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The Physical Chemistry of Silatranes

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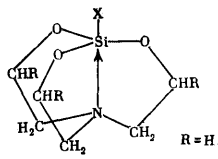
The present state and evolution of the theoretical ideas concerning the steric and electronic structures of silatranes as well as certain characteristics of their reactivity are analysed critically. The decisive influence of the hypervalent X-Si ← N bond on the physicochemical and spectroscopic characteristics of silatranes is demonstrated.
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I. INTRODUCTION

The considerable interest in the chemistry of silatranes arose primarily because they have been found to include a number of substances with high and specific biological activities[1-4].



R = H, CH_3, or CF_3.

The molecular structure of silatranes is of special interest, since they are the first representatives of stable inner-complex organic derivatives of pentacoordinate silicon and have been studied in very high detail by a wide variety of physical methods. The development of the theory of their structure is undoubtedly an important contribution to the creation of the theoretical foundations and practical chemistry of metalloatranes. The aim of this review is to describe the present state and evolution of the theoretical ideas about the steric and electronic structures of silatranes and to discuss certain features of their reactivity.

II. 1-SUBSTITUTED SILATRANES

The first mention of silatranes appeared in 1960–1961 in a patent[5] and in a letter to the Editor[6]. They reported the formation of silatranes by the reaction of organyltriethoxysilanes $XSi(OC_2H_5)_3$ with tris-(2-hydroxyethyl)amine $(HOCH_2CH_2)_3N$:

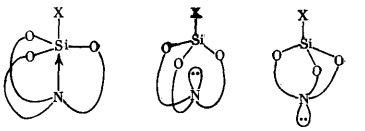
$$XSi(OC_2H_5)_3 + (HOCH_2CH_2)_3N \rightarrow XSi(OCH_2CH_2)_3N + 3C_2H_5OH .$$

The formation of silatranes in this reaction is unexpected, because the interaction of two trifunctional reagents as a rule results in the formation of polymers. Subsequent comparison of the chemical properties of silatranes and model compounds—organyltriethoxysilanes and triethanolamine—enabled the authors[6] to arrive at the following findings: (1) the nitrogen atom in silatranes is inert with respect to methyl iodide; (2) silatranes are more resistant to hydrolysis than the corresponding triethoxysilanes. On this basis, it was in fact suggested[6] that silatranes are the first representatives of organic compounds of pentacoordinate silicon containing the hitherto unknown intramolecular coordinate bond Si ← N.

Owing to the outward attractiveness and simplicity of this hypothesis, the absolute majority of the results of subsequent studies on silatranes were interpreted within its framework without further stipulations[1,2,7]. However, the above facts can be accounted for qualitatively without resorting to this hypothesis. For example, the reduced basicity of the nitrogen atom can be regarded as a consequence of the steric inaccessibility of its lone electron pair (LEP) in the *endo*-form of the silatrane molecule, stabilised by non-valence and electrostatic interaction. Below we shall attempt to analyse critically the results of physicochemical studies on silatranes from the standpoint of the choice of one of the two alternative hypotheses.

1. The Steric Structure

The classical theory of the structure of organic compounds permits three possible structures of silatranes[1]:



(Ia) (Ib) (Ic)

Structure (Ia) is planar-concave with a pentacoordinate silicon atom and a tetracoordinate nitrogen atom; structure (Ib) is convex-concave with a tetracoordinate silicon atom and a tervalent nitrogen atom; structure (Ic) (*exo*) is convex-convex and the heteroatoms are in the same valence state as in structure (Ib). Structure (Ic) can be rejected for silatranes on the grounds that the nitrogen atom in silatranes lacks basic properties[1,6,7]. Evidently the existence of silatranes in forms (Ia) and (Ib) would correspond to the first and second of the above hypotheses respectively.

It would seem that a decision can be reached concerning the alternative structures by resorting to X-ray diffraction. Table 1 presents the results of X-ray diffraction studies on a number of 1-substituted silatranes. In the molecules of the absolute majority of the compounds investigated the nitrogen atom is displaced from the plane of the neighbouring carbon atoms in the direction of the silicon atom (*endo*-orientation). The coordination polyhedron around the silicon atom consists of a distorted trigonal bipyramid, in the equatorial plane of which three oxygen atoms are accommodated, while the vertices contain the nitrogen atom and the α-atom of the substituent X. However, the deviations of the form of the coordination polyhedron from the ideal bipyramid are considerable. The average X–Si–O angles

(the values of which reflect to some extent the valence state of the silicon atom) are intermediate between the valence angles of compounds of tetravalent (109.5°) and pentacoordinate (90°) silicon atoms. On the basis of the valence angles, one cannot therefore decide reliably whether the steric structure of silatranes corresponds to distorted forms (Ia) or (Ib).

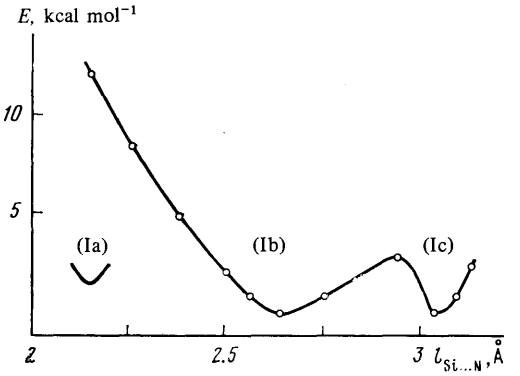
Table 1. The steric structures of 1-substituted silatranes.

X	Axial characteristics		Equatorial characteristics*		Refs.
	l_{X-Si}, Å	l_{Si-N}, Å	l_{Si-O}, Å	X-Si-O angle	
Cl	2.15	2.02	1.65	—	8
$ClCH_2$	1.91	2.12	1.67	97.4°	9
$Cl(CH_2)_3$	1.88	2.18	1.66	97.2°	10
mNO_2Ph	1.90	2.12	1.66	95.8°	11
Ph(α-form)	1.88	2.19	1.66	97.1°	12
Ph(β-form)	1.91	2.15	1.65	96.6°	13
Ph(γ-form)	1.89	2.13	1.65	96.0°	14
C_2H_5	1.88	2.21	1.66	—	15
$[(CH_3)_2C_6H_5P]_2ClPt$	2.29	2.89	1.65	108.8°	16,17

*The average Si–O bond lengths and X–Si–O angles are quoted.

The Si...N internuclear distances in the molecules of silatranes (Table 1) are much greater than the sum of the covalent values (1.8 Å), but are smaller than the sum of the van der Waals radii (3.1 Å) of the silicon and nitrogen atoms. This permitted the assignment of the structure of silatranes to form (Ia) without any ambiguity. On the basis of a qualitative inspection of the Si...N internuclear distance, one can be certain that there is a definite interaction between the silicon and nitrogen atoms in silatrane molecules. However, without additional arguments it is impossible to identify such interaction with the Si←N coordinate bond. Indeed one can assume with just as much certainty that the real structure of silatranes corresponds to a minimum in the conformational energy of form (Ib), in which the internuclear distance depends on the degree of non-valence interactions, the latter being in many respects determined by the nature of the substituent X. This hypothesis seemingly received indirect support by the detection of the *trans*-{PtCl[$Si(OCH_2CH_2)_3N$].[$P(CH_3)_2C_6H_5$]} molecule in a kind of *endo*-form[16,17]. The silicon atom in this molecule has a tetrahedral structure and the nitrogen atom is only slightly displaced from the plane of the three carbon atoms linked to it (by 0.07 Å). It is believed[16] that the tetrahedral structure of the silicon atom in this silatrane is caused by the considerable steric hindrance due to the structure of the Si-substituent as well as the low electronegativity of the latter. The nearly planar disposition of the nitrogen atom was explained by the intense steric interactions of the three methylene groups surrounding it.

To elucidate the relative role of the conformational and electronic factors determining the structure of silatrane molecules, the dependence of the chain energy on the Si...N internuclear distance has been investigated for the 1-methyl silatrane molecule by the Westheimer–Kitaigorodskii method[18,19]. It was found that the real structure of the 1-methyl silatrane molecule corresponds to the minimum conformational energy in form (Ia) alone; the latter is more stable to the extent of 8.5 kcal mole^{-1} than structure (Ib) (for the same Si...N internuclear distance). It was thus possible to demonstrate that conformational factors play a major role in the formation of the steric structure of silatranes, tending to increase the coordination number of the silicon atom to five. At the same time, the conformational energy of the *endo*-form (Ia) proved to be fairly close to the value calculated for the *exo*-form (Ic), which does not really exist and the barrier to the (Ic)→(Ia) transition does not exceed 2 kcal mole^{-1} (see Figure). Consequently conformational factors cannot account for the experimentally observed stability of the *endo*-form (Ia). This leads to the conclusion that the main factor determining the high stability of form (Ia) is the considerable contribution of the Si←N valence interaction energy to the overall energy of silatrane molecules†. Subsequently this conclusion was confirmed by quantum-chemical calculations[21].



