CRYSTAL STRUCTURE DETERMINATIONS OF ORGANOSILICON COMPOUNDS

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Abstract

Crystal structures of organosilicon compounds studied in collaboration between the Institute of Inorganic Chemistry Technical University and the X-ray diffraction group of the Central Research Institute of Chemistry HAS are reviewed. The structures of the following classed of compounds are discussed: silatranes, N,N'-diarylcyclodisilazanes, di- and oligosilanes and related germyl compounds and miscellaneous organosilicon compounds.

The study of organosilicon compounds at the Institute of Inorganic Chemistry, Technical University of Budapest has been in progress since 1950. The investigation of the molecular structure has always played a central role in this research. In 1972, at the Central Research Institute for Chemistry of the Hungarian Academy of Sciences, X-ray crystal structure determinations of organosilicon compounds also began. Since that year, the structures of 38 compounds have been determined in cooperation. The most important data obtained from X-ray structure analyses together with a few relevant conclusions concerning the molecular structures are summarized in the present paper.

All structure determinations were performed using diffractometer data. Intensities in most cases were collected on an Enraf-Nonius CAD-4 computer controlled four-circle diffractometer. The conventional crystallographic R-values fall in the range of 0.04—0.09. The compounds studied may be classified as follows:

1. Silatranes
2. N,N'-diarylcyclodisilazanes
3. Di- and oligosilanes and related germyl compounds
4. Miscellaneous organosilicon compounds

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1. Silatranes

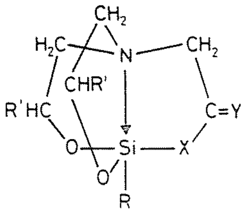
The general formula of silatranes are depicted in Fig. 1, the characteristic geometrical data are listed in Table 1 (Fig. 1, Table 1).

Using available data from the literature and our own measurements, the factors affecting the length of the Si←N dative bonds can be classified as follows:

- the electron-withdrawing or releasing properties of the R-substituent attached to the silicon atom,
- the number of the equatorial oxygen atoms,
- the basicity of the nitrogen atom,
- the structure of the SiOCCN five-membered rings,
- the substituents in the five-membered rings,
- steric effects.

The $d(\mathrm{Si}\leftarrow\mathrm{N})$ bond distance is correlated with the Sanderson-electronegativity ($\bar{X}_R$) of the substituent R as follows [17]:

$$d(\mathrm{Si}\leftarrow\mathrm{N}) = 302.1\bar{X}_R^{-0.257} \quad (\mathrm{pm})$$



	R	X	Y	R'
1	β-C_6H_5	O	H_2	H
2	γ-C_6H_5	O	H_2	H
3	CH_3	O	H_2	H
4	p-FC_6H_4	O	O	H
5	m-$CF_3C_6H_4$	O	O	H
6	m-ClC_6H_4O	O	H_2	H
7	F	O	H_2	H
8	p-$CH_3C_6H_4$	O	H_2	H
9	p-$CH_3C_6H_4$	O	HCH_3	CH_3
10	C_6H_5	CH_2	H_2	H
11	p-$CH_3C_6H_4O$	O	H_2	H
12	C_6H_5	O	O	H
13	CH_3	O	O	H
14	γ-$HO(CH_2)_3$	O	H_2	H
15	p-$CH_3C_6H_4$	CH_2	H_2	H
16	γ-$HS(CH_2)_3$	O	H_2	H

Fig. 1. The general formula of silatranes

Table 1

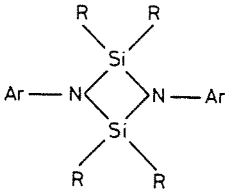
Characteristic geometric data of silatranes

No	$d(\mathrm{Si}\leftarrow\mathrm{N})$ (pm)	ΔSi (pm)	ΔN (pm)	α(NSiO) (°)	Ref.
1	215.6(4)	20	38	83.3	[1]
2	213.2(4)	18	39	83.7	[2, 3]
3	217.5(4)	21	38	82.7	[4]
4	212.9(3)	20	39	83.2	[5]
5	210.6(3)	19	39	83.5	[5]
6	207.9(2)	14	40	85.3	[6]
7	204.2(1)	12	39	85.9	[7]
8	216.9(2)	20	37	82.9	[8]
9	223.6(3)	24	36	81.8	[8]
10	229.1(1)	27	36	81.1	[9]
11	210.7(2)	15	37	84.7	[10, 11]
12	211.9(3)	19	39	83.4	[12]
13	213.4(1)	21	38	82.8	[13]
14	217.3(2)	21	37	82.7	[14]
15	229.0(2)	26	35	81.2	[15]
16	217.7(4)	21	37	82.7	[16]

2. N,N′-diarylcyclodisilazanes

Fig. 2 depicts the general formula of the molecules studied, the characteristic geometric data are shown in Table 2 (Fig. 2, Table 2).

