BOND STRUCTURE OF OLIGOSILANES AND THEIR DERIVATIVES

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It is well known that the ultraviolet absorption of linear homo oligomers and polymers of the fourth group elements indicates a bathochromic shift with increasing polymerization degree [1].

Table 1

Ultraviolet absorption peaks of compounds R-(Z)$_n$-R (in Å)

Z	Type of excitation	n = oligomerization degree								
		1	2	3	4	5	6	7	8	∞
—CH₂—	σ—σ*	~1250	~1350	~1450						~1500
—SiR₂—	σ—σ*	~1600	1900	2150	2350	2500	2600		2720	~2900
—GeR₂—	σ—σ*	~1650	1900	2150	2300	2400				
—SnR₂—	σ—σ*	1850	2100				2460			
—S—	n—σ*	1950 2170	1950 2500	1830 2120 2900	2120 2900				1900 2250 2800	
—C=C—	π—π*	1800	2280	2740	3140	3450	3750		4200	~7000

According to the data in Table I a bathochromic shift of slight extent can be observed even for hydrocarbons. However, it can be explained with the increasing number of the energy levels of molecular orbitals, thus the σ — σ* transition energy decreases. In the case of polyenes the highest occupied π and the lowest unoccupied π* energy levels gradually approach each other due to the conjugation effect. For this reason the bathochromic shift is considerable in this case. The trend is the same in the ultraviolet transitions observed for peralkylated oligosilanes, oligogermanes and oligostannanes, and the extent of the bathochromic shift can be characterized as occurring between the two extreme cases mentioned.

This interesting effect was considered in several studies and it was explained by the specific electron structure of silicon, germanium and tin. The oligosilanes were of particular interest. C. G. PITT and co-workers [2] assumed an electron transition between a σ orbital belonging to the silicon-silicon chain and a π^* level generated from the d orbital of silicon.

H. BOCK and W. ENSSLIN [3] disproved the participation of the silicon d orbital.

The autors, on the basis of SÁNDORFFY's C-model, tried to prove by LCBO-MO calculations that only the sp³ hybrid orbitals of silicon were responsible for the formation of silicon-silicon bond.

According to this explanation — in contrast with the opinion of other scientists — the d orbitals of silicon do not take part in the bond, that is $(d—d)\pi$ interaction does not exist. In the LCBO-MO calculations the geminal interaction of silicon atoms, in addition to the vicinal resonance integrals, was taken into consideration. This implies the assumption of so-called σ conjugation, based on the finding that the measured ionization energies and the eigenvalues calculated by the LCBO-MO method showed a linear correlation.

In the light of these investigations if appeared promising to study the bond structure of carbon-carbon and silicon-silicon bonds by all-valence methods. We have not dealt with germanium-germanium and tin-tin bond because of the difficulties of the calculations.

Our recently developed all-valence electron method, named LCVO-MO method, provided the results illustrated in Fig. 1 for methane, ethane, monosilane and disilane.

In Fig. 1 it can be seen that the partial charge of the hydrogens is more positive in methane than in silane. In accordance with the quantumchemical calculations the positive charge of the hydrogens in monosilane can be explained by the effect of the d_{xy}, d_{xz} and d_{yz} orbitals of silicon, which decrease the electron density on the hydrogen atoms because of some back-donation. The bond order of the silicon-hydrogen bond is larger than that of the carbon-hydrogen bond.

It also can be observed that the electrons are found not only along the carbon-hydrogen and silicon-hydrogen bonds but also in the direction of the line connecting the hydrogen atoms. This secondary hydrogen-hydrogen bond order is larger in methane due to the smaller distance.

