of the weak Si—O dipoles to undergo intramolecular compensation as a result of which each Si—O dipole is associated with a dipole having the opposite orientation (O—Si). The intramolecular compensation of the individual dipoles has been confirmed by the insignificant change of the dipole moment with increase of the molecular weight of polydiorganosiloxanes.

Bearing in mind the polarity of the Si—O bond, many physical properties of polydiorganosiloxanes (the fact that they are hydrophobic, their compressibility, surface properties, etc.) can be explained solely in terms of the helical macromolecular structure forming a "coil" with "protruding" hydrocarbon groups[139,347,350,360]. However, one should not forget that the effect of the $(p \rightarrow d)_\pi$ bonding in the Si—O—Si system should also weaken the intermolecular interaction.

According to ^{1}H NMR data, segmental motion, which has been attributed to chain drift, takes place in polydimethylsiloxane even at very low temperatures (−136°C).[365-372] The segmental mobility of polydimethylsiloxane raw rubber is much higher than that of natural raw rubber[373]. Comparison of the dielectric properties of polydimethylsiloxane with ^{1}H NMR and X-ray diffraction data suggested[365] that motion of the second kind, preceding the onset of chain rotation, occurs in the crystalline polymer appreciably below the melting point of the crystals. The activation energy for the rotation of the polydimethylsiloxane chain calculated from the ^{1}H NMR data is 8 J mole^{-1}.[365]

The methyl groups in polydimethylsiloxanes rotate unusually readily about the Si—O bonds even at 196°C.[368-371]‡ Such rotation of the methyl groups is probably one cause of the increased distances between the macrochains and of the weakened intermolecular interaction in polydimethylsiloxanes[370]. On the other hand, the rotation of the phenyl groups at low temperatures is fully hindered and even at room temperature their rotation is somewhat retarded[371]. The consequences of the ease of rotation of the methyl groups is the high molar volume and the low density of the cohesion energy[139,350] of polydimethylsiloxane. The average molar volume of the Me_2SiO unit is 75.5 ml mole^{-1}.[374] The low density of the cohesion energy of polydimethylsiloxane, which is appreciably lower than for other polymers, is in fact responsible for the low boiling points, low heats of evaporation, low surface tensions, high compressibilities and low dielectric constants of liquid polydimethylsiloxanes and also for the low heats of fusion and moderate adhesion [energy] of high-molecular-weight polydimethylsiloxanes.

The weakness of the intermolecular forces is also manifested in a number of other properties of polydimethylsiloxanes. The lower ultrasonic velocities in polydimethylsiloxanes compared with the majority of organic liquids having similar densities[139,375,376] indicate a loose packing and a weak intermolecular interaction of the siloxane molecules.

Polydimethylsiloxane becomes rubber-like only when its molecular weight is fairly high (about 10^6) and when its molecular weight is 4×10^5 it flows in the cold although it remains solid. In contrast to other types of raw rubber, unfilled vulcanised polydimethylsiloxane specimens have a very low strength (2—5 kgf cm^{-2}).[377] A characteristic feature of siloxane raw rubbers is also an appreciably smaller decrease of strength with increase of temperature than for other elastomers[377].

Among all the known elastomers, polydimethylsiloxane raw rubber has the lowest glass point (−123°C).[378] The high rate of crystallisation of polydimethylsiloxane raw rubber, which crystallises rapidly at −54°C without supercooling, has also been explained by the weak intermolecular interactions and mobility of the siloxane molecules at low temperatures[379,380].

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‡ The anomalously high mobility of the methyl groups, attributed to the "out-of-plane" deformations of the Si—O—Si bonds, has also been observed in an X-ray diffraction study of structures containing the planar six-membered siloxane ring[25,29].

The substitution of methyl groups in polydimethylsiloxane by vinyl groups does not affect the mobility of the polymeric chains[371]. The introduction of 3,3,3-trifluoropropyl groups has little effect on the molecular motion[371], but the replacement of the dimethylsiloxane units by methylphenylsiloxane[372] or diphenylsiloxane[371] units greatly hinders such motion. On the other hand, the substitution of methyl groups in polydimethylsiloxane by hydrogen atoms increases the mobility of the siloxane chains[372].

Thus the mobility of the polysiloxane molecules decreases in the sequence

$$[H(Me)SiO]_n > [Me_2SiO]_n > [CH_2{=}CH(Me)SiO]_n > [Pr(Me)SiO]_n > [Me(Ph)SiO]_n > [Ph_2SiO]_n.$$

The results of studies on the polysiloxanes by ^{1}H NMR agree well with data for the thermodynamic flexibility of polymeric siloxane molecules obtained in a study of solutions of the polymers by light scattering, osmometry, and viscometry[381-387]. Although the rotation of the polymeric chain about the Si—O bond is restricted to some extent (the unperturbed mean square distance between the ends of the polymeric molecule is much greater than the value calculated theoretically for free rotation), nevertheless the flexibility of the siloxane molecule is much greater than that of other polymeric chains[381-387].