The phenyl rings in these molecules (with the exception of the 19 *o*-tolyl derivative) are nearly coplanar with the cyclodisilazane ring. The different conformation of 19 is not exclusively attributable to steric factors but also to electron effects. The formation of the planar structures may be explained by



	Ar	R
17	C_6H_5	CH_3
18	C_6H_5	C_6H_5
19	o-$CH_3C_6H_4$	CH_3
20	m-$CH_3C_6H_4$	CH_3
21	p-$CH_3C_6H_4$	CH_3
22	o-ClC_6H_4	CH_3
23	o-$CH_3OC_6H_4$	CH_3
24	m-$CF_3C_6H_4$	CH_3

Fig. 2. The general formula of cyclodisilazanes

delocalization, and Si . . . Cl or Si . . . O non-bonded interactions. A comparative NMR study revealed that conformations observed in the solid state are the dominant conformations in solutions.

Table 2

Characteristic geometric data of cyclodisilazanes

No.	*d*(Si-N) (pm)	Si-N-Si (°)	N-Si-N (°)	Dihedral angle (°)	Ref.
17	173.9(3) 174.9(3)	94.3(1)	85.7(1)	5.1	[18]
18	174.3(2) 174.7(2)	95.8(2)	84.1(2)	3.5	[19]
19	173.7(2) 174.0(2)	93.2(2)	86.8(2)	89.6	[20]
20	173.5(2) 173.7(2)	94.8(2)	85.2(2)	5.6(1)	[21]
21	173.6(2) 174.5(2)	94.4(1)	85.6(1)	8.4(1)	[21]
22	175.6(2) 175.6(2)	94.9(2)	85.1(2)	3.8(1)	[22]
23	173.7(2) 175.7(2)	95.8(1)	84.2(1)	7.4(1)	[23]
24	174.4(2) 174.9(2)	94.9(2)	85.2(1)	4.5(1)	[24]

3. Di- and oligosilanes and the related germyl-compounds

The general formula of the compounds containing Si—Si or Si—Ge bonds are shown in Fig. 3 and relevant structural parameters are given in Table 3 (Fig. 3, Table 3).

The crystal structures of disilanes, polysilanes and cyclopolysilanes were determined in order to reveal the structural and conformational features of a number of basic types of compounds. Their conformations have been compared to the analogous carbon compounds. Polysilanes gained increased interest because of their practical applications as photo resistors. Disilanes and analogous germyl-silanes have been used as ligands to transition metal complexes. Structural studies (X-ray and NMR) on the iron complexes have been performed. The silyl group bound to the transition metal displays electron donor capacity, which is even more pronounced in the case of the germyl-silyl ligand.

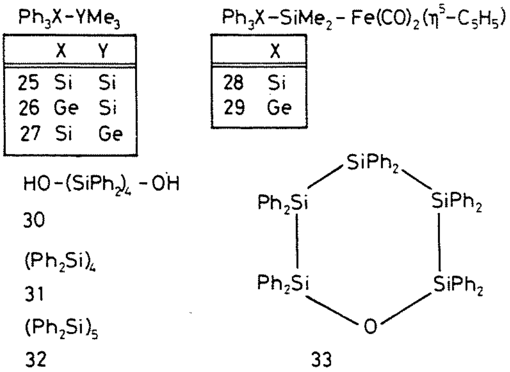


Fig. 3. The general formulae of the compounds containing Si—Si or Si—Ge bonds

Table 3

Characteristic geometric data of di- and oligosilanes and related germyl compounds