Dependence of the conformational energy E of the 1-methylsilatrane molecule on the distance between the silicon and nitrogen atoms ($l_{Si...N}$).

According to X-ray diffraction data[8–15,22], the three five-membered heterocycles in the molecules of 1-substituted silatranes are non-planar. They have the shape of an envelope bent as a rule along the N–Cβ line. The molecules of all the silatranes investigated are distributed in crystals at distances which are determined by the van der Waals interactions. The crystal structures of 1-methylsilatrane[23,24] and 1-phenylsilatrane[12–14] exhibit polymorphism. The existence of several crystalline modifications (α, β, and γ) of the last compound was explained by the different conformations of the silatrane skeleton.

The dipole moments of silatranes are extremely high (5–9 D);[25–27] they are several times greater than the values for the corresponding organyltriethoxysilanes (1.5–2 D). This was assessed[25] as evidence for the existence of silatranes in form (Ia). The dipole moment of the $Si(OCH_2CH_2)_3N$ fragment in both the *exo*-form (Ic) and the *endo*-form (Ia), calculated by an additive scheme[25] without taking account the moment of the Si←N bond, proved to be significantly smaller

†It has been possible to show recently[20] that the stabilisation of structure (Ib) by electrostatic interaction is possible only for unrealistically high dipole moments of the polar bonds (Si–O, O–C).

(by 4–5 D) than the experimental value. Since data for the molecular structure had not yet been obtained in our calculations[25] it was necessary to employ bond lengths and angles which proved to be far from realistic. Analysis of the results led the authors[25] to the conclusion that silatranes exist in form (Ia) and have a very high (up to 8 D) dipole moment of the Si←N bond; however, this conclusion cannot be regarded as reliable for the reason stated above.

According to ^{1}H NMR data[1,28,29], three five-membered atrane half-rings in silatrane molecules are independent and completely identical. The chemical equivalence of the geminal protons of the methylene groups shows that the non-planar half-rings Si–O–C–C–N are involved in rapid (in terms of the NMR scale) conformational transitions. Analysis of the constants for the spin–spin coupling between the protons of the substituted ring of 3-methyl derivatives of silatranes indicates the *endo*-orientation of the LEP of the nitrogen atom in their molecules[30]. However, an unambiguous choice between forms (Ia) and (Ib) of silatrane molecules cannot be made on this basis.

2. Electronic Structure of 1-Substituted Silatranes

The adoption of the hypothesis that silatranes contain the Si←N bond imposes a number of requirements on their electronic structure[31,32]. Firstly the formation of such a bond must be accompanied by a rearrangement of the electron cloud of the silicon and nitrogen atoms and to some extent also of their immediate environment. This type of rearrangement should be manifested in a comparative analysis of the physicochemical properties of silatranes and the corresponding model systems sensitive to changes in electron distribution. Secondly, the collective properties# of silatranes cannot be understood without taking into account the characteristics of the Si←N bond. Thirdly, the nature of the dependence of the physicochemical properties of silatranes on the nature of the substituent at the silicon atom is determined by the presence of the Si←N bond. On the other hand, the hypothesis of the stabilisation of the silatrane skeleton as a result of non-valence interaction does not require the fulfilment of these conditions.

At the very beginning of the development of the chemistry of silatranes it was already claimed intuitively[1] that the degree of interaction between the nitrogen and silicon atoms and the length of the Si←N bond in silatrane molecules must be determined by the nature of the substituent X. With increasing electronegativity of the latter, a strengthening of the Si←N bond is to be expected. This was indeed established experimentally by X-ray diffraction analysis of silatranes (Table 1). The dependence of the Si...N internuclear distance in silatrane molecules on the Taft inductive constant (σ^*) of the substituent X at the silicon atom is linear[8,33]: $l_{Si\leftarrow N} = 2.20 - 0.0636\sigma^*$.

In silatrane molecules the displacement Δ of the silicon atom from the equatorial plane containing the three oxygen atoms in the direction of the substituent X is linked to the Si←N bond length by the relation[22] $l_{Si\leftarrow N} - \Delta = d$, where d is the distance from the nitrogen atom to the equatorial plane of the trigonal bipyramid; the value of d in the series of 1-substituted silatranes is then approximately the same and amounts to 2.00 ± 0.05 Å. It has been suggested that this is due to the competition of the non-valence interactions between the substituent and oxygen atoms, on the one hand, and the strain forces in the heterocycles, on the other. Later[15], on the basis of the analysis of more extensive experimental data, it was found that both Δ and d vary linearly with the Si←N bond length: $\Delta = -1.052 + 0.576 l_{Si\leftarrow N}$ and $d = 1.055 + 0.422 l_{Si\leftarrow N}$. Comparison of these relations shows that the length of the transannular Si←N bond in the molecules of 1-substituted silatrane changes mainly owing to the displacement of the silicon (and not nitrogen) atom relative to the equatorial plane of the distorted trigonal bipyramid. It was assumed that this indicates a decisive influence of the electronic interactions on the structure of silatrane molecules[15].

Despite the fact that this claim is valid, it in no way follows from the considerations presented above. For a more correct analysis of the changes in the degree of interaction between the silicon and nitrogen atoms, it is necessary to compare the values of Δ with the distance between the nitrogen atoms and the plane formed by the three neighbouring carbon atoms (Δ') and not with the value of d.[33] $\Delta = 0.48$ Å and $\Delta' = 0.13$ Å correspond to the minimum conformational energy of the 1-methylsilatrane molecule in form (Ib).[18] On the other hand, owing to the valence interaction in real 1-alkylsilatrane molecules the values of Δ and Δ' are lower and higher respectively than those indicated above. With increase of the Si←N bond strength, Δ diminishes and Δ' increases[34], the extent of the changes in these quantities being virtually identical in the series of silatranes whose structures have been investigated[33]. Consequently, under the influence of the substituent X, identical changes take place in the valence states of the nitrogen and silicon atoms. This agrees well with the results of studies of silatranes by other physical methods[35].

The value of $l_{Si\leftarrow N} = 1.83$ Å corresponds to the intercept which the plot of Δ against l_{Si-N} makes on the abscissa axis[15]. On this basis, it has been concluded[15] that the "ideal" length of the transannular Si←N bond is equal to the covalent Si–N bond length. The linear dependence of $l_{Si\leftarrow N}$ on the Taft inductive constant σ^*_X shows[8] that in an "ideal" silatrane the substituent X should have $\sigma^* = 5.4$. This value is extremely close to that known for the $R_3\overset{+}{N}$- group. It is therefore logical to assume that the 1-azaniasilatrane structure $[R_3N\rightarrow Si(OCH_2CH_2)_3N]^+A^-$ corresponds to the concept of the "ideal" silatrane. Hence it follows that there is no complete electron transfer from the nitrogen atom to the silicon atom in the molecules of the silatranes investigated hitherto.

Structural studies on silatranes have shown[14,15,22] that the Si–O bond lengths in their molecules and in model triethoxysilanes are virtually the same. It has come to be believed that this is due to the compensation of the enhancement of σ-bonding by the weakening of the $d_\pi - p_\pi$ interaction between the oxygen and silicon atoms when the silicon atom passes to the pentacoordinate state. However, evidence has been adduced (which must be regarded as incorrect) also in support of the $p_\pi - p_\pi$ interaction between the same atom[36].

In a series of 1-organylsilatranes the Si–O bond length hardly changes[14,15,22] and the longest Si←N bonds correspond to the shortest C–Si bonds[14]. This shows that the *trans*-influence of the substituents is characteristic of silatranes.

