# NITROGEN-CONTAINING ORGANOSILICON COMPOUNDS

## XI. Dipole Moments and Structure of Some Azasilacyclanes*

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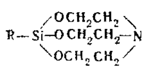
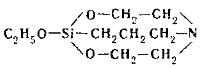
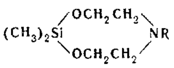
The dipole moments of 1-ethoxy-2-carbasilatrane (1-ethoxy-2,8-dioxa-5-aza-1-silabicyclo [3,3,3]undecane (II)), and of 1,1-dimethyl-2,8-dioxa-5-aza-1-silacyclooctane (III) have been investigated. The presence of a transannular Si←N coordination bond (weaker than in the 1-ethoxysilatrane I) in II and its absence from III has been established.

An investigation of the dipole moments of the silatranes I has enabled the existence of a transannular donor-acceptor Si←N bond in these compounds to be demonstrated [2]. Its presence is also shown by the inertness of I to methyl iodide [3].


I


II


III

a R=H; b R=$CH_3$

The rate of neutralization of II with perchloric acid in glacial acetic acid [4] considerably exceeds the rate of neutralization of the silatranes (I) which may be connected with the decrease in the transannular interaction of the Si and N atoms in II because of the replacement of one of the electronegative oxygen atoms by a methylene group. Some decrease in the Si ← N donor-acceptor interaction in II as compared with the 1-ethoxysilatrane I (R = $C_2H_5O$) is also shown by the measurement of the dipole moment of II that we have carried out. However, the relatively high exaltation (3.9 D) of the experimental value of the dipole moment of II (4.71D) as compared with that calculated without taking the Si ← N donor-acceptor interaction into account (0.8 D) indicates the presence of an Si ← N coordination bond in these compounds. In agreement with this, II does not react with methyl iodide even on prolonged heating.

The cyclic organosilicon diethanolamine derivative III has also been ascribed a structure with a pentacovalent silicon atom [5, 6]. However, compound IIIb, unlike I and II, reacts vigorously with methyl iodide forming the corresponding methiodide. The measured dipole moments of IIIa and IIIb are 2.83 and 2.52 D, respectively. These values are only 0.5–1 D higher than the moments calculated for the fixed "boat" and "crown" configurations and show the absence of a well-defined donor-acceptor bond between the nitrogen and silicon atoms in these compounds.

## EXPERIMENTAL

Compound II was obtained by the reaction of 3-aminopropyltriethoxysilane with ethylene oxide in ethanolic solution [7], IIIa was synthesized from dimethyl bis(ethylamino)silane and diethanolamine [1], and IIIb was obtained for the first time (from diethoxydimethylsilane and N-methyldiethanolamine by the method of Voronkov and Romadan [8]). IIIb: bp 55° C (5 mm), $n_D^{20}$ 1.4475, $d_4^{20}$0.9914, $MR_D$ 47.29. Found, %: C 48.08; H 9.82; N 7.85. Calculated for $C_7H_{17}NO_2Si$, %: C 47.96, H 9.77, N 7.99; $MR_D$ 47.37. Methiodide of IIIb. Found, %: I 40.33. Calculated for $C_8H_{20}INO_2Si$, %: I 40.00.

The dipole moments were determined by benzene solution at 25° C by the method of heterodyne beats [9]. The molecular refractions were calculated from the refractive indices of benzene solutions. The atomic polarization was taken as 15% of $MR_D$. The experimental figures and the calculated values of the dipole moments are given in the table.

## REFERENCES

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Dipole Moments of II and III

| Compound | $f_n$, molar fractions | ε | d | $MR_D$ | $\mu_{exp}$, D | $\mu_{calc}$, D | $\mu_{exp} - \mu_{calc}$, D |
|---|---|---|---|---|---|---|---|
| $C_6H_6$ | 0.000000 | 2.2740 | 0.8734 | | | | |
| I (R=$C_2H_5O$) | | | | | 6.29* | 0.5 | 5.8 |
| II | 0.000564 | 2.2833 | 0.8739 | 56.02 | 4.71 | 0.8 | 3.9 |
| | 0.000870 | 2.2936 | 0.8740 | | | | |
| | 0.000886 | 2.3020 | 0.8741 | | | | |
| | 0.001179 | 2.3178 | 0.8744 | | | | |
| IIIa | 0.002586 | 2.3087 | 0.8740 | 42.33 | 2.83 | 2.3**<br>1.8*** | 0.5<br>1.0 |
| | 0.004699 | 2.3363 | 0.8741 | | | | |
| | 0.008535 | 2.3514 | 0.8744 | | | | |
| IIIb | 0.003913 | 2.3116 | 0.8748 | 42.29 | 2.52 | 2.0**<br>1.9*** | 0.5<br>0.6 |
| | 0.004976 | 2.3170 | 0.8750 | | | | |
| | 0.005009 | 2.3226 | | | | | |
| | 0.005214 | 2.3224 | 0.8749 | | | | |

*Literature data [2].
**"Crown" form.
***"Boat" form.

