THE MOLECULAR ASSOCIATION OF SMALL ORGANOSILICON HETEROCYCLES AND THEIR ANALOGS

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The molecular association of derivatives of the 1-silacycloalkanes $CH_2(CH_2)_{n-1}SiXY$ and their saturated and unsaturated noncyclic analogs has been studied by cryoscopy in cyclohexane. It has been established that in this series of heterocycles the tendency to association falls with an increase in their size and is a maximum in the case of the silacyclobutanes (n = 4). Derivatives of 1-silacyclobutane are associated considerably more strongly than their noncyclic analogs $CH_2{=\!=}CH(CH_3)XiXY$ and $CH_3CH_2(CH_3)SiXY$. The relationship found between the degree of association and the structure is in harmony with the results of studies of molecular association by UV spectroscopy and also with data on reactivities.

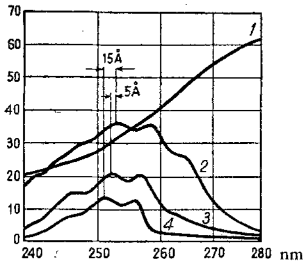
Recently, Voronkov and Deich [1], using cryoscopy in cyclohexane, have demonstrated the association of the chloro(organyl)silanes. They came to the conclusion that the main factor determining the degree of association of compounds of the type R_nSiX_{4-n} (n = = 1–3) is the steric effect of the organic substituents on the silicon atom. In particular, it was found that an increase in the length of the n-alkyl radicals in the alkylchlorosilanes substantially lowers the degree of association. Branching of the alkyl radicals suppresses association to an even greater extent.

In the opinion of these authors [1], the molecular association of the chlorosilanes in nonpolar solvents (for cyclohexane $\mu = 0$) is due to the partial transition of the unshared pairs of electrons of the chlorine atoms into the vacant 3d orbitals of the silicon atom of another molecule.

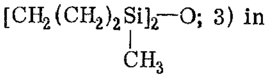
Derivatives of 1-silacyclobutane are characterized by an anomalous reactivity both in substitution on an endocyclic silicon atom [2–5] and in the case of addition to the Si—C bond of the ring [6–8]. In our opinion, this is due to structural features of the endocyclic silicon atom [9] in the silacyclobutanes and, particularly, to the favorable conditions in the case of these compounds for the formation of transition complexes with hybridization of the sp^3d or the sp^3d^2 type [10, 11].

In view of this, we have carried out an investigation of the donor-acceptor interaction in strained four-membered organosilicon heterocycles by various physicochemical methods.

Efimova and Babich [2] have studied the capacity for molecular association of some organosilicon heterocycles by UV spectroscopy. The absorption spectra of pyridine in solutions of various organosilicon compounds show that the greatest bathochromic displacement and increase in intensity are found in the case of 1,1-dimethyl-1-silacyclobutane (as compared with 1,1-dimethyl-1-silacyclopentane and some cyclic tetraalkylsilanes). In the case of the disiloxane $[CH_2(CH_2)_2Si(CH_3)]_2O$, this effect, calculated to one $CH_2(CH_2)_2Si(CH_3)$ group, decreases (see figure). This phenomenon is apparently a consequence of donor-acceptor interaction of the $CH_2(CH_2)_2Si\!<\!\leftarrow\!NC_5H_5$ type.



UV absorption spectra of pyridine in various solvents: 1) pure solvent; 2) in the disiloxane

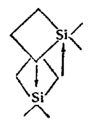

$[\underset{\displaystyle CH_3}{CH_2(CH_2)_2\overset{}{Si}}]_2\text{—}O$; 3) in

dimethylsilacyclobutane; 4) in hexane.

The smaller bathochromic shift in the case of 1-silacyclobutane derivatives, in which there is an electron-donating substitutent on the endocyclic silicon atom is in good agreement with this hypothesis. All the effects mentioned, although they do lie outside the range of experimental error, are nevertheless very slight.

In this work we have studied the molecular association of organo-silicon heterocycles and some of their noncyclic analogs by the method used by Voronkov and Deich [1]. The results obtained are given in the table.

It can be seen from this that the highest capacity for association in all the series investigated (compounds I–IV, VIII, X) are possessed by derivatives of 1-silacyclobutane. At the same time, in contrast to Voronkov and Deich's results, association is found not only in the case of the chlorosilanes but to an equal extent for the silahydrocarbons. In the latter case there is possibly intermolecular interaction of the type:



The degree of association in the series of 1,1-dimethyl-1-silacycloalkanes $CH_2(CH_2)_{n-1}Si(CH_3)_2$ (compounds

Table

Molecular Weights and Degrees of Dissociation (a) of the Silacycloalkanes and Their Analogs