The parallel variation of the energies of the 2p levels of the silicon atom and the 1s level of the nitrogen atom in 1-substituted silatranes has been demonstrated by the method of photoelectron spectroscopy for chemical analysis (ESCA).[37] This finding is consistent with the hypothesis that the Si←N bond exists in silatranes (i.e. that there is a charge transfer from the nitrogen atom to the silicon atom). According to

#Properties which are determined, to a first approximation, by the sum of the properties of the individual bonds.

photoelectron spectroscopic (PES) data[38], the ionisation potentials of the 2*p* level of the nitrogen atom in the molecules of 1-hydro-, 1-methyl-, and 1-ethoxy-silatranes are higher than in triethanolamine. The authors explained this by the σ-donation of the LED of the nitrogen atom to the 3*d* orbital of the silicon atom. The approximate constancy of the first ionisation potentials for silatranes with X = H and C_2H_5O was somewhat unexpected. However, one should note that the interpretation of the PES data for silatranes in the study of Cradock et al.[38] is not reliable. The levels were assigned on the basis of symmetry considerations, which is clearly insufficient in the analysis of the PES of such complex molecules.

X-Ray electronic spectra of silatranes have been studied[36,39,40]. The chemical shifts of the K_α lines of the silicon atoms, calculated by an additive scheme on the assumption of the tetravalent state of the silicon atom, proved to be greater than the experimental values. The difference is fundamental and supports the structure with a pentacoordinate silicon atom. It has been suggested[39] that the Si←N bond in silatrane molecules is responsible for the reduced effective charge on the silicon atom (i.e. for the increased electron density at this atom) and hence for the reduced chemical shift of the K_α line. This conclusion cannot be regarded as rigorously justified, because the formula $\Delta E_l = Kq_{eff}$, used to determine the effective charges, presupposes the equality of the constant k for compounds of tetra- and penta-coordinate silicon, which is extremely doubtful.

A hypsochromic shift of the absorption band of the $N(CH_2)_3$ group relative to the spectrum of triethanolamine, in which the LEP of the nitrogen atom is free, has been observed in the ultraviolet spectra of 1-substituted silatranes (X = C_2H_5, CH_3, or H).[41] This confirms the hypothesis that the Si←N bond is present in silatranes, since the higher binding energy of the lone electron pair in silatrane is in fact responsible for the hypsochromic shift. Analysis of the ultraviolet absorption spectra of 1-aryloxysilatranes leads to the conclusion[42] that the bands due to the aryloxy-groups (200–300 nm) are insensitive to the coordination interaction of the silicon and nitrogen atoms.

Absorption bands in the range 560–590 cm^{-1}, which are absent from the spectra of model compounds, are characteristic of the infrared spectra of silatranes[1,43–48]. These frequencies were assigned to the stretching vibrations of the Si←N bond on the grounds that the vibrations of the covalent Si–N bonds in aminosilanes are in the range 780–830 cm^{-1}, while the vibration frequency of the coordinate bond should be lower[1,43]. The integral intensity A of this band in the spectra of a series of 1-organoxysilatranes of the type $RO\overset{\downarrow}{S}i(OCH_2CH_2)_3\overset{\downarrow}{N}$ depends on the nature of the substituent[44,45]. There should be strong kinematic interactions between the vibrations of the collinear X–Si and Si←N fragments, as a result of which the stretching vibration frequency of the Si←N bond should be displaced towards lower values with increase of the atomic weight of the substituent at the silicon atom. Such a shift has indeed been observed[44,49] in the series of 1-substituted silatranes with X = H, F, Cl, or Br, which also confirms the validity of the assignment of the ν band to the Si←N vibration. The introduction of symmetry coordinates permitted the calculation of the force field of the 1-hydrosilatrane molecule[45]. The force constant of the Si←N bond proved to be 1.2×10^6 cm^{-2}, which is several times smaller than the force constants of covalent bonds.

Evidence has recently been presented[46] showing that the assignment of the 560–590 cm^{-1} band in the infrared spectra of silatranes to the Si←N bond vibrations is erroneous. According to some data[44,45], the integral intensities A_ν of this band are as a rule inversely proportional to its intensity at the maximum. On the other hand, according to Voronkov et al.[46] (although the latter do not in fact quote specific results for the compound investigated previously[44,45]), the half-widths of such bands are constant, which led them to the belief that the measurements of the values of A_ν in the earlier investigations[44,45] were methodologically incorrect. The integral intensity of this band, measured for the first time for the series of 1-alkyl- and *C*-substituted silatranes, proved to be independent of the nature of the substituent at the silicon atom[46]; this constitutes important evidence against the assignment of the band in the range 560–590 cm^{-1} to ν(Si→N). It is so far difficult to solve ultimately the problem of the assignment of this band. For example, despite the use of the same method for the determination of the integral intensities (the Iogansen method) in the studies described in Refs. 44 and 46, the values of A_{570} obtained for 1-ethoxysilatrane differ sharply (9250 and 1612 litre cm^{-2} mol^{-1} respectively). Yet another argument against the assignment of the 560–590 cm^{-1} band to the Si←N vibration is based on the hypothesis that such vibrations (symmetry A_1) should be inactive in Raman spectra§. Furthermore, the intensity ratio $A_{570}/A_{790} = 0.1$ in the infrared spectrum of 1-ethylthiomethyl-3-methylsilatrane, while in the Raman spectrum it increases to **0.3.**[46]

On the basis of the above considerations and the presence of a band in the region of 600 cm^{-1} in the infrared spectra of certain di- and tri-cyclic structures (including those of metalloatranes), the 560–590 cm^{-1} band in the infrared spectra of silatranes has been assigned[46] to the skeletal vibrations. If this hypothesis is adopted, it is not clear why, despite the significant deformation of the atrane molecular skeleton on substitution of the $O_{(2)}$ atom by the methylene group[7] or after the introduction of methyl groups in the 3-, 7-, and 10-positions[1,7,46], the frequency of the above vibration remains constant. At the same time the 560–590 cm^{-1} band has not been observed[16] in the infrared spectrum of the bicyclic *trans*-{PtCl[Si$(OCH_2CH_2)_3$N][P$(CH_3)_2C_6H_5$]} molecule, in which there is virtually no Si←N bond according to X-ray diffraction data[16,17]. We believe that this factor shows unambiguously that the presence of the Si←N bond is an essential condition for the manifestation of the band at 560–590 cm^{-1} in the infrared spectra of silatranes.

We may note that the 560–590 cm^{-1} band in the infrared spectra of Si- and C-substituted silatranes has been assigned to the fully symmetrical vibrations of the SiO_3 group[47]. It has also been suggested[48] that the moderately intense bands in the region of 300 cm^{-1} should be assigned to the Si←N bond vibrations. Thus one must admit that the problem of the direct manifestation of the Si←N bond vibrations in the infrared spectra of silatranes still remains essentially open.

At the same time, the bathochromic shift of the ν(H–Si) band in the spectrum of hydrosilatrane relative to triethoxysilane[1,6,43] as well as the appreciably lower ν_{as}(C–Si) and ν(Hal–Si) frequencies in the infrared spectra of 1-alkyl-[43] and 1-halogeno-silatranes[49,51] compared with the corresponding derivatives of triethoxysilane confirm indirectly the presence of the Si←N bond in silatranes.

A change in the nature of the substituent at the silicon atom has approximately the same influence on the degrees of electronic shielding of the protons of both OCH_2 and CH_2N groups in the ^1H NMR spectra of silatranes[1,28,29,38],

§This is a clear misunderstanding, since the A_1 vibrations are active in both Raman and infrared spectra[50].

[52–54]. This is responsible for the constancy of the difference between the chemical shifts of these protons (in a given solvent) for all 1-substituted silatranes (Table 2). The results show that the electronic influence of the substituent at the silicon atom is transmitted not only via the system of σ-bonds of the atrane half-rings (SiOCCN) but also via the Si←N bonds. The same feature can be seen also in the variation of the spin–spin coupling constants $^1J(^{13}C-^1H)$ for the OCH_2 and CH_2N groups[53]. It follows from statistical considerations that the Si←N bond transmits the influence of the substituent X more effectively than each of the Si–O bonds. Thus ^1H NMR data indicate one of the most significant features of silatranes—the *trans*-influence of the substituent at the silicon atom on the nitrogen atom.

Table 2. NMR parameters of 1-substituted silatranes.

X	^1H chemical shifts, p.p.m.*		^{29}Si chemical shifts, p.p.m.	
	δ_{OCH_2}	δ_{CH_2N}	δ_{Si}	$\Delta\delta_{Si}^{**}$
H	3.830	2.868	−83.6	17.6
CH_3	3.779	2.806	−65.7	21.7
CH_3CH_2	3.777	2.802	−67.1	21.2
$ClCH_2$	3.858	2.886	−77.2	21.1
$BrCH_2$	3.853	2.879	−77.7	21.5
ICH_2	3.839	2.860	−77.0	22.3
$H_2C=CH$	3.829	7.850	−83.5	23.2
Cl_2CH	3.930	2.962	−83.2	14.8
C_6H_5	3.905	2.915	−80.5	21.1
CH_3CH_2O	3.837	2.836	−94.7	12.3
F	3.906	2.950	−101.1	16.1

*Values extrapolated to infinite dilution in $CHCl_3$.

