

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

Alexey N. Egorochkin <sup>a</sup>, Mikhail G. Voronkov <sup>b</sup>, Olga V. Kuznetsova <sup>a,\*</sup>, Olga V. Novikova <sup>a</sup>

<sup>a</sup> G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 603950 Nizhny Novgorod, Russia

<sup>b</sup> A.E. Favorsky Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russia

Received 16 May 2007; received in revised form 18 September 2007; accepted 24 September 2007

Available online 29 September 2007

## Abstract

The literature data on X substituent influence on the  $^1H$ ,  $^{29}Si$  and  $^{15}N$  NMR chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) of Si-substituted silatranes  $XSi(OCH_2CH_2)_3N$ , as well as  $M-N$  bond lengths ( $d$ ) in atranes  $XM(OCH_2CH_2)_3N$  ( $M = C, Si, Ge, Sn, Pb$ ) have been analyzed. It was established for the first time that the  $\delta$ ,  $J$  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%.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Silatranes; NMR spectra; Substituent effects; Atranes; Polarizability effect;  $M \leftarrow N$  bond lengths

## 1. Introduction

The first representatives of five-coordinated silicon compounds – silatranes  $XSi(OCH_2CH_2)_3N$  – attract scientists' interest for a long time [1]. The participation of the nitrogen atom in the transannular  $Si \leftarrow N$  bonding as well as the structure with a nearly trigonal-bipyramidal silicon atom impart some peculiar chemical [1] and biological properties [11] 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  $Si \leftarrow N$  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  $Si \leftarrow N$  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  $\sigma^*$ -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.

\* Corresponding author. Tel.: +7 831 4627795; fax: +7 831 4627497.  
E-mail address: [olga@iomc.ras.ru](mailto:olga@iomc.ras.ru) (O.V. Kuznetsova).

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:

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

where  $E$  is the energy of electrostatic stabilization of the charge  $q$ ,  $\alpha$  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  $Si \leftarrow N$  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  $\delta$  and  $J$  values [6–14]. The  $\delta$  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 ( $\delta, J$ ) are related to free energy of dissociation  $\Delta G^\ddagger$  of the  $Si \leftarrow N$  bonds by the general linear equation

$$P = k\Delta G^\ddagger + l \quad (2)$$

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  $\Delta G^\ddagger$  (kJ mol<sup>-1</sup>) and order  $P(SiN)$  of  $Si \leftarrow N$  bonds, NMR chemical shifts  $\delta$  (ppm) in silatranes  $XSi(OCH_2CH_2)_3N$ ;  $\delta_{Ge}(^{15}N)$  chemical shifts (ppm) in germatranes  $XGe(OCH_2CH_2)_3N$

X	Property $P$	$\Delta G^\ddagger^a$	$P(SiN)^a$	$\delta(^1H)^b$	$\delta^{cr}(^{29}Si)^c$	$\delta^c(^{29}Si)^d$	$\delta^{cr}(^{15}N)^e$	$\delta^d(^{15}N)^f$	$\delta^c(^{15}N)^f$	$\delta_{Ge}^c(^{15}N)^h$	$\delta_{Ge}^d(^{15}N)^h$
	Solvent	DMSO- $d_6$	DMSO- $d_6$	CHCl <sub>3</sub>	Solid-state	CHCl <sub>3</sub>	Solid-state	DMSO- $d_6$	CDCl <sub>3</sub>	CHCl <sub>3</sub>	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>i</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 <sub>2</sub> C=CH		–	–	–	–83.4	–81.1	–	–	–	–	–
HC≡C		–	–	3.89	–	–	–	–	–	–	–
ClCH <sub>2</sub>		–	–	–	–81.9	–79.9	–	–	–	–	–
Cl <sub>2</sub> CH		–	–	–	–89.4	–87.6	–	–	–	–	–
HO		–	–	3.84	–	–	–	–	–	–	–
MeO		60.2	0.29	3.84	–	–	–350.1	–351.3	–352.7 <sup>g</sup>	–	–
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

<sup>a</sup> Ref. [6].

<sup>b</sup> OCH<sub>2</sub>-<sup>1</sup>H, Ref. [7].

<sup>c</sup> Refs. [1k,8].

<sup>d</sup> Refs. [1k,9].

<sup>e</sup> Refs. [1k,10].

<sup>f</sup> Refs. [1k,11].

<sup>g</sup> In CHCl<sub>3</sub>.

<sup>h</sup> Ref. [12].