As far as the bond structure of ethane and disilane is concerned, the bond order of the carbon-carbon bond in ethane is about ~ 1, the analogous silicon-silicon bond order in disilane, however, is larger, its value being about ~ 1.40. On the basis of the calculations it can be concluded that the silicon-silicon bond order consists mostly of the σ connection between the sp³ hybrid orbitals with a value of 1.1525 and in a considerable degree of the so-called

σ—d effect corresponding to the interaction between the sp^3 orbitals and the neighbouring d orbitals. The latter gives a bond order of 0.215. The $(d$—$d)\pi$ interaction can be neglected since its value is 0.0255.

Accordingly the silicon-silicon bond essentially has a σ character which is the consequence of the $(sp^3$—$sp^3)\sigma$ effect and the double $(sp^3$—$d)\sigma$ effects. On the other hand $(d$—$d)\pi$ interaction practically does not occur.

It should mentioned that when hydrogens are replaced by electron-donating substituents, the proportion of the $(d$—$d)\pi$ bond is somewhat increased. This is the case in 1,2-dimethoxy-disilane and 1,2-difluoro-disilane molecules.

There is a $(d$—$p)\pi$ effect, for example, between the d orbitals of silicon and the lone pairs of oxygen and fluorine, respectively, and at the same time
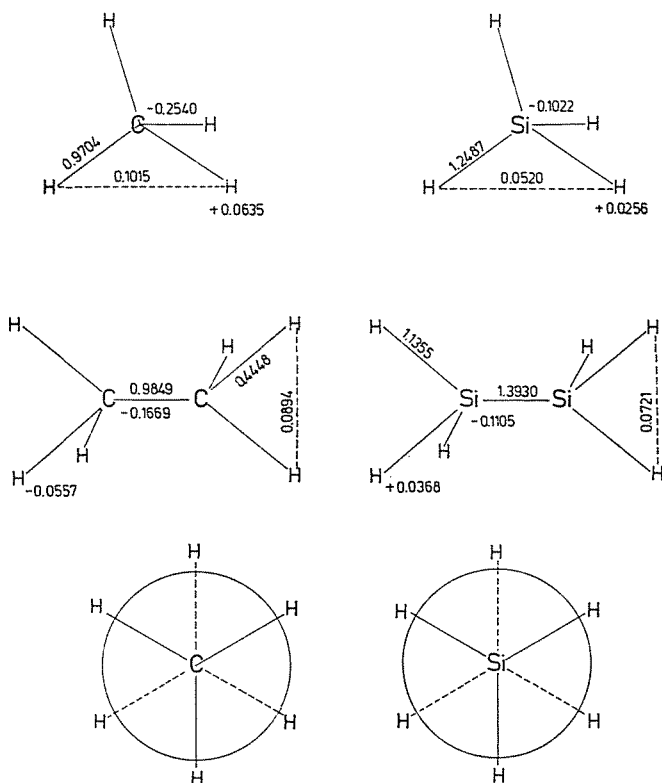
$$P_{SiSi} \; (\sigma) \; = \; 1.1525$$
$$P_{SiSi} \; (\sigma\text{-}d) \; = \; 0.2150$$
$$P_{SiSi} \; (d\text{-}d)\pi \; = \; 0.0255$$

Fig. 1. The partial charge and bond order values of methane, silane, ethane, and disilane.

$$(CH_3O)SiH_2 \longrightarrow SiH_2(OCH_3)$$

$$FSiH_2 \longrightarrow SiH_2F$$

$$CH_2 = CH \longrightarrow Si(CH_3)_2 \longrightarrow Si(CH_3)_2 \longrightarrow CH = CH_2$$

$$\overset{\displaystyle |}{-Si} \overset{1}{\underset{\displaystyle |}{\longrightarrow}} \overset{\displaystyle |}{\underset{\displaystyle |}{Si}} -$$

$$CH_2 \overset{1.9838}{=\!=\!=} CH \overset{1.1789}{\underline{\qquad}} Si \overset{1.0008}{\underline{\qquad}} Si \underline{\qquad} CH = CH_2$$
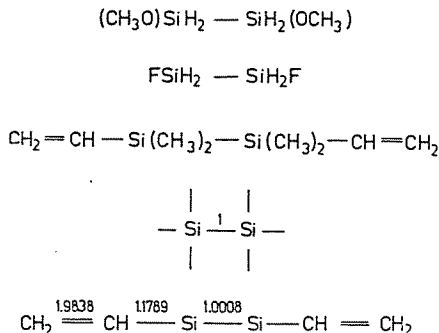
Fig. 2

the $(d-d)\pi$ effect of the two neighbouring silicon atoms also increases because of the transconjugation (Fig. 2).

