Reports of the Academy of Sciences of the USSR

Academician K. A. ANDRIANOV, E. I. FEDIN,

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1965. Vol. 163, No. 4

CHEMISTRY

Academician K. A. ANDRIANOV, E. I. FEDIN,
G. V. KOTRELEV, I. V. GORSKAYA

HIGH-RESOLUTION PROTON MAGNETIC RESONANCE OF ORGANOCYCLOSILAZANES

A study of the structure of methylvinylcyclosilazanes by means of infrared and ultraviolet spectroscopy showed that in these compounds there is interaction between the π-electrons of the double bond and the free d-orbitals of silicon (^{1}). Taking into account the possibility of delocalization of the free electrons on nitrogen with the formation of a single conjugated system along the contour of the ring, one might expect an effect of transmission of conjugation of different vinyl groups through the silazane ring. However, in the cited work it was noted that the absorption coefficient of the vinyl group ε in the ultraviolet spectrum has a value not characteristic of an aromatic system of conjugated bonds. Apparently, in the present case, because of the asymmetry of the heterocyclic molecule, the most energetically favorable conformation is not planar, but a chair-shaped conformation, characteristic of saturated carbon rings of the cyclohexane type.

Such a structure of methylvinylcyclosilazanes, as well as of other cyclosilazanes with different substituents at the silicon atom, precludes the formation of an aromatic system with equalized electron density, since overlap of the p-electron clouds of the nitrogen pair and the d-orbitals of silicon in different parts of the molecule will be nonuniform. In this case, a system of localized three-center bonds may possibly be formed.

It was of definite interest to study the structure of various organocyclosilazanes by the method of high-resolution proton resonance—

Table 1

No.	Compound	δ, ppm: CH_3	δ, ppm: R_{aliph}	δ, ppm: R_{arom}	δ, ppm: $R_{alkynyl}$	
1	$((CH_3)_2SiNH)_3$	0.38				1.04
2	$((CH_3)_2SiNH)_4$	0.52				1.30

No.	Compound	δ, ppm: CH_3	δ, ppm: R_{aliph}	δ, ppm: R_{arom}	δ, ppm: $R_{alkynyl}$	
3	$(CH_3C_2H_5SiNH)_3$	0.350.47	0.800.87			1.11
4	$(CH_3C_4H_9SiNH)_3$	0.200.47	0.770.95			1.10
5	$(CH_3C_8H_{13}SiNH)_3$	0.180.44	0.84			1.19
6	$(CH_3C_6H_5SiNH)_3$	0.380.73		8.008.30		1.10
7	$(CH_3)_5C_6H_5(SiNH)_3$	0.380.59		7.888.18		1.38
8	$(CH_3CH_2 =$ $CHSiNH)_3$	0.380.80			6.00	
9	$(CH_3CH_2 =$ $CHSiNH)_4$	0.380.78			6.02	
10	$(CH_3)_3Si-$ $NH-$ $Si(CH_3)_3$	0.11				1.30
11	$C_6H_5\backslash Si-$ $NH-$ $Si/C_6H_5(CH_3)_2$	0.11		7.417.60		0.53
12	$(C_6H_5)_2\backslash SiNHSi(CH_3)_3CH_3/$	0.10		7.768.01		0.71

and, on the basis of the chemical shifts of various protons, to draw conclusions about the distribution of electron density in the organosilazane ring. A study of six- and eight-membered dialkyl-, alkyl-, aryl-, and alkylalkynylcyclosilazanes showed that the chemical shift of the protons at nitrogen does not depend on the structure of the rings or on their organic substituents and is close to the chemical shift of linear organocyclosilazanes (Table 1). The magnitude of the chemical shift of the protons at nitrogen in organocyclosilazanes and in linear organosilazanes is close to that for organic secondary amines and differs sharply from the magnitudes of the chemical shifts of protons at nitrogen in organic nitrogen-containing conjugated cyclic systems. These data are consistent with the concept of the nonplanar structure of the indicated organocyclosilazanes. Confirmation of the nonplanar structure of silazane rings is also provided by the splitting of the peaks of the protons of the methyl groups at silicon. Thus, from literature data it is known that the protons of methyl groups located in axial and equatorial positions with respect to the plane of the ring give different chemical shifts (2). In this case, the organocyclosilazane should have the following spatial structure:

Spatial structure of organocyclosilazane ring

where R is alkyl, aryl, or alkenyl; *a* is the axial direction of the bond; *e* is the equatorial direction of the bond.

Such a structure corresponds to the trans isomer, the formation of which is always possible under the conditions of ammonolysis of diorganodichlorosilanes.

In this approach to the structure of organocyclosilazanes, it is also necessary to take into account the fact that, in addition to the above chair-type conformation, the presence of energetically less favorable bath-type conformations and others, as well as their mutual interconversion, is possible. Replacement of one methyl group at each silicon atom in dimethylcyclosilazanes by other organic groups will apparently hinder the transition from one conformation to another. As a result, fixation of a definite conformation will occur.

Hence it is clear that the size and nature of the organic radicals at the silicon atom will have a considerable influence on the structure of organocyclosilazanes, and this, in turn, should be reflected in the nuclear magnetic resonance spectra.

Thus, from the data in Table 1 it is evident that, in the case of dimethylcyclosilazanes, only one peak is observed, corresponding to the protons of the methyl groups. The methyl groups in these rings, owing to conformational transitions, are equivalent, as a result of which splitting of the peaks of the corresponding protons does not occur. Compounds 3, 4, 5, 6, 7, 8, and 9 have a distinctly expressed splitting of the peaks of the methyl-group protons, which indicates the presence of nonplanar conformations.

Thus, our investigations of organocyclosilazanes by the method of nuclear magnetic resonance show the absence of a single conjugated system in the ring as a consequence of failure to satisfy the principal condition for the formation of aromatic systems—coplanarity. Despite the interaction of the unshared electron pair of nitrogen with the *d*-orbitals of silicon, the σ-bonds impose definite restrictions on electron delocalization with the formation of an aligned electron cloud along the contour of the ring.

Experimental Part

Compounds 1, 2, 3, 6, 7, 8, 9, 10, 11, 12 (Table 1) were obtained as a result of the ammonolysis reaction of the corresponding organochlorosilanes according to the following procedure: gaseous ammonia was passed through a 20% solution of the organochlorosilane in benzene at a temperature of 20–25° until complete neutralization of the chlorosilane; the ammonium chloride was filtered off, the benzene was distilled off from the solution, and the ammonolysis products were distilled under vacuum. The constants of the isolated organosilazanes agreed with the literature data.

Compounds 4 and 5 were obtained by the same procedure and had the following constants: $(CH_3C_4H_9SiNH)_3$. B.p. 126–128° C / 1 mm; n_D^{20} 1.4600; d_4^{20} 0.9074. $(CH_3C_6H_{13}SiNH)_3$. B.p. 171–173° C / 1 mm; n_D^{20} 1.4642; d_4^{20} 0.8938.

The spectra of the organosilazanes were recorded at room temperature on a TsLA-5535 instrument. The operating frequency was 40 MHz. Magnetic field sweep was used. For recording the spectra, 10% solutions of the substances under study in CCl_4 were prepared. TMS was used as the reference standard.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
15.III.1965

Cited Literature

1. K. A. Andrianov, I. Khaiduk, L. M. Khananashvili, DAN, **150**, No. 1, 93 (1963).

2. L. W. Breed, R. L. Elliott, Inorg. Chem., **3**, No. 11, 1622 (1964).

Note: Figure translations are in progress. See original paper for figures.