Table 2  
Spin–spin coupling constants  $J$  (Hz) in silatranes  $XSi(OCH_2CH_2)_3Na$

X	$J$	$^1J^d(^{15}N-^{29}Si)$		$^1J^d(^{15}N-^{13}C)$		$^2J^c(^{15}N-C-^{13}C)$		$^3J^d(^{15}N-C-C-^1H)$
		Solvent	DMSO- $d_6$	CDCl $_3$	DMSO- $d_6$	CDCl $_3$	DMSO- $d_6$	CDCl $_3$
H		2.05	1.10	6.75	7.04	1.10	1.25	2.15
Me		0.70	0.40	7.08	7.43	1.35	1.43	2.25
Ph		1.43	0.66	6.97	7.15	1.10	1.29	2.20
MeO		1.65	1.17	6.82	7.04	1.10	0.95	2.16
Cl		3.37	1.98	6.31	6.64	0.73	0.63	2.05

<sup>a</sup> Refs. [6,13,14].

Table 3  
Coefficients ( $k$  and  $l$ ) of equations  $P = k\Delta G^\ddagger + l$ , standard deviations ( $S_k$  and  $S_l$ ), standard errors of approximation ( $S_Y$ ), correlation coefficients ( $r$ )<sup>a</sup>

Property $P^b$	Equation	$k$	$l$	$S_k$	$S_l$	$S_Y$	$r$
$\delta^d(^{15}N)$	(3)	0.630	-390.8	0.12	7.6	1.2	0.946
$^1J^d(^{15}N-^{29}Si)$	(4)	0.200	-10.38	0.003	0.17	0.03	0.999
$^1J^d(^{15}N-^{13}C)$	(5)	-0.059	10.41	0.005	0.32	0.05	0.989
$^2J^c(^{15}N-C-^{13}C)$	(6)	-0.044	3.76	0.006	0.34	0.05	0.978
$^3J^d(^{15}N-C-C-^1H)$	(7)	-0.015	3.07	0.001	0.06	0.01	0.994

<sup>a</sup> Sample size  $n = 5$ ; X = H, Me, Ph, MeO, Cl.

<sup>b</sup> In DMSO- $d_6$ .

energy of dissociation  $\Delta G^\ddagger$  of Si ← N bonds due to substituents X is linearly related to the change in  $P$  properties [ $\delta^d(^{15}N)$ ,  $^1J^d(^{15}N-^{29}Si)$ ,  $^1J^d(^{15}N-^{13}C)$ ,  $^2J^c(^{15}N-C-^{13}C)$ , and  $^3J^d(^{15}N-C-C-^1H)$ ] of the silatrane molecules due to these substituents. We suppose that the other  $P$  properties [ $P(SiN)$ ,  $\delta(^1H)$ ,  $\delta^{cr}(^{29}Si)$ ,  $\delta^c(^{29}Si)$ ,  $\delta^{cr}(^{15}N)$ ,  $\delta^c(^{15}N)$ ,  $\delta_{Ge}^c(^{15}N)$ , and  $\delta_{Ge}^d(^{15}N)$ ] also obey the LFER concept.

In practice, the LFER is used in the form of the Hammett–Taft correlation equations. For the so-called classic reaction series 1,4- $XC_6H_4R_C^q$ , where substituents X are located at large distance  $d$  from the reaction centre  $R_C$  bearing positive or negative charge  $q$ , correlation equation are as follows:

$$P = P_H + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-), \quad (8)$$

where  $P$  are the chemical (logarithms of equilibrium and reaction rate constants) and physical properties;  $P_H$  is  $P$  value when X = H;  $\sigma_I$  is the universal inductive constant of substituent X, which is independent of the type of  $R_C$ ;  $\sigma_R$ ,  $\sigma_R^+$  and  $\sigma_R^-$  are the parameters characterizing the resonance effect of X substituent in the presence, respectively, of small, large positive, and large negative charge on the reaction (indicator) centre  $R_C^q$ . The  $a$  and  $b$  coefficients depend on the type of the  $R_C$  centre.

In these series the charge  $q$  may be localized on the reaction centre  $R_C$  or partially delocalized over the benzene ring. If delocalization is a negligibly small the polarizability effect is not observed. This is explained by large distance  $d$  that leads to negligibly small values of  $E$  in Eq. (1).

In the so-called non-classic reaction series the distance  $d$  between the charged reaction (indicator) centre  $R_C^q$  and substituents X is less than in the classic ones. For this reason, in the non-classic reaction series the electrostatic inter-

action, which energy  $E$  is described by Eq. (1), is always non-zero. Moreover, as noted above, in some intermolecular complexes  $X_nD^{q+} \cdot A^{q-}Hal_m$  electrostatic interaction (i.e. polarizability effect) exceeds 50% from total effect of substituents X [4]. For the non-classic reaction series the Hammett–Taft correlation equations take the form:

$$P = P_H + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-) + c\sigma_\alpha, \quad (9)$$

where  $\sigma_\alpha$  is the universal constant characterizing the polarizability effect of substituent X. The other symbols in Eqs. (8) and (9) are identical.