**$\Delta\delta_{Si} = \delta_{Si}(X-Si(OCH_2CH_2)_3N) - \delta_{Si}(X-Si(OCH_2CH_3)_3)$.

When the nitrogen atom passes to the cationic state or its LEP is involved in a coordinate bond, the ^1H NMR absorption line of the protons of the methylene group linked to the nitrogen atom usually undergoes a paramagnetic shift of approximately 0.5–0.8 p.p.m. However, the chemical shifts of the CH_2N protons in the ^1H NMR spectra of silatranes are only slightly greater than in those of the acyclic and monocyclic analogues[29,52], where there is no Si←N bond. The observed difference between the chemical shifts of the CH_2N protons of silatranes and their analogues shows that the degree of transfer of the LEP of the nitrogen atom to the silicon atom is insignificant. This purely qualitative conclusion (which conflicts with the hypothesis put forward at one time[1,25] that the Si←N bond is highly polar) was later proved quantitatively[21,27,35,55].

The chemical shifts of the OCH_2 and CH_2N protons of 1-alkyl- and 1-alkenylsilatranes are correlated with the inductive substituent constant σ*.[29,52,56] However, 1-aryloxy- and 1-alkoxy-silatranes deviate from this relation. This has been explained[29,52] by the superposition of the effect due to the $d_\pi - p_\pi$ interaction of the silicon atom with the oxygen atom of the aryloxy- or alkoxy-group.

An equation for joint correlation of the σ_{CH_2N} and the field and resonance constants (F and R) of the substituent X has been found for a number of 1-alkyl or aryl- and 1-aryloxy- or alkoxy-silatranes[53]. ^1H NMR data also show that the distribution of electron density in silatranes depends also on the steric influence of the substituent at silicon atom[29,52]. The chemical shifts of the ^{13}C NMR signal of the atrane skeleton in silatrane molecules depend comparatively little on the nature of the substituent on the silicon atom [$\delta(C_N) = 51$ p.p.m. and $\delta(C_0) = 57$ p.p.m.].[53] This is probably caused by the damping effect of the readily polarisable C–H bonds in the silatrane molecules, which can compensate for the change in the charges on the α- and β-carbon atoms induced by the substituent X.

Despite the involvement of the nitrogen atom of silatranes in the Si←N coordinate bond, the ^{14}N NMR lines in their spectra are appreciably broadened (X = CH_3, $\Delta\nu = 2211$ Hz; X = H, $\Delta\nu = 638$ Hz).[57] The authors explain this by the local asymmetry of the nitrogen atom in the silatrane molecules and by the increase of the C–N–C valence angles. The isolation of the contribution of the Si←N bond to the ^{14}N shielding constant for silatranes is complicated by a number of factors. Among these, the main one is the cyclisation effect, which is of a distinctly diamagnetic type. At the same time, the change in the ^{14}N chemical shifts (by 9 p.p.m.) when the hydrogen atom in the 1-hydrosilatrane molecule ($\delta_N = -355$ p.p.m.) is replaced by the methyl group[57] is approximately equal to the downfield shift of the ^{14}N resonance of trialkylamines or their salts when the hydrogen atom at α-carbon atom is substituted by the methyl group. This kind of analogy in the behaviour of δ_N is caused by the formally similar mechanisms of the transmission of the effective substituent to the indicator centre (^{14}N) in the X–C–N and X–Si–N fragments.

In the NMR spectra of 1-substituted silatranes the ^{29}Si line is displaced upfield with increase of the electronegativity of the substituent X.[53,58,59] A similar dependence has been observed also for Si-substituted triethoxysilane $XSi(OCH_2H_5)_3$.[53,59] Consequently the presence of the Si←N bond in silatranes cannot be inferred from the nature of the change in the $\delta(^{29}Si)$ as the substituent X is varied. At the same time, the ^{29}Si signals in the NMR spectra of silatranes are appreciably displaced upfield compared with the signals observed in the NMR spectra of model Si-substituted triethoxysilanes (Table 2). This increase of the shielding cannot be accounted for either by the cyclisation effect (usually causing a downfield shift of the signals[60]) or by the influence of the high electronegativity of the nitrogen atom. The implication is that the factors which do not characterise directly the presence of the Si←N bond are unable to explain the upfield shift of the ^{29}Si NMR signal of silatranes relative to Si-substituted triethoxysilanes.

However, the increase of the shielding constants of the nuclei with increase of the coordination number of the atom, a fact which has not so far been accounted for theoretically, is widely known in ^{11}B, ^{29}Si, ^{119}Sn, ^{199}Hg, etc. NMR. On this basis one must conclude that the nature of the ^{29}Si NMR spectra of silatranes rigorously demonstrates the presence of the Si←N bond in their molecules. If one adopts the reasonable, at first sight, hypothesis that the presence of the Si←N bond is responsible for the increased electron density at the silicon atom (compared with model systems) and one takes into account the familiar[60,61] V-shaped relation between the chemical shift and the atomic charge, then one should expect a downfield shift of the ^{29}Si signal of silatranes. It was therefore necessary to assume[53,59] that, in contrast to Si-substituted triethoxysilanes, the ^{29}Si shifts of silatranes are determined not only by the effective charge of silicon atom but also by a certain positive coordination contribution δ_{coord}. The magnitude of the latter increases with increasing degree of the Si←N interaction.

The proposed interpretation explains why the absolute values of $|\Delta\delta Si = \delta Si(silatrane) - \delta Si(triethoxysilane)|$ decrease in parallel with increase of the degree of the Si←N interaction in silatrane molecules[53]. On the other hand, the hypothesis of the reduced electronic charge on the silicon atom in silatranes hinders the explanation of the observed relations, although it does provide a formal explanation of the upfield shift of the ^{29}Si signal in their NMR spectra. All these findings show that, like the majority of other spectroscopic characteristics of silatranes, their ^{29}Si NMR chemical shifts are not determined solely by the contribution of the charge on the central atom.

An increase of the degree of shielding (compared with the corresponding Si-substituted triethoxysilanes) of the nuclei of the atoms forming part of the composition of the substituent at the silicon is also characteristic of silatranes[1,29,52,53,58]. ^{13}C and ^{19}F linked directly to the silicon atom are the only exceptions[58]. The pentacoordinate state of the silicon atom in silatrane molecules is responsible for the increase of the spin–spin coupling constants $^1J(^{29}Si^{13}C)$ and $^2J(^{29}Si^1H)$ and for the decrease of $^1J(^{29}Si^1H)$ and $^1J(^{29}Si^{19}F)$ compared with the corresponding derivatives of tetravalent silicon[58]. The above properties are probably common to all derivatives of Group IVB elements containing a heteroatom with an increased coordination number.

Before silatranes were studied by ^1H NMR,[29,52] the hypothesis of the high polarity of the Si←N bond in their molecules aroused no doubts. This conviction was based on the determination and calculations of the dipole moments of silatranes[1,25]. The appearance of new data on the geometry of the silatrane molecules enabled one of the present authors and his coworkers[27,55] to recalculate their dipole moments on the basis of an additive scheme. It was found[55] that the Si←N bond dipole moment in 1-alkyl- and 1-aryl-silatranes does not exceed 2.20 D, which corresponds to the transfer of approximately 0.2*e* from the nitrogen to the silicon atom. At the same time the validity of the earlier conclusion[25] that the high dipole moments of silatranes cannot be explained without taking into account the contribution of the Si←N bond moment was demonstrated. Similar results were obtained in another study[27], where the dipole moment of the Si←N bond in 1-methylsilatrane was estimated as 1.38 D.

The dipole moments of silatranes depend not only on the electronic effect of the substituent X and hence also on the internuclear Si...X distance, as assumed before, but also on the conformational features of the heterocyclic skeleton of the molecules[55]. The revised values of μ(Si←N) are of fundamental importance for the theory of the structure of silatranes. In the study of 1-methylsilatrane solutions in dioxan measurements were made of the molar Kerr constants, the total polarisation, and the molecular anisotropy[62]. The determination of these molecular characteristics made it possible to establish, within the framework of the additive scheme for the calculation of bond polarisabilities, that the Si←N bond in silatranes is characterised by an appreciable anisotropy of its polarisability. The conformations of a number of silatranes containing a carbofunctional substituent were established by the same methods[63].