No	*d*(Si-Si) (pm)	*d*(Si-C_{ar}) (pm)		Ref.
25	235.5(1)	188.6(1) 186.2(2)[b]		[25]
26	238.4(1)[a]	186.3(3)[b]		[26]
27	239.4(1)[a]	188.5(1)		[24]
28	237.4(1)	188.1(3) 188.7(3)[b]	*d*(Si-Fe): 234.6(1)	[27]
29	240.5(2)[a]	188.1(6)[b]	*d*(Si-Fe): 232.8(2)	[26]
30	236.9(3)	187.6(3)	*d*(Si-O): 164.7(4)	[28]
31	237.7(3)	188.6(2)	α(SiSiSi): 89.6(1)°	[29]
32	239.5(8)	189.6(5)	α(SiSiSi): 104.5(6)°	[30]
33	239.1(1) 237.3(2)	187.7(7)	*d*(Si-O): 164.1(3); α(SiOSi): 146.0(5)°	[31]

[a]: *d*(Si-Ge)
[b]: *d*(Si-C_{methyl})

4. Miscellaneous organosilicon compounds

Miscellaneous organosilicon compounds studied are shown in Fig. 4.

In tetraphenylsilane 34 the asymmetric unit is 1/4th of the molecules [32, 33]. Characteristic geometrical features: Si—C_{ar}: 187.3(4) pm, C(1)′—Si—, —C(1)-C(2): 172.8(4)^0, the dihedral angle formed by the plane of the phenyl ring with the *a*-*a* base plane: 49.7(5)^0.

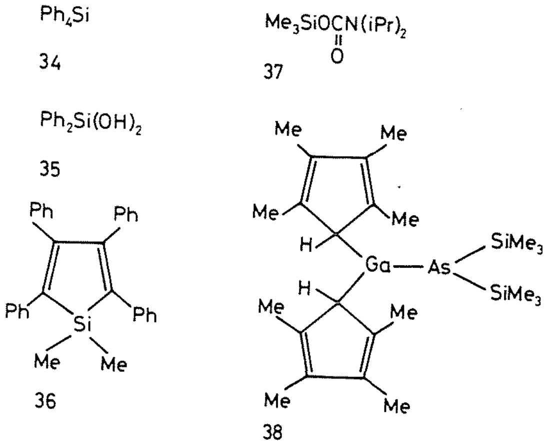


Fig. 4. The formulae of miscellaneous organosilicon compounds

In diphenylsilanediol 35 the asymmetric unit contains 3 independent molecules [34]. The average bond distances and angles are as follows: Si—O: 164.1(2) pm; Si—C: 185.5(3) pm; O—Si—O: 109.5(1.8)°; C—Si—C: 113.0(7)°; O—Si—C: 108.6(6)°. The complex hydrogen bond system forms a peculiar arrangement of the molecules about the *c* crystallographic axis. In this arrangement, the molecules linked by hydrogen bonds, turn their polar OH groups towards each other, and direct their apolar phenyl rings outward.

In dimethyl-tetraphenyl-silacyclopentadiene 36 the 2 molecules of the asymmetric unit mainly differ in the rotations of the phenyl rings with respect to the silole moiety, presumably due to crystal packing forces [35]. Averaged bond lengths and angles: Si—C(endocyclic): 186.6(3) pm; Si—C(exocyclic): 185.5(2) pm; C═C: 135.8(2) pm; C—C: 151.1(2) pm; C—Si—C(endocyclic): 92.7(1)°; Si—C—C: 107.6(2)°; C—C—C: 116.0(1)°. The observed molecular geometry is consistent with a partial delocalization through the silicon atom and not the butadiene system.

The conformation of the trimethylsilyl-N,N-diisopropylcarbamate 37 was studied in solution (NMR) and solid state (X-ray diffraction) [36]. The study revealed that crystals were formed from the preferred conformer in solution. This conformer is characterized by a weak C═O . . . H—C hydrogen bond. The molecule posesses a crystallographic mirror plane: atoms Si—O——CO—N(CH_2) lie in this plane. Geometrical data suggest that the electrons of the carbamate group extend to the Si atom. The non-bonded CO . . . Si distance (289.4 pm) is considerably shorter than the sum of the van der Waals radii (340 pm).

The arsinogallane compound 38 is a precursor to the GaAs semiconductor, and its crystal structure determination provided structural data for the rarely studied As—Si bond [37]. Relevant bond lengths: As—Si: 235.5(8) and 232.8(8) pm; Ga—As: 243.3(4) pm.

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