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*For part X, see [1].

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# PHENOLIC DERIVATIVES OF 2-PYRONE

## II. Transformations of 1,1-Dichloro-5-(2',5'-dimethoxyphenyl)-1,3-pentadien-5-one*

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The cyclization of 1,1-dichloro-5-(2',5'-dimethoxyphenyl)-1,3-pentadien-5-one and the product of its partial demethylation leading to the corresponding derivatives of 2-pyrone and 2-(β,β-dichlorovinyl)-6-methoxy-4-chromanone has been studied. Irradiation causes the dimerization of 1,1-dichloro-5-(2',5'-dimethoxyphenyl)-1,3-pentadien-5-one.

During its formation from 2,5-dimethoxyacetophenone and 1, 1, 1, 3-tetrachloro-3-ethoxypropane, 1,1-dichloro-5-(2',5'-dimethoxyphenyl)-1,3-pentadien-5-one (I) undergoes partial demethylation to 1,1-dichloro-5-(2'-hydroxy-5'-methoxyphenyl)-1,3-pentadien-5-one (II). The structure of II has been confirmed by independent synthesis and by its conversion into I. Compound II, like 1,1-dichloro-5-(2'-hydroxyphenyl)-1,3-pentadien-5-one [1] can be cyclized in two directions—with the formation of 6-(2'-hydroxy-5'-methoxyphenyl)-2-pyrone (III) and of 2-(β,β-dichlorovinyl)-6-methoxy-4-chromanone (IV). Under the same conditions, I gives only 6-(2',5'-dimethoxyphe-

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*For part I, see [1].

Properties and Analytical Data of the Compounds Synthesized

| Compound | Mp, °C | UV spectra* | | IR spectra** | | Empirical formula | Found, % | | | Calculated, % | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\lambda_{max}$, nm | log ε | $\nu_{C=O}$, см$^{-1}$ | $\nu_{OH}$, см$^{-1}$ | | C | H | Cl | C | H | Cl | |
| I | 106–107 | 372; 298,5; 220 | 3.628; 4.421; 4.162 | 1646 | — | $C_{13}H_{12}Cl_2O_3$[a] | 54.69 | 4.00 | 24.33 | 54.37 | 4.21 | 24.70 | 90.1 |
| II | 108–109 | 310; 407; 220 | 4.441; 3.682; 4.104 | 1575 | —[b] | $C_{12}H_{10}Cl_2O_3$ | 52.56 | 3.76 | 26.27 | 52.77 | 3.69 | 25.96 | 80.5 |
| V | 98–99 | — | — | 1725 | — | $C_{13}H_{12}O_4$ | 67.03 | 5.09 | — | 67.23 | 5.21 | — | 95.8 |
| III | 161.5–162.5 | 375; 325; 242; 221 | 4.100; 3.886; 3.823; 4.328 | 1702 | 3210 | $C_{12}H_{10}O_4$ | 65.84 | 4.55 | — | 66.05 | 4.62 | — | 30.0 |
| IV | 86–86.5 | 350; 256; 225,5 | 3.582; 3.886; 4.386 | 1690 | — | $C_{12}H_{10}Cl_2O_3$ | 52.61 | 3.80 | 25.86 | 52.77 | 3.69 | 25.96 | 18.0 |
| VI | 142–142.5 | 338; 252 | 3.894; 4.130 | 1666 | — | $C_{26}H_{24}Cl_4O_6$[c] | 54.70 | 4.20 | 24.72 | 54.37 | 4.21 | 24.70 | 100.0 |

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* EPF-3 ultraviolet spectrophotometer, solvent ethanol.

** UR-10 infrared spectrophotometer, in the form of a mull in paraffin oil.

[a] 2,4-Dinitrophenylhydrazone of **I**—mp 192-193° C. Found, %: N 11.96. Calculated for $C_{19}H_{16}Cl_2N_4O_6$, %: N 11.99. [b] Absent because of a hydrogen bond. [c] Molecular weight, found: 570 (cryoscopically); calculated: 574.