The molecular ions $(M-X)^+$ in the mass-spectra of silatranes[64,65] exhibit a high intensity (from 48.5 to 33.9%). This indicates the stability of the silatrane ring on electron impact, which can be accounted for by the presence of the Si←N coordinate bond. When the substituent X is extracted, the latter is converted into the "covalent" Si–N bond, where the nitrogen atom is in the ammonium state.

The influence of the silatrane skeleton on the properties of the Si-substituent have been frequently considered. The ^{35}Cl NQR frequencies for 1-chloroalkyl- and 1-chlorovinyl-silatranes are somewhat lower than for the corresponding acylic analogues[54]. This is consistent with the hypothesis that there is a coordination interaction in silatranes between the silicon and nitrogen atoms, which increases the +*I* effect of the silatranyl group. The inductive constant of the silatranyl group has been determined as −1.2 by employing familiar[66,67] linear relations between the ^{35}Cl NQR frequencies and the σ_X^* constants for the $H_2C{=}CClX$ and $XX'CCl_2$ series. This value indicates a distinctly σ-donor character of the $-\overset{\downarrow}{Si}(OCH_2CH_2)_3N$ group. The high σ-donor capacity of the silatranyl group has also been confirmed by ^1H, ^{13}C, and ^{19}F NMR.[28,29,52,53,58,68–70]

The quantitative estimate of the inductive effect of the silatranyl group, obtained[70] on the basis of ^{13}C NMR data for 1-phenyl silatrane ($\sigma^* = -0.9$) is lower in absolute magnitude than that determined[54] by ^{35}Cl NQR. This discrepancy is most probably independent of the difference between the reliabilities of the correlation equations employed, based on data found by different methods (^{35}Cl NQR and ^{13}C NMR). It can probably be explained by the fact that the σ-donor properties of the silatranyl group are not constant and depend on the nature of the substituent at the silicon atom. The latter in fact determines the degree of transannular interaction in silatrane molecules and hence the increased, compared with $Si(OR)_3$ groups, electron-donating capacity of the silatranyl fragment $-\overset{\downarrow}{Si}(OCH_2CH_2)_3N$ (see below). The quantitative estimate of the inductive effect of the silatranylmethyl group $-CH_2-\overset{\downarrow}{Si}(OCH_2CH_2)_3N$ ($\sigma^* = 0.8$)[69] is consistent with the value of $\sigma^*[-\overset{\downarrow}{Si}(OCH_2CH_2)_3N]$ obtained from ^{35}Cl NQR data.

It has been suggested[54] that there may be a coordination interaction between the chlorine and silicon (oxygen) atoms in the 1-(γ-chloropropyl)silatrane molecule. However, this was subsequently disproved experimentally[10].

Thus, despite the fact that, in the majority of the studies examined the isolation of the contribution of the Si←N bond to the properties of silatranes investigated has been achieved only at a qualitative level (and frequently very artificially), the results obtained convincingly demonstrate a significant change in the electron clouds of the silicon and nitrogen atoms as well as their immediate environment in silatrane molecules. Together with the characteristic influence of the nature of the substituent at the silicon atom on the properties of silatranes this indicates unambiguously the presence of the Si←N bond in their molecules. The existing experimental data cannot be accounted for within the framework of the alternative model (the stabilisation of the silatrane skeleton by non-valence and electrostatic interactions). At the same time, in view of the lack of experimental and theoretical estimates of the Si←N bond energy, the problem of the causes of the stability of silatranes, which is crucial for the theory of their structure, remained in fact open for a long time.

To solve this problem, the total energies of the 1-hydrosilatrane molecules and the most significant points on the potential function for the *endo–exo* transition were calculated[21] by the CNDO/2 method in terms of a novel parametrisation. It was shown that the *endo*-form is energetically more favourable than the *exo*-form (by 60 kcal mol^{-1}). The high value of the calculated barrier to the transition of the *endo*-form (Ia) into the *exo*-form (Ic) (~64 kcal mol^{-1}) and its low value (~4 kcal mol^{-1}) for the reverse transition demonstrated that the *exo*-form does not exist.

The energies of the skeletal bonds of the silatrane molecule do not actually change on transition from the *endo*- to

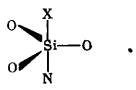
the *exo*-form (more precisely the changes in them are negligible compared with their absolute values). The decrease of the Si←N bond energy by more than an order of magnitude is unique and extremely symptomatic. Hence we may conclude that the main factor stabilising the *endo*-form of the silatrane molecule is the bonding interaction between the silicon and nitrogen atoms. The energy of the Si←N bond in the *endo*-form (Ia) of the 1-hydrosilatrane molecule can be regarded as close to 24–25 kcal mol^{-1}¶.

Analysis of the populations of the hybrid orbitals of the nitrogen atom indicates unambiguously the involvement of its LEP in the formation of the Si←N bond. The calculated degree of transfer of electron density from the nitrogen to the silicon atom in the hydrosilatrane molecule (~0.2*e*) agrees well with the earlier estimate obtained by analysing the dipole moments of silatranes[55].

The results of conformational[18,19] and quantum-chemical[21] analyses suggest[35,72] that the cause of the existence of the intramolecular Si←N bond in silatranes and the virtual absence of the formation of a similar intermolecular bond when organyltriethoxysilanes react with amines consists in the fundamental difference between the free energy profiles for the formation of the intra- and intermolecular hypervalent X–Si–N linkages. The energetically favourable transition of the silatrane molecule from the *exo*- to the *endo*-form occurs with retention of the conformational entropy. This follows from the existence, as the reaction coordinate r_{Si-N} is altered, of only two stable states and the dissociation of the intermolecular complex is characterised by a monotonic increase of the entropy.

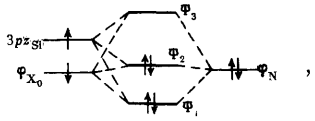
The problem of the nature of the interaction between the silicon and nitrogen atoms in silatranes is particularly significant. *Only one mechanism of their mutual binding was in* essence considered in previous studies: the donor–acceptor interaction of the LEP of the nitrogen atom with the vacant 3*d* orbitals of the silicon atom having a suitable symmetry[1,28,38,73]. However, as shown above, this mechanism cannot explain logically certain results of physicochemical studies on silatranes. Futhermore, the concept of hybridisation involving 3*d* orbitals, particularly in the case of non-transition elements, has been recently subjected to serious and constructive criticism[74]. The problem of both the nature of the Si←N bond in silatranes and of the influence of the substituents at the silicon atom on the energetics of the molecule and the steric structure of the silatrane skeleton therefore clearly had to be reconsidered.

An attempt has been made[75] to treat the electronic and steric structures of silatranes within the framework of the model of hypervalent linkages[76]. A significant factor in the consideration of the electronic structure of silatranes is the isolation of the molecular fragment of greatest structural and chemical importance. This is the silicon atom and its immediate environment, which has approximately the symmetry of a trigonal bipyramid:



For a more logical determination of the influence of the substituent X on the equilibrium properties of silatranes, one can assume that, for a "standard" substituent X_0, the geometry of the local environment of the silicon atom corresponds rigorously to the ideal trigonal bipyramid†. Three sp^2-hybridised orbitals can be constructed from the four valence orbitals of the silicon atom (3*s*, $3p_x$, $3p_y$, and $3p_z$). The hybrid orbitals are involved in the formation of three "normal" equivalent equatorial Si–O bonds. The orbitals of the axial atoms (one from each atom) can then interact with the single $3p_z$ orbital of the central silicon atom common to all of them. According to the molecular orbital (MO) theory, this should lead to the formation of three three-orbital, three-centre MO.

In the case where the central atom is less electronegative than the axial atoms, this can be represented schematically as follows:



where ϕ_{X_0} and ϕ_N are the hybrid or the pure orbitals of the axial atoms used to construct the MO, ψ_1 is a bonding MO, ψ_2 a weakly bonding MO with a node in the region of the weaker bond (for the X–A–X fragment, the ψ_2 orbital becomes non-bonding), and ψ_3 an antibonding MO. The filling of ψ_2 with electrons corresponds to the model of hypervalent linkages and distinguishes such linkages from the "normal" bonds for which only bonding MO are filled with electrons. It can be readily shown that the filling of the ψ_1 orbital with electrons in the model of hypervalent linkages ensures the required energy gain in the interaction of three atomic orbitals.

