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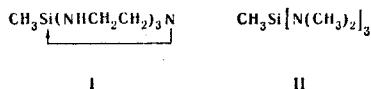
¹H, ¹³C, and ²⁹Si NMR SPECTRA OF 1-METHYLAZASILATRANE

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Considerable shielding of the ¹H and ²⁹Si nuclei due to transannular nitrogen–silicon coupling, which is expressed more clearly than in the case of silatranes, was established on the basis of ¹H, ¹³C, and ²⁹Si NMR data for the methylsilyl group in 1-methyl-2,5,8,9-tetraaza-1-silatricyclo[3.3.3.0^{1,5}]undecane (1-methylazasilatrane) and a comparison of these data with the data for the methyl[tris(dimethylamino)]silane model. It is shown that the change in the hybridization of the silicon atom associated with the increase in its coordination number is not only reflected in the chemical shifts but also leads to an increase in ¹J_{CH} and ²J_{SiH}.

We have measured the chemical shifts of the ¹H, ¹³C, and ²⁹Si nuclei and the constants of spin–spin coupling between them for the methylsilyl group in the molecules of the recently synthesized 1-methyl-2,5,8,9-tetraaza-1-silatricyclo[3.3.3.0^{1,5}]undecane [1-methylazasilatrane (I)] [1] and the model compound methyl[tris(dimethylamino)]silane (II) (Table 1).



The existence of transannular nitrogen–silicon coupling in the I molecule ensures appreciably greater, as compared with II, shielding of the hydrogen and silicon-29 nuclei of the CH_3-Si fragment. The difference in the ²⁹Si chemical shifts in these compounds is also due to the paramagnetic contribution (+16 ppm) [2] of the three "additional" methyl groups attached to the nitrogen atom in model compound II. Thus the contribution of the $\text{N} \rightarrow \text{Si}$ coordinate bond to shielding of silicon-29 in 1-methylazasilatrane I is ~ 34 ppm. According to our data, the differences in the chemical shifts of silicon-29 between organylsilatranes $\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$ and the corresponding organyltrioxysilanes $\text{RSi}(\text{OCH}_2\text{CH}_3)_3$ are 20–25 ppm. It may therefore be assumed that the transannular nitrogen–silicon coupling in the azasilatranes is expressed more clearly than in silatranes. The latter assumption is also in agreement with the results of a study of the dipole moments of these compounds [1].

The change in the hybridization of the silicon atom in the I molecule due to the increase in its coordination number leads to an appreciable decrease in its electronegativity. This is reflected not only in the ¹H and

TABLE 1. Parameters of the NMR Spectra of 1-Methylazasilatrane and Methyl[tris(dimethylamino)]silane

Compound	Chemical shifts, ppm			SSCC, Hz	
	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	$\delta(^{29}\text{Si})$	^{13}C	^{29}SiH
I	-0,37	+2,46	-68,5	113,7	5,6
II	-0,01	-6,36	-16,3	117,2	6,3

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²⁹Si chemical shifts but also in the ¹J_{CH} and ²J_{SiH} constants, which are lower in the case of I than in the case of II. The shift in the resonance of the ¹³C atom in the methyl group of I, as compared with II, to weak field is apparently due to the change in the three-dimensional structure of the silicon atom (the silicon atom in sila-tranes has a trigonal-bipyramidal configuration, whereas in silanes it has a tetrahedral configuration). An indirect confirmation of this is afforded by the shift to weak field of the signals of the alkyl substituent in the ¹³C NMR spectra of alkyltrichlorostannanes during complexing [3].

We noted similar changes in ¹J_{CH}, ²J_{SiH}, and δ (¹³C) during a comparison of the NMR spectra of methyl-triethoxysilane.

EXPERIMENTAL

The synthesis of I and II was described in [1]. The measurements were made from 10% solutions of the compounds in chloroform (with tetramethylsilane as the internal standard) with a Tesla BS 487C NMR spectrometer equipped with an adapter (developed in the Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR) for heteronuclear ¹H-²⁹Si double resonance [4].

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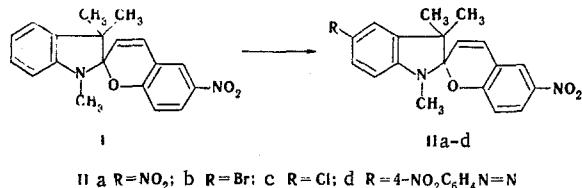
SOME SUBSTITUTION REACTIONS IN A NUMBER OF PHOTOCHEMICAL INDOLINE SPIROCHROMENES

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The corresponding 5-substituted compounds are formed in the halogenation, nitration, and diazo coupling of 1,3,3-trimethyl-6'-nitroindoline-2-spiro-2'-[2H]chromene.

A large amount of research has been devoted to synthetic and photochemical studies in the series of photochromic spirochromenes, but very little study has been devoted to the chemical properties of these compounds, which are of importance in both a theoretical and practical respect. Continuing our research on the reactivities of indolinespirochromenes [1], we accomplished the halogenation, nitration, and diazo coupling of spirochromene I.



The nitration of spirochromene I by the action of nitric acid in acetic anhydride or in concentrated sulfuric acid and by treatment with sodium nitrite in acetic acid and subsequent oxidation of the resulting nitroso compound by air oxidation lead smoothly to the corresponding 5-nitro-substituted spirochromene (IIa). We confirmed the structure of the spirochromene by alternative synthesis from 5-nitro-1,3,3-trimethyl-2-methyleneindoline (V) and 5-nitrosalicylaldehyde:

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