Taking the silicon-silicon bond order in hexamethyldisilane to be unity and carrying out a simplified quantumchemical calculation, the results show, as can be seen in the figure, that the bond order in the vinyl group of divinyl-tetramethyldisilane is 1.9838, whereas the silicon-carbon bond order is larger than unity, its value is 1.1789, and at the same time the silicon-silicon bond order shows an insignificant increase as compared to disilane (1.0008). These results showed unambiguously that the $(d-d)\pi$ interaction may be neglected even in the case when electron donating groups are attached to silicon.

To interprete the results of both the ultraviolet and photoelectron spectroscopic investigations for linear and cyclic permethylated oligosilanes simplified LCVO-MO calculations were carried out, in which the effect of the methyl groups was neglected, only the silicon atoms in the main chain were included into the calculation and the d orbitals of silicon were not taken into account since their role could be neglected in the first approach as pointed out above.

Table 2 demonstrates that the calculated orbital energies and the corresponding ionization energies show a good correlation. The orbital energies and the ionization energies can be compared on the basis of Koopmans's theorem. The agreement is good between the calculated and experimental ultraviolet singlet transition energies. In the spectrum of the Si_5 linear molecule two absorption bands, which can be calculated independently, overlap each other, and only the mean value of the calculated peaks can be observed as absorption maximum. This calculated value (in brackets) agrees fairly well with the experimental transition energy.

The results confirmed that the effect of silicon d orbitals can be neglected. The splitting of ionization energies and the bathochromic shift with increasing oligomerization degree are the consequence of σ conjugation. The σ conjugation is much larger for silicon-silicon chains as compared with carbon-carbon chains,

Table 2

Orbital energies and electron excitation energies (calculated by C. I.) of permethylated oligosilanes

		E_i	I	$^1E_\nu$ (calc.)	$^1E_\nu$ (exp.)
Si$_2$		−10,90	8.69	6.2321	6.2132
Si$_3$	a$_g$	−11.23	9.14	5.7666	5.7666
	b$_u$	−10.95	8.19		
Si$_4$	a$_g$	−11.36	9.30	5.3030	5.2766
	b$_u$	−11.27	8.76		
	a$_g$	−10.81	7.98		
Si$_5$	a	−11.42		4.5846	
	b	−11.41		5.0669	
	a	−11.11		(4.83)	4.96
	b	−10.76			
cycl. Si$_6$	a$_{1g}$	−11.73	9.78	4.8093	(4.86)
	e$_g$	−11.40	9.12	5.3678	(5.3448)
	e$_u$	−11.12	8.16		
	a$_{1u}$	−10.99	7.79		
cycl. Si$_5$	a$_1'$	−11.7088	9.80		
	e$_2'$	−11.2585	8.91		
	e$_1'$	−11.1202	7.94		

because the diffuse sp^3 hybrid orbital of silicon represents a stronger geminal interaction than that of carbon as a consequence of larger overlapping. The situation is illustrated in Fig. 3.
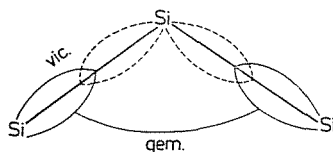
Fig. 3. The vicinal and geminal overlapping of the sp^3 hybrid orbitals in the trisilane molecule

Interesting results were obtained as to the bond order (Fig. 4).