The first evident consequence arising from the model is that the influence of the σ-linked substituent can be transmitted only via the $3p_z$ orbital of the central atom. This explains the *trans*-influence of the substituent characteristic of silatranes. The expression defining the effect of the bonding between the Si and N atoms can be formulated as follows for a three-level system:

$$\Delta E_{SiN} = \beta^2_{Si^0N} \Big/ \left(\alpha^0_{Si} + \frac{\beta^2_{Si^0X^0}}{\alpha^0_{Si} - \alpha^0_X} - \alpha^0_N \right),$$

where α and β are the Coulombic and resonance integrals, subscript 0 refers to the initial atomic levels, and the ratio $\beta^2_{Si^0N}/(\alpha_{Si^0N} - \alpha_{X^0})$ characterises the decrease of the effect of the bonding between the Si and N levels as a result of the X_0–Si interaction.

It follows from this expression that, with increase of the X–Si bond strength, the Si–N interaction in silatranes is weakened. Furthermore, the change in the Si←N bond energy depends significantly also on the electronegativities of the silicon and nitrogen atom (the Coulombic integrals α_{Si} and α_N). The conclusion that the silicon atom is displaced from the equatorial plane formed by the three oxygen atoms on transition from X_0 to X_i is natural. Indeed, the strengthening of one part of the X–Si–N fragment and the weakening of the other constitutes in essence the "expulsion" of the silicon atom from the equatorial plane. The greater the effect of the strengthening (and weakening) of one of the components of the fragment compared with the standard value, the greater should be the displacement Δ from this plane#.

¶The presence of the Si←N bond in the 1-methylsilatrane molecule was also confirmed by the 4NDO method[71].

†Such a "standard" substituent is the $R_3\dot{N}$ group.

#The sign of Δ depends on the relative values of α_{X_0} and α_{X_i}.

When the contribution of the 3s orbital is neglected and for $|\alpha_{X_i}| > |\alpha_{Si}|$, an increase of the electronegativity of the substituent X should weaken the X–Si bond and enhance the Si←N interaction. If $|\alpha_X| < |\alpha_{Si}|$, variation of the substituent X leads to a parallel variation of the X–Si and Si←N bond strengths. Analysis of the experimental data for the steric structure of silatranes[14] fully confirmed the conclusions of Voronkov and coworkers[75]. In agreement with the theory, the weakest Si←N interaction is observed for a silatrane in which the silicon atom is linked to the atom of a transition metal (Pt: $|\alpha_{Pt}| \ll |\alpha_{Si}|$).[16,17] In this molecule the non-valence interactions make the dominant contribution to the stabilisation of the silatrane skeleton. Indeed, the optimum geometry of the silatrane ring in relation to the non-valence interactions, corresponding to a structure without bonding[18], is fairly close to the experimental structure[16,17].

The proposed model readily explains the destabilising resonance§ influence of the *p*- or π-donor Si-substituents in silatrane molecules, which is caused by the filling with electrons of the antibonding level of the hypervalent X–Si–N linkage as a result of which the degree of Si→N bonding diminishes.

The X–Si bond in silatranes is known[8,14,22,64] to be weakened¶, i.e. its length is increased, compared with the corresponding $X-Si_{sp^3}$ bond. This can apparently be accounted for by the fact that the hypervalent linkages are always weaker than the normal covalent bonds. The disposition and filling with electrons of the atomic levels corresponding to the experimental and theoretical results[21], which is illustrated in the diagram, clearly show that the degree of charge transfer from the donor orbital ϕ_N to the $3p_z$ orbital of the silicon atom is less than unity. The Si←N bond strength should increase with increase of the polarity of the bond. As the ionisation potential of the central atom increases, the energy of the bonding orbital falls, i.e. the hypervalent structure in fact becomes less stable (other conditions being equal). Comparison of the ionisation potentials of the carbon and silicon atoms (11.25 and 8.15 eV) explains why it is difficult to obtain carba-atrane†. On this basis, one may expect an increase of the bonding effect when the silicon atom in silatranes is replaced by a germanium or tin atom and also when the nitrogen atom is replaced by a phosphorus atom.

Thus the above investigation shows that the interaction between the silicon and nitrogen atoms in silatranes is due to the hypervalent bonding between these atoms and the substituent at the silicon atom. Despite a number of assumptions, the hypervalent bond model describes more realistically, in our view, the electronic and steric structures of silatranes than the widely held hypothesis of the sp^3d hybridisation of the silicon atom.

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§This influence has not been established experimentally quite so convincingly as the inductive effect. It has been observed in the analysis of the ^1H NMR and ESCA spectra as well as the kinetics of the hydrolysis of silatranes.

¶In the limiting case which obtains under electron impact, the hypervalent X–Si–N linkage is converted into the usual covalent linkage in the substituted ammonium ion $[\overset{\downarrow}{\underset{\downarrow}{Si}}(OCH_2CH_2)_3\overset{\downarrow}{\underset{\downarrow}{N}}]^+$ formed.

†A recent analysis[77] demonstrated the possibility of the existence of the stable hypervalent linkage X–C←P.

3. Donor–Acceptor Properties of Silatranes

The study of the mechanism of the hydrolysis of silatranes provided definite ideas about their donor–acceptor properties. The influence of the substituent at the silicon atom on the rate of hydrolysis of silatranes has been studied in both neutral[7,78,79] and in acid media[79–81]. The hydrolysis in a neutral medium is described satisfactorily by a first-order equation. The silatranes investigated can be divided into two reaction series. The first includes 1-alkylsilatranes and the second 1-alkoxy-derivatives. Linear relations between the logarithms of the rate constants for the hydrolytic reactions ($\lg k$) and the inductive constants of the substituent at the nitrogen atom (σ^*) have been observed for both series.

In the reaction series of 1-alkylsilatranes an increase of the inductive constant of the substituent X accelerates the hydrolysis. The high reaction constant $\rho = +4.76$ indicates a high degree of polarity of the transition state in which the silicon atom acquires a considerable negative charge.

The values of $\lg k$ for 1-vinyl- and 1-phenyl-silatranes deviate significantly from the linear correlation plot for 1-alkyl derivatives. This can be explained by the $p\pi-d\pi$ interaction of the above substituents at the silicon atom, which reduces the electron-accepting effect of X. A better explanation, from modern standpoints, consists in π-donation to the antibonding orbital of the hypervalent X–Si←N linkage. The same causes are probably responsible also for the lower than expected (in view of the high electronegativity of the alkoxy-groups) rate constants for the hydrolysis of 1-alkoxysilatranes. The reaction constant $\rho = 2.60$ for these compounds is smaller than for 1-alkylsilatranes. The results led to the conclusion that the rate-limiting stage in hydrolysis in a neutral medium is nucleophilic attack by a water molecule or an OH^- ion on the silicon atom.

The rate of hydrolysis of silatranes in an acid medium[79–81] is considerably higher than in a neutral medium. The influence of the substituent at the silicon atom is also different. With increase of the electronegativity of the latter, the rate constants for the hydrolysis of silatranes decrease appreciably, which made it necessary to assume[79,80] that the rate-limiting stage in the acid hydrolysis of silatranes is electrophilic attack by a hydronium ion on the oxygen atom with simultaneous transfer of the hydration shell to the silicon atom. The subsequent stages of the hydrolysis (in the first place the rupture of the Si–O) bond are probably very fast.

A somewhat different mechanism[82] has been proposed for the acid hydrolysis of the Si-substituted derivatives of tribenzosilatrane $X-\overset{\downarrow}{\underset{\downarrow}{Si}}(OC_6H_4)_3\overset{\downarrow}{\underset{\downarrow}{N}}$. The protonation of the oxygen atom is fast; on the other hand, the slow stage of the reaction is the dissociation of the Si–O bond in the protonated molecule. In both cases the possibility of the protonation of the nitrogen atom (as the initial and slowest step of the hydrolytic reaction in an acid medium) is rejected owing to its weak nucleophilic properties due to the steric inaccessibility of the LEP. On the other hand, evidence has been obtained[81] showing that the slowest stage of the hydrolytic reaction is the *endo–exo* transition of the silatrane molecule accompanied by the cleavage of the Si←N bond, which is followed by the protonation of the nitrogen atom in the transition state. This evidence is based on the analysis of the kinetic isotope effect observed in the hydrolysis. The proposed mechanism explains naturally the influence of the nature of the substituent at the silicon atom on the rate of the process.

The experimental activation energy for the hydrolysis of 1-phenylsilatrane (22 kcal mol^{-1}) [81] agrees satisfactorily with the Si←N bond energy in 1-hydrosilatrane estimated by the CNDO/2 method[21].

