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NMR spectra of silatranes and M ← N (M = C, Si, Ge, Sn, Pb) bond lengths in atranes: Substituent effects

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Abstract

The literature data on X substituent influence on the ^{1}H, ^{29}Si and ^{15}N NMR chemical shifts (δ) and coupling constants (J) of Si-substituted silatranes $\mathrm{X\underleftarrow{Si(OCH_2CH_2)_3N}}$, as well as M–N bond lengths (d) in atranes $\mathrm{X\underleftarrow{M(OCH_2CH_2)_3N}}$ (M = C, Si, Ge, Sn, Pb) have been analyzed. It was established for the first time that the δ, J and d values depend not only on the inductive and resonance effects but also on the polarizability of X substituents. The polarizability contribution ranges from 8% to 25%.
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Keywords: Silatranes; NMR spectra; Substituent effects; Atranes; Polarizability effect; M ← N bond lengths

1. Introduction

The first representatives of five-coordinated silicon compounds – silatranes $\mathrm{X\underleftarrow{Si(OCH_2CH_2)_3N}}$ – attract scientists' interest for a long time [1]. The participation of the nitrogen atom in the transannular Si ← N bonding as well as the structure with a nearly trigonal-bipyramidal silicon atom impart some peculiar chemical [1] and biological properties [1l] to the silatranes. Molecular and stereoelectronic structure as well as physical properties of silatranes have been studied over many years [1,2]. The vibrational, ultraviolet, photoelectron, NMR, NQR spectroscopy, X-ray diffraction, mass-spectrometry, dielectrometry, thermochemistry, electrochemistry, and quantum chemistry techniques have been used to reveal a profound effect of X substituents, bound to the silicon atom, on the length of the Si ← N donor–acceptor bond as well as on the structure of silatranes. The investigations testify that the influence of substituents X on the physical properties of silatranes cannot be properly explained by only inductive effect and conjugation [1k].

Recently we have shown [2] that the third component of intramolecular interaction in silatranes exists along with inductive and resonance effects of substituents X. The appearance of this component is caused by the intramolecular charge transfer from the nitrogen atom to the silicon one because of the transannular Si ← N bonding. Consequently, the silicon atom acquires a partial negative charge q^-. Apparently, the charge q^- is not localized on the Si atom but is delocalized over the SiO_3 moiety. Delocalization of the q^- charge seems to be of a rather complex character. On the one hand, the charge is shifted from the Si atom to the more electronegative oxygen atoms. On the other hand, the silicon atom with respect to the oxygen atom is a resonance acceptor (d, n-conjugation effect). This effect includes the participation of unoccupied 3d-orbitals of Si and of antibonding σ^*-orbitals of the Si–X bonds [3]. Despite the complexity of charge q^- distribution over the SiO_3 moiety, the fact of the charge q^- transfer from the N atom to the SiO_3 fragment is well established. According to the existing estimates [1k], the charge transfer from the N atom to Si atom in 1-organylsilatranes is approximately 0.2 e.

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It is remarkable that intramolecular charge transfer in silatranes is formally similar to the intermolecular charge transfer in donor–acceptor complexes $X_nD^{q+} \cdot A^{q-}Hal_m$ (D = N, O, S; A = B, Al, Ga, Sn, Sb; Hal = F, Cl, Br) [4]. In these complexes charge transfer from the donor molecule X_nD to the acceptor molecule $AHal_m$ gives rise to a partial positive charge q^+ on donor centre *D*. The charge q^+ on the *D* centre of the complexes $X_nD^{q+} \cdot A^{q-}Hal_m$ and the charge q^- on the SiO_3 fragment of silatranes polarize the substituents X, thus inducing the dipoles in the X. Electrostatic interaction of the induced dipole moment with the charge q^+ in the $X_nD \cdot AHal_m$ complexes and with the charge q^- in silatranes is described by the equation:

$$E = -q^2\alpha/(2\varepsilon r^4), \qquad (1)$$

where *E* is the energy of electrostatic stabilization of the charge *q*, α is the substituent polarizability and *d* is the distance between the induced dipole and the charge *q* [5].