The silicon-silicon bond order assumed to be 1 in disilane is only 0.9882 in trisilane. In this molecule the bond order between the two terminal silicon atoms in geminal position is rather considerable, 0.3721, and this is an evidence of σ-conjugation. In tetrasilane the silicon-silicon bond order decreases again
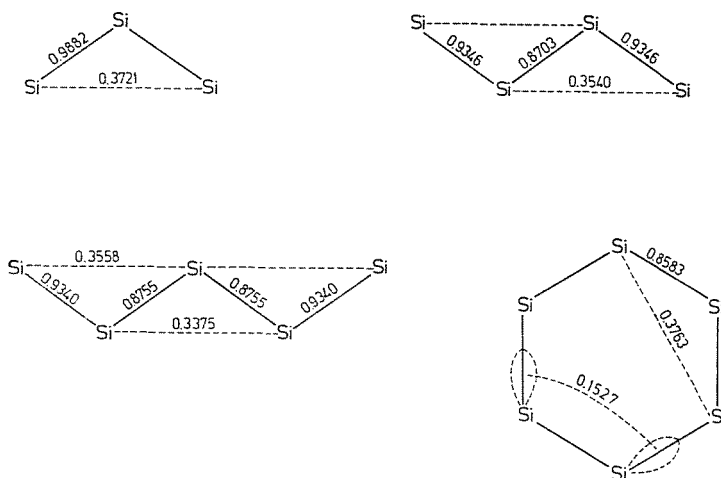

Fig. 4. The bond order of trisilane, tetrasilane, pentasilane and cyclic hexasilane

to 0.8703, but the bond order between silicon atoms in positions 1 and 2 is different. The corresponding values for pentasilane are 0.8755 and 0.9340, respectively. The geminal bond order ranges between 0.3721 and 0.3375. In the cyclic hexasilane the silicon-silicon bond order is the smallest with a value of 0.8583. On the other hand, the largest secondary bond order is found here: its value equals 0.3763. Besides, there is a contribution from the overlap of the sp^3 hybrid orbitals of two neighbouring silicon atoms directed apart from each other. The latter effect cannot be observed, of course, in linear oligosilanes and results in an increased conjugation for cyclic oligosilanes. This fact is responsible for the special properties of cyclic oligosilanes as compared with the linear ones.

The bond order values prove that the strength of the silicon-silicon bond decreases with increasing degrees of oligomerization. For this reason the degradation of oligosilanes at high temperatures increases with the degree of oligomerization.

In Fig. 5 we summarized orbital energy levels in linear and cyclic oligosilanes.

It is clear from this figure that the σ and σ^* levels approach with increasing degree of oligomerization and this results in a bathochromic shift. At the same time more and more one-electron ionization steps have to be observed,

depending on the symmetry of the molecule and on the number of silicon atoms. The calculated energy levels are in a full agreement with the results of photoelectron spectroscopic investigations. Thus one ionization energy appears in the photoelectron spectrum of disilane, two and three ionization energies are characteristic for trisilane and tetrasilane, respectively. Three ionization energies with an intensity ratio of $2 : 2 : 1$ can be observed for cyclic pentasilane, and the spectrum of cyclic hexasilane indicates four ionization energies with an intensity ratio of $1 : 2 : 2 : 1$.
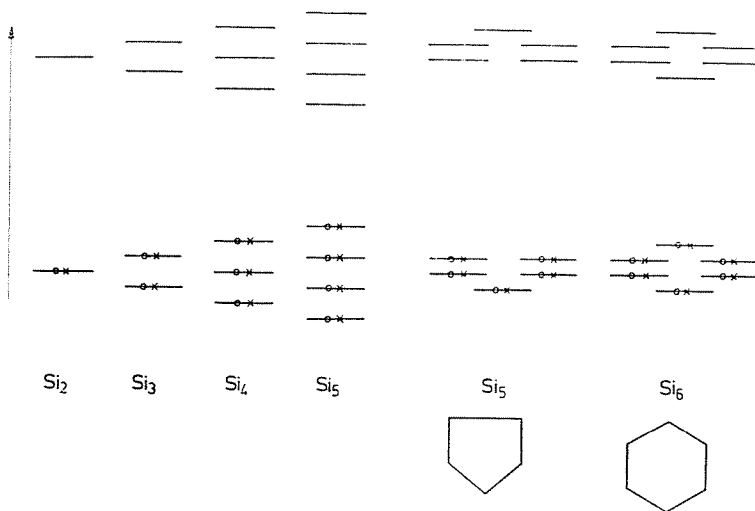