One of the most important pieces of chemical evidence for the involvement of the nitrogen atom in the transannular interaction with the silicon atom and hence for the pentacoordinate state of the latter in silatrane molecules is their inability to form methiodides as well as the low rate of their interaction with perchloric acid[1,6,7,73]. It is therefore not surprising that a number of studies have been made on the possibility of the formation of complexes of silatranes with other electron-accepting reagents. 1:1 complexes with certain Lewis acids ($TiCl_4$, $AlCl_3$) have been obtained for a series of 1-substituted silatranes; the structure of these complexes has been studied by infrared spectroscopy[83]; after the interaction of 1-ethoxysilatrane with $TiCl_4$, it was possible to isolate a 2:1 complex. In the infrared spectra of these complexes the bands assigned previously[1,7,43] to the Si←N coordinate bond persist, while the ν(Si–O) bands undergo a regular displacement. This led to the hypothesis[83] that the nitrogen atom in the silatrane molecule is not involved in the donor–acceptor interaction with Lewis acids. One of the oxygen atoms functions as the nucleophilic centre of the silatrane molecules in the complexes.

The isolation of the pure 1:1 hydrochloride of 1,3,7,10-tetramethylsilatrane, which is unstable in air, and analysis of its infrared spectrum led to the assertion[84] that the nitrogen atom is the centre of coordination with the HCl molecule. Evidence for this has been based on the fact that the infrared spectrum of the hydrochloride contains absorption bands of the stretching vibrations of the hydroxy-groups, which usually appear in the region of 3200–3300 cm^{-1}. This indicates the retention of the Si–O–C bonds in the complex-formation process. A group of bands characteristic of trialkylamine hydrochlorides was observed in the range 2500–2800 cm^{-1}. It was found that in the infrared spectrum of the hydrochloride of 1,3,7,10-tetramethylsilatrane all the absorption bands characteristic of the silatrane itself, including the 560–590 cm^{-1} band, are retained. Since this band has been assigned to the vibrations of the silatrane skeleton[46], its presence in the spectrum has been interpreted[84] as evidence for the retention of this skeleton in the complex. In this connection we may note that there is no absorption at 560–590 cm^{-1} in the infrared spectrum of the platinum derivative, which contains no transannular Si←N bond[16]. It is correct to assume[83] that the presence of the 560–590 cm^{-1} band in the infrared spectra of the complexes of silatranes with Lewis acids is evidence for the retention of the Si←N bond in these compounds. One cannot rule out the possibility that the hydrochloride of 1,3,7,10-tetramethylsilatrane is an oxonium derivative or a clathrate compound.

The ability of the nitrogen atom in certain 1-substituted silatranes to participate in complex formation with tetracyanoethylene (TCE) has been reported[84]. However, later convincing evidence was obtained[81] showing that the nitrogen atoms in silatrane molecules do not interact with TCE. The application of the EPR method and analysis of data published previously[84] established[85] that the absorption bands in the range 20000–25000 cm^{-1}, assigned[84] to the silatrane–TCE complex, are in fact due to the TCE radical-anion (and its conversion product). The formation of the TEC radical-anions is due to the electron transfer from the nitrogen atoms of impurity molecules present in the test substances in very small amounts. Carefully purified 1-alkylsilatranes do not give rise to a colour and EPR signals in systems with TCE.[85]

At the same time, it has been shown by ultraviolet spectroscopy[69] that 1-phenyl- and 1-benzyl-silatranes form charge-transfer complexes with TCE. However, in these two cases the donor centre is the aromatic substituent at the silicon atom. Analysis of the absorption bands in the spectra of these complexes shows convincingly that the silatranyl substituent is a better electron donor than the $Si(OC_2H_5)_3$ group. Silatranes are able to form hydrogen bonds with chloroform[26,52]. The composition of some of these associated species has been established by measuring the dielectric losses[86]; the proton acceptors in these compounds are oxygen atoms.

1-Methylsilatrane is capable of forming complexes with lanthanide shift reagents[87]. The interpretation of the paramagnetic shifts in the ^1H NMR spectrum of 1-methylsilatrane induced by europium trisdipivaloylmethanate [Eu(DPM)$_3$] (a lanthanide shift reagent) was based[88] on a comparison of the relative observed chemical shifts with the values calculated from McConnell's formula[89]. The best agreement (in terms of the *R*-factor) with experiment is obtained on the hypothesis that 90% of the 1-methylsilatrane molecules are involved in coordination with the acceptor via the oxygen atoms, while the remaining 10% are coordinated via the nitrogen atom. The 1-methylsilatrane molecule assumed to be coordinated with the shift reagent via the nitrogen atom should exist in the *endo*-form according to the calculation. However, the electron pair of the nitrogen atom in such a structure is known to be inaccessible to electrophilic attack. We believe that the results of the calculation[88] cannot be regarded as convincing demonstration of the involvement of the nitrogen atom in silatrane molecules in complex formation with Eu(DPM)$_3$. This is due to a number of fundamental difficulties which arise when the method of shift reagents is used in structural chemistry[90,91].

The conclusion that the nitrogen atom in silatranes is able to participate in complex formation was reached also on the basis of the study of the ^1H NMR of certain representatives of this class (X = CH_3, $ClCH_2$, or Cl) in the presence of paramagnetic complexes of $NiCl_2$ or $CoCl_2$ with 1-ethylimidazole[92]. In the systems investigated the induced shifts could be recorded reliably only in the presence of an excess of the paramagnetic complex by a factor of 1.5–2, which indicates an exceptionally low capacity of silatranes for coordination (the addition of individual $NiCl_2$ or $CoCl_2$ salts does not cause any changes in the ^1H NMR spectra of silatranes). It was found that there is a significant upfield shift of the signals due to the CH_2N protons, and not OCH_2 protons, in the ^1H NMR spectra of silatranes under the influence of these paramagnetic complexes. This served as the basis for the assumption that the nitrogen atom is a centre of coordination. However, the shifts induced by the Ni^{2+} and Co^{2+} complexes are largely of the contact type. Consequently, their values depend not only on the geometrical factor but also on the nature of the distribution of spin density in the adducts.

Thus there are at present no convincing grounds for the assertion that the lone electron pair of the nitrogen atom can be involved in the formation of complexes by silatranes with weak Lewis acids.

By virtue of the high dipole moments of silatranes, many of their properties should depend significantly on the polarity of the medium. The mechanism of the influence of the polar solvent reduces to non-specific interactions which induce the formation of solvates and the dissociation of the self-associated silatrane species, which leads ultimately to the perturbation of the most readily polarisable hypervalent X–Si←N linkage.

The phenomenon is illustrated by the recently observed dependence of the stretching vibration frequencies of the Si–H bonds in 1-hydrosilatrane (but not trialkoxysilane) on the solvent polarity and temperature[93]. With increase of the dielectric constant of the medium, the frequencies ν(Si–H) diminish, which corresponds to a weakening of the H–Si bond owing to the enhancement of the interaction between the silicon and nitrogen atoms. A significant influence of the medium on the properties of silatranes has also been observed in the study of the ^{1}H NMR spectra[53].

Further investigation of the interaction in silatrane–solvent systems may throw light also on the hitherto completely obscure problem of the mechanism of the formation of complexes by silatranes.

III. *C*-SUBSTITUTED SILATRANES

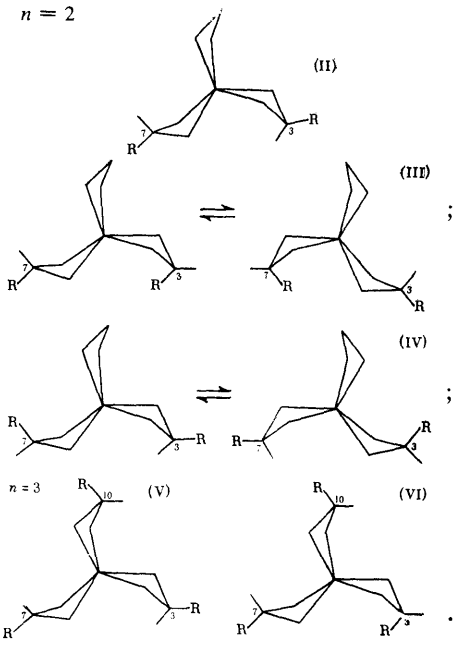
The study of the influence of the substituents R at the carbon atoms of the silatrane skeleton yields interesting information about the steric and electronic structures of silatranes. Successive substitution of the hydrogen atoms in the 3-, 7-, and 10-positions in chloroalkylsilatranes by methyl groups (i.e. R=CH_3) leads to an increase of the dipole moments[27]. It has been suggested that this is due to the conformational distortions of the atrane skeleton induced by the introduction of the methyl groups or by changes in its electronic structure.