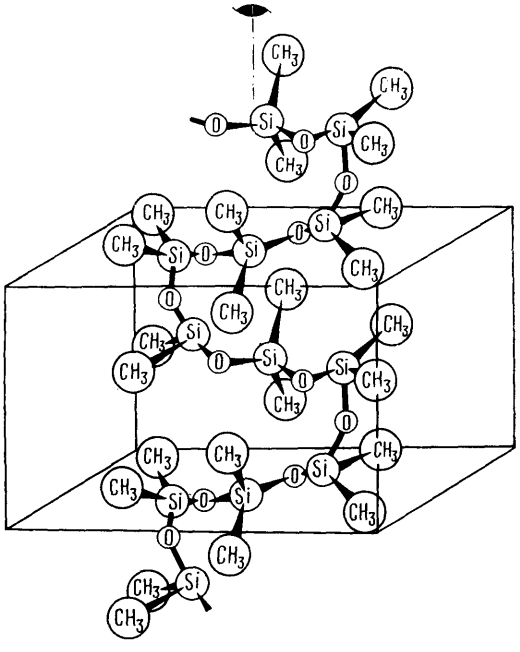


Figure 2. The crystal structure of polydimethylsiloxane[21].

The results of a calorimetric study of the mixing of polydimethylsiloxane with various solvents also led to the conclusion that the molecules of this polymer are very flexible[360,363,364]. This is likewise indicated by the appreciable atomic polarisations P_a and the anomalously short dielectric relaxation times of disiloxanes[99] and cyclosiloxanes[388]. The similarity of the P_a for hexamethyldisiloxane and D_3 [388] demonstrates a significantly lower flexibility of the Si—O bonds in D_3. On the other hand, judging from the value of P_a, the flexibility of the siloxane bonds in the relatively unstrained D_4 ring is much greater and close to their flexibility in linear polydimethylsiloxanes[99].

The great flexibility of the SiOSi angles is responsible for the possibility of the existence of many cyclosiloxanes in the form of several conformers equally probably on energy grounds, which are readily interconverted[28,389,390]. The results of calculations of the overlap integrals of the d and p orbitals for various configurations of siloxane rings agree well with this hypothesis[391].

Two crystalline modifications (orthorhombic and triclinic) and three modifications have been isolated for A$_3$ § and A$_4$ respectively[390].

According to spectroscopic data, only one conformation is possible for dimethylcyclosiloxanes with an odd number of siloxane units ($n > 3$), in which all the silicon atoms are in the same plane and all the oxygen atoms are in another plane parallel to it[392]. When n is even, two (or more) conformations of cyclic siloxanes are possible. The folded D_4 ring can exist in the form of three conformers of different symmetries. One of these is present in the gas and liquid phases[393] and two others in the crystalline state. In the low-temperature modification of D_4, four oxygen atoms and four silicon atoms are located in two separate planes disposed at an angle of 30°.[61] Certain octaorganosilsesquioxanes also exist in the form of two modifications[389].

X-Ray diffraction studies on silicates demonstrate the existence of different equilibrium conformations also in cyclic silicate anions, which is due to the high flexibility of the siloxane chain[61].

Spectroscopic studies and thermodynamic calculations have led to the conclusion that rotation about the Si—O bond in siloxanes is virtually free (the potential barrier does not exceed several tens of kcal mole^{-1}).[9,382,393] Nevertheless rotation about the siloxane bond is apparently always restricted to some extent in all compounds and the energy barrier depends appreciably on the nature of the substituents at the silicon atoms.

The flexibility of the polysiloxane molecule decreases following the substitution of the methyl groups at the silicon atoms by propyl[394], trifluoropropyl[384], or phenyl[384] groups. In the presence of two phenyl groups at the same silicon atom, the flexibility of the siloxane polymer is significantly smaller than that of the methylphenylsiloxane polymer with the same content of phenyl groups.

Thus the thermodynamic flexibility of polymethylphenylsiloxane corresponds to that of the dimethylsiloxane—diphenylsiloxane copolymer containing 25—30 mole % of diphenylsiloxane units[385,386].

The flexibility of the siloxane molecule decreases particularly appreciably on passing from a linear to a "ladder" structure; although the rotational mobilities of the phenyl group in the linear methylphenylsiloxane and the ladder phenylsiloxane $[PhSiO_{1.5}]_n$ polymers are approximately the same, the rigidity of the latter is appreciably greater[395-402]. The number of units (50) in the segment of the ladder phenylsiloxane is ten times greater than in the segment of the methylphenylsiloxane polymer[89,395,401].

The thermodynamic flexibility of polydimethylsiloxane is increased by the introduction of phenylene groups into the siloxane chain[402].

Certain problems of the effect of the nature of the siloxane bond on the properties of oxygen compounds of

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§ A = $C_6H_5(CH_3)SiO$.

silicon, which were not considered here owing to the limited space available, are dealt with in monographs and reviews[56,403-405].

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