Fig. 5. σ and σ^* energy-levels of oligo-silanes

All our calculated results and the experimental data prove the existance of σ conjugation which is the consequence of the geminal interaction between the diffuse sp^3 hybrid orbitals of silicon atoms. Of course, in addition to this dominant effect there is also a σ—d effect which is superimposed on the σ bond structure. The $(d$—$d)\pi$ effect can be neglected in the interpretation of chemical properties.

Based on the similarity of the carbon-carbon and silicon-silicon bond and on the larger bond distance for silicon it could be expected that the rotational possibility around the silicon-silicon bond axis was hindered in a smaller degree than in the case of the analogous hydrocarbons.

We investigated, in co-operation with prof. Hengge from Graz, the rotation possibilities of some disubstituted tetramethyldisilane derivatives by means of dipolmetry [4]. We studied the effect of the following substituents: hydrogen, fluorine, chlorine, bromine, iodine, methoxy, methylthio.

On the basis of the data in Table 3 it can be seen that for all derivatives, with the exception of the hydrogen compound, the experimental dipole moment

<div align="center">

Table 3

Dipole moments and conformation data of $X_2Si_2(CH_3)_4$

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X	μ_{exp} D.	μ_{rot} D.	$\Delta\mu$	μ_t	μ_g	$x_{\bar{g}}$
H	1.25	1.25	0	0	1.533	—
F	1.91	2.294	0.384	0	2.809	0.4623
Cl	1.96	2.800	0.840	0	3.429	0.3267
Br	1.78	3.147	1.367	0	3.854	0.2133
I	1.47	3.28	1.810	0	4.017	0.1339
OCH_3	1.38	2.161	0.781	1.396	3.872	0
SCH_3	1.86	2.245	0.385	1.615	3.629	0.0810

is smaller than the calculated value, assuming free rotation. The difference between the experimental and calculated values increases with larger sterical requirement of the substituent. The molar fraction of the gauche conformation "X_g" can be calculated using the following equation:

$$X_g = \frac{\breve{\mu}^2 - \mu_t^2}{\mu_g^2 - \mu_t^2}$$

where $\breve{\mu}$ is the experimental dipole moment, μ_g and μ_t the dipole moments belonging to the gauche and trans conformation, respectively. The data in Table 3 show that steric hindrance increases in the following order: H < F < < Cl < Br < I < SCH_3 < OCH_3. There is practically free rotation in the case of hydrogen substitution, and the rotation is totally hindered for the methoxy derivative where only the trans position is possible.

It is known from similar investigations that in 1,2-dichloroethane the gauche conformation represents only 19 mol percents, whereas in the analogous 1,2-dichlorotetramethyldisilane the ratio of the gauche conformation is 33%. This result proves that the larger silicon-silicon bond distance as compared with the carbon-carbon bond provides a larger rotational possibility in accordance with our mentioned findings.

Summary

1. It was found that the silicon-silicon bond is similar to the carbon-carbon bond. In the case of oligosilanes the difference between the two kinds of bonds appeared in the σ conjugation of greater extent for silicon, owing to the more diffuse sp^3 hybrid orbitals of silicon, and this results in larger splitting of the ionization energies and in a more considerable bathochromic shift in the ultraviolet absorption values.

2. The longer silicon-silicon bond offers a larger rotational possibility for silicon derivatives.

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