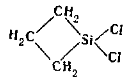
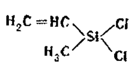
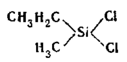
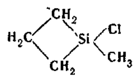
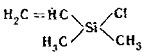
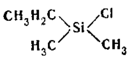
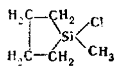
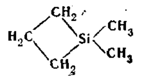
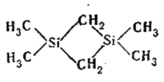
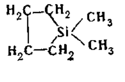
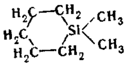
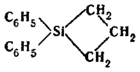
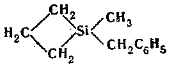
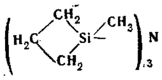
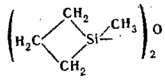
Compound	Formula	C, g/kg	Δt, °C	Molecular weight		a=M/M'
				found (M)	calculated (M')	
I		5.33 9.80 18.80	0.518 0.955 1.809	208.1 208 210	141	1.48 1.48 1.49
II		4.36 8.58 15.32	0.480 0.940 1.664	183.5 184.8 186	141	1.30 1.31 1.32
III		5.10 7.15 13.22	0.587 0.810 1.502	175 178.3 178	143	1.23 1.25 1.25
IV		6.10 10.50 15.25	0.722 1.252 1.840	170.3 169 167	120.5	1.41 1.40 1.39
V		4.10 7.44 12.42	0.682 1.231 2.079	121.1 122 121	120.5	1.00 1.01 1.00
VI		4.33 8.59 13.25	0.565 1.115 1.740	154.5 156 154	122.5	1.26 1.28 1.26
VII		7.15 11.90 20.40	0.841 1.370 2.360	172 176 175	157	1.24 1.23 1.24
VIII		4.31 8.35 10.91	0.618 1.225 1.587	141 139 139.8	100	1.41 1.39 1.40
IX		4.35 8.19 13.70	0.599 1.151 1.914	143 143.4 144.5	144	1.0 1.0 1.0
X	$(CH_3)_3SiCH{=}CH_2$	3.91 7.73 11.70	0.675 1.565 1.970	117 118 120	100	1.17 1.18 1.20
XI	$ClCH_2Si(CH_3)_3$	4.10 8.15 14.05	0.527 1.057 1.840	157 156 154	122.5	1.28 1.27 1.26
XII	$Cl_2CHSi(CH_3)_3$	6.84 11.38 18.91	0.710 1.192 1.960	195 192 194.5	157	1.24 1.23 1.24
XIII		4.34 6.29 14.11	0.630 0.920 2.055	139 137.8 139	114	1.22 1.20 1.22

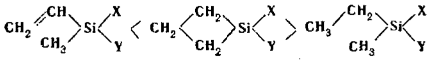
Table (continued)

Compound	Formula	C, g/kg	Δ*t*, °C	Molecular weight		*a*=*M*/*M'*
				found (M)	calculated (M')	
XIV		6.43 6.03 18.28	0.970 0.910 2.740	134 134 134.6	122	1.10 1.10 1.11
XV		5.20 9.81 15.69	0.476 0.891 1.570	220 222 220	224	1.0 1.0 1.0
XVI		4.73 9.58 14.60	0.555 1.118 1.700	172.2 173 173	176	1.0 1.0 1.0
XVII		7.07 12.83 18.10	0.545 0.980 1.380	262 265 265	269	1.0 1.0 1.0
XVIII		4.76 8.56 13.39	0.541 0.957 1.498	178 182 180.2	186	1.0 1.0 1.0
XIX	$[(CH_3)_3Si]_3N$	4.71 7.72 14.30	0.417 0.676 1.255	228 231 230	233	1.0 1.0 1.0
XX	$[CH_2=CH(CH_3)_2Si]NH$	4.83 8.39 11.89	0.540 0.947 1.330	180 179 180	185	1.0 1.0 1.0

VIII, XIII, XIV) decreases with an increase in the size and dimensions of the ring.

This feature is in agreement with the dependence of the reactivity on the size of the ring observed in a number of reactions [2–5].

In all cases, the degree of association of the silacyclobutanes is higher than for their saturated and unsaturated noncyclic analogs:



$X = Y = CH_3$, Cl or $X = CH_3$, $Y = Cl$

In the case of compounds with a well-defined "τ effect" (silazanes, siloxanes, and compounds with phenyl radicals on the silicon atoms: XV, XVII–XX), as in the case of organosilicon compounds containing carbofunctional groups with a negative inductive effect (XI, XII, the degree of association depends both on the steric factor and on the inductive effect and the "τ effect" of the substituents. However, it is difficult to evaluate the contribution of each of the effects mentioned by using the results of only the method described.

EXPERIMENTAL

All the compounds studied were carefully purified by distillation through a column or in vacuum. Their purity, checked by gas-liquid chromatography, was not less than 99%, and their physical constants (bp, n_D^{20}, d_4^{20}) corresponded to literature data.

The molecular weights, determined by the cryoscopic method, were close to the calculated values. Chemically pure cyclohexane was dried over sodium and was twice redistilled through a column over sodium. The molecular weight was calculated from the formula $M = KC/\Delta t$, where K is the cryoscopic constant (For C_6H_{12}, K = 20.2° C) [12], C is the concentration of the substance studied in 1000 g of solvent, and Δt is the depression of the melting point of the solution (in ° C).

The degree of association a was determined from the ratio $a = M/M'$, where M is the experimental and M' the theoretical value of the molecular weight.

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