At the same time the dipole moment of 1-phenyl-2-homosilatrane $C_6H_5Si(OCH_2CH_2CH_2)(OCH_2)_2N$ hardly changes when methyl groups are introduced into the 8- and 11-positions[94]. The intensity of the $(M-X)^+$ ions in the mass-spectra of 3-mono-, 3,7-di-, and 3,7,10-trimethyl derivatives of 1-chloroalkylsilatranes decreases linearly with increase of the number of methyl groups in the molecule[64]. The authors explained this by the increased strength of the Si–C bond, since, owing to the inductive influence of the *C*-methyl substituents, there is an increase of the electron density at the silicon atom and a weakening of the degree of the transannular interaction of the latter with the nitrogen atom. The ^{35}Cl NQR frequencies for 1-chloroalkyl-3,7-10-trimethylsilatranes are higher than for their *C*-unsubstituted analogues[54]. These data are consistent with the decrease following the introduction of the *C*-methyl group in the electron-donating capacity of the silatrane skeleton, which is caused by the weakening of the Si←N bond. Previously[54] this decrease was attributed to the distortion of the geometry of the silatrane skeleton arising when methyl groups are introduced.

The introduction of methyl groups in the 3-, 7-, and 10-positions in the silatrane skeleton reduces the hydrolysis rate constant[79,81]. This has been explained[79] by the increased order and hence strength of the Si–O bond. Within the framework of the proposed mechanism of the hydrolytic process (with the protonation of oxygen atoms as the rate-limiting stage), this hypothesis appears likely. In terms of the alternative concept (where protonation of the nitrogen atom is the primary step), the observed behaviour cannot be explained[81]. However, on the basis of the proposed mechanism for the hydrolytic reaction[81], one can assume that the introduction of *C*-methyl groups into the silatrane skeleton reduces its conformational mobility, hindering thereby the *endo–exo* isomerisation of the molecule.

As methyl groups accumulate, the intensity of the band in the range 560–590 cm^{-1} increases in the infrared spectra of 3-mono-, 3,7-di-, and 3,7,10-trimethylsilatranes[46]. However, without a correct identification of the band under discussion, it is so far impossible to explain the effect.

According to ^{1}H NMR data, Si-substituted 3-methylsilatranes exist as a single diastereoisomer with a pseudoequatorrial orientation of the substituent[30,52]; Si-substituted 3,7-dimethylsilatranes and 3,7,10-trimethylsilatranes consist of mixtures of the following diastereoisomers[53,95]:



Judging from the spin–spin coupling constants between the protons of the substituted atrane half-rings, all the methyl groups of isomer (V) as well as the 7- and 10-groups of isomer (VI) are oriented pseudoequatorially, while the 3-CH_3 group of isomer (VI) is disposed pseudoaxially. In diastereoisomer (II) both methyl groups are pseudoequatorial, but the substituted atrane half-rings are non-equivalent. On the other hand, in diastereoisomers (III) and (IV) the substituted half-rings are equivalent in pairs owing to the high conformational mobility of these isomers, the conformational changes being accompanied by a rapid *ae–ea* reorientation of the *C*-substituents.

A change in the temperature of solutions of 3,7-dimethyl-, and 3,7,10-trimethylsilatranes in various solvents from −80° to +200 °C does not alter the relative positions of their ^{1}H NMR lines[95]. This shows that the height of the barrier to the conversion of the *C*-substituted rings in silatrane molecules is very small (<2 kcal mol^{-1}). However, the differences between the strain energies of the rings substituted pseudoequatorially and pseudoaxially are fairly large. These two factors fully explain the existence of molecules of 3-methyl-substituted silatranes as well as diastereoisomers (V) and (VI) in a single energetically favourable conformation. The same causes are responsible for the ease of the conformational transitions between the two states (III) and (IV) which are degenerate with respect to energy. Furthermore, the equatorial–axial and not equatorial–equatorial orientation of the 3,7-substituents in isomers (III) and (IV) shows that the non-concerted conversion of the three five-membered rings is forbidden by virtue of the high strain energies of the asymmetric structure. This is confirmed by the results of conformational calculations[20]. Thus the conformational transitions of the silatrane skeleton are collective and take place with retention of C_3 symmetry.

Analogous conclusions were reached[96] in a ^{19}F NMR study of the stereochemistry of the *C*-(trifluoromethyl)silatranes# ($R = CF_3$). Naturally, the strain arising in the axial orientation should influence the extent of the transannular Si←N interaction. The shielding constants for the protons of the substituent at the silicon atom and the ^{29}Si nuclei in the case of *C*-substituted silatranes are greater for the less strained diastereoisomers[53].

The sum total of the data presented above requires a reconsideration of the problem of the influence of *C*-substituents on the spectroscopic and physicochemical properties of silatranes substituted in the 3-, 7-, 10-positions and the formulation of a series of new experimental approaches to its solution. The point is that all the characteristics of 3,7-di- and 3,7,10-tri-substituted silatranes obtained hitherto must be regarded as integral characteristics referring to a mixture of stereoisomers. This constitutes one of the causes of the evident conflict between the conclusions based on the change in the properties of silatranes following their successive *C*-substitution. Hence it is necessary to separate the above mixtures into individual components and to study in detail the physicochemical and spectroscopic properties of the latter. In analysing the results, particular attention must be paid to the stereodynamic characteristics of each isomer§. The solution of the problem formulated here can play a significant role in the practical applications of the silatranes. Data indicating the biological activity of *C*-substituted silatranes already exist[97]. One must assume that their optically active isomers will be still more effective.

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The structural studies on silatranes make a fundamental contribution to the development of a general theory of the structure of organic compounds containing the atoms of pentacoordinate silicon and its neighbours in the Periodic System.

Analysis of the results of physicochemical studies on silatranes indicates a significant influence of the hypervalent—Si←N linkage on their steric and electronic structures and in many instances also on their reactivity. At the same time, the extensive experimental data accumulated point to an urgent need for the solution of a number of new vital problems in the structural chemistry of silatranes. These involve in the first place a theoretical study of the structure and spectroscopic characteristics, an experimental determination of the thermodynamic parameters, and a systematic study of the reactivity and of the influence of the medium on the physical and chemical properties of silatranes.

The solution of all these problems will not only prove to be extremely useful for the theory of chemical structure and reactivity but will also permit a deeper understanding of the nature of the biological activity of silatranes.

During the preparation of the manuscript for the press, a number of new studies, extending the available ideas about silatranes, were published. A monograph[97] and a brief review[98] devoted to silatranes appeared. The concept of the hypervalent nature of the bonding in the axial fragments of silatrane molecules has been confirmed[99] by the CNDO/2 method (in terms of two parametrisations) in relation to 1-hydro- and 1-fluoro-silatranes. The constancy of the hypervalent X–Si←N bond order when the nature of the substituent X is varied has been demonstrated[33]. An increase of the degree of Si←N interaction in silatrane molecules with increasing proton-donating capacity, polarity, and polarisability of the medium has been observed by infrared spectroscopy[100] and ^{15}N and ^{29}Si NMR.[101,102] The solvent effects diminish with increasing strength of the Si←N bond under the influence of the 1-substituent[102]. According to ^{29}Si NMR data for the solid state[103], the influence of the crystal field on the state of the Si←N bond in silatrane molecules does not exceed the effect of a highly polar solvent. The influence of the nature of the 1-substituent in silatranes on the ^{15}N NMR chemical shifts has been studied[104,105]. The spin–spin interaction between the ^{15}N and ^{29}Si nuclei has been observed[104] in relation to 1-chloromethylsilatrane. The relaxation times of the ^{29}Si and ^{13}C nuclei have been studied by NMR.[106] The pathways leading to the dissociative ionisation of 1-substituted silatranes on electron impact have been examined[107]. Arguments supporting the manifestation of the ν(Si←N) stretching vibration band in the infrared spectra at frequencies below 400 cm^{-1} have been obtained[108]. It has been shown by EPR [109] that unstable silatranyl radicals are formed in the oxidation-reduction reactions of 1-hydrosilatrane.

#For these diastereoisomers, a further spin–spin interaction between the fluorine nuclei separated by eight valence bonds was observed for the first time.

§This must be taken in account also in a more detailed analysis of the known properties of *C*-unsubstituted and 3-substituted silatranes.

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