This dependence points to the fact that the stereoelectronic structure of molecules and complexes, containing excess charge on the reaction centre, depends not only on the inductive and resonance effects of the substituents but also on electrostatic interaction, i.e. polarizability effect. This assumption has been earlier proved by our group for various properties of the donor–acceptor complexes $X_nD \cdot AHal_m$ [4] and silatranes [2]. In the $X_nD \cdot AHal_m$ complexes the contribution of polarizability effect to the total effect of substituents is 15–56%. Influence of polarizability effect on the dipole moments of the molecules, the length of the Si ← N bonds, and the electrochemical oxidation potentials in silatranes is comparatively small (13–18%).

The aim of this work was to study the substituent effects on the NMR chemical shifts and coupling constants of silatranes. Much valuable information on the polarizability effect in silatranes can be hoped for.

2. Results and discussion

The NMR chemical shifts and the spin–spin coupling constants in the NMR spectra of silatranes and germatranes depend on their concentration in solution as well as on nature of the solvent used [1,6–14]. It should be taken into consideration when studying the influence of substituent X on the δ and *J* values [6–14]. The δ and *J* values, taken from [6–14], are given in Tables 1 and 2.

Chemical shifts $\delta(^{15}N)$ and spin–spin coupling constants $^1J(^{15}N–^{29}Si)$ are often considered as a direct measure of the transannular interaction in Si-substituted silatranes [1k,6].

We have found that some physical properties (δ, *J*) are related to free energy of dissociation $\Delta G^{\neq}$ of the Si ← N bonds by the general linear equation

$$P = k\Delta G^{\neq} + l \qquad (2)$$

According to Eqs. (2)–(7), the influence of X substituents on *P* properties indicated in Table 3 can be considered using the linear free energy relationships (LFER, see, e.g., Ref. [15]). In other words, the change in the free

Table 1
Free energy of dissociation $\Delta G^{\neq}$ (kJ mol^{-1}) and order *P*(SiN) of Si ← N bonds, NMR chemical shifts δ (ppm) in silatranes $\underleftarrow{XSi(OCH_2CH_2)_3N}$; $\delta_{Ge}(^{15}N)$ chemical shifts (ppm) in germatranes $\underleftarrow{XGe(OCH_2CH_2)_3N}$

X	Property *P*	$\Delta G^{\neq a}$	$P(SiN)^a$	$\delta(^1H)^b$	$\delta^{cr}(^{29}Si)^c$	$\delta^c(^{29}Si)^d$	$\delta^{cr}(^{15}N)^e$	$\delta^d(^{15}N)^f$	$\delta^c(^{15}N)^f$	$\delta^c_{Ge}(^{15}N)^h$	$\delta^d_{Ge}(^{15}N)^h$
	Solvent	DMSO-d_6	DMSO-d_6	$CHCl_3$	Solid-state	$CHCl_3$	Solid-state	DMSO-d_6	$CDCl_3$	$CHCl_3$	DMSO
H		61.9	0.32	3.83	–	–	−351.6	−353.0	−354.4	–	–
Me		55.2	0.19	3.78	−70.8	−64.4	−355.6	−356.4	−359.4	−367.1	−365.8
Et		–	–	3.78	−68.7	−64.3	–	–	–	–	–
i-Pr		–	–	3.75	–	–	–	–	–	–	–
Ph		59.0	0.27	3.91	−82.9	−80.2	−353.6	−354.4	−356.3	−366.3	−365.0
$H_2C{=}CH$		–	–	–	−83.4	−81.1	–	–	–	–	–
$HC{\equiv}C$		–	–	3.89	–	–	–	–	–	–	–
$ClCH_2$		–	–	–	−81.9	−79.9	–	–	–	–	–
Cl_2CH		–	–	–	−89.4	−87.6	–	–	–	–	–
HO		–	–	3.84	–	–	–	–	–	–	–
MeO		60.2	0.29	3.84	–	–	−350.1	−351.3	−352.7[g]	–	–
EtO		–	–	3.84	−96.0	−94.7	−350.1	–	−353.3	−362.9	−362.4
PhO		–	–	3.92	–	–	–	–	–	–	–
F		–	–	3.91	−101.5	−100.5	–	–	–	–	–
Cl		68.6	0.41	3.97	–	–	−348.1	−347.8	−348.8	−360.3	−359.8
Br		–	–	4.01	–	–	–	–	−348.0	−360.0	−358.6

[a] Ref. [6].
[b] $OCH_2–^1H$, Ref. [7].
[c] Refs. [1k,8].
[d] Refs. [1k,9].
[e] Refs. [1k,10].
[f] Refs. [1k,11].
[g] In $CHCl_3$.
[h] Ref. [12].