It is much more convenient to use the constants  $\sigma_\alpha$  than make complex and sometimes ambiguous calculations according to the formula (1) [5]. The constants  $\sigma_\alpha$  for many X substituents have been calculated by non-empirical quantum-chemical methods [16]. The  $\sigma$ -constants used are given in Table 4.

The foregoing will make it possible to prove the existence of the polarizability effect as well as to calculate its value. Statistical significance of the  $c\sigma_\alpha$  term in Eq. (9) is proof of the existence of this effect. Therefore, first we should consider Eqs. (8) and (9), relating the properties  $P$  of silatranes, given in Table 1, to effects of substituents X (Table 5).

From Table 5 it follows that for all the studied properties  $P$  ( $\Delta G^\ddagger$ ,  $P(SiN)$ ,  $\delta$ ,  $J$ ) three-parameter equations of (9) type have higher statistical characteristics than two-parameter equation (8). On going from Eq. (8) to the corresponding Eq. (9) the correlation coefficients  $r$  increase, whereas standard approximation errors  $S_Y$  decrease. It means that the term  $c\sigma_\alpha$  in Eqs. (11), (13), (15), (17), (19), (21), (23), (25), (27), (29), (31), (33), (35), (37), (39), (41), (43) and (45) is statistically significant. In other words, in the mentioned three-parameter general equation (9) the value

Table 4  
Inductive  $\sigma_I$ , resonance  $\sigma_R$ ,  $\sigma_R^+$ ,  $\sigma_R^-$  and polarizability  $\sigma_x$  constants of X substituents<sup>a</sup>

X	$\sigma_I$	$\sigma_R$	$\sigma_R^+$	$\sigma_R^-$	$\sigma_x$
H	0	0	0	0	0
Me	-0.05	-0.12	-0.26	-0.13	-0.35
Et	-0.05	-0.10	-0.25	-0.14	-0.49
<i>i</i> -Pr	-0.03	-0.12	-0.25	-0.12	-0.62
Ph	0.12	-0.13	-0.30	-0.10	-0.81
H <sub>2</sub> C=CH	0.13	-0.17	-0.29	-	-0.50
HC≡C	0.22	0.01	0.00	0.31	-0.60
ClCH <sub>2</sub>	0.13	-0.01	-0.14	-	-0.54
Cl <sub>2</sub> CH	0.31	0.01	-0.15	-	-0.62
Me <sub>2</sub> N	0.15	-0.98	-1.85	-0.27	-0.44
HO	0.33	-0.70	-1.25	-0.70	-0.03
MeO	0.29	-0.56	-1.07	-0.55	-0.17
EtO	0.26	-0.50	-1.07	-0.54	-0.23
PhO	0.37	-0.40	-0.87	-0.47	-0.38
F	0.45	-0.39	-0.52	-0.48	0.13
Cl	0.42	-0.19	-0.31	-0.23	-0.43
Br	0.45	-0.22	-0.30	-0.20	-0.59

<sup>a</sup> Refs. [2,4,16].

of the coefficient  $c$  is higher than standard deviation  $S_c$ . Consequently, the properties  $P$  ( $\Delta G^\ddagger$ ,  $P(\text{SiN})$ ,  $\delta$ ,  $J$ ) of silatranes depend on inductive, resonance and polarizability effect of the substituents X bound to the silicon atom.

Inductive Ind, resonance Res and polarization Pol contributions to the overall change of the properties  $P$  under the influence of substituents X can be calculated by representing Eq. (9) as follows:

$$P = P_H + \text{Ind} + \text{Res} + \text{Pol} \quad (46)$$

According to Table 6, the polarizability contribution Pol ranges from 8% to 25%. Let us briefly consider some peculiarities of the polarizability effect in silatranes and germatranes.

1. Polarizability effect of substituents X affects various properties of silatranes such as the dipole moments of the molecules, the dipole moments and the length of the Si ← N bonds, the electrochemical oxidation poten-

Table 5  
Coefficients ( $P_H$ ,  $a$ ,  $b$ , and  $c$ ) of equations  $P = P_H + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-)$  and  $P = P_H + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-) + c\sigma_x$ , standard deviations ( $S_P$ ,  $S_a$ ,  $S_b$ , and  $S_c$ ), standard errors of approximation ( $S_Y$ ), correlation coefficients ( $r$ ) and sample size ( $n$ )

Property $P$	Equation	Resonance constant	$P_H$	$a$	$b$	$c$	$S_P$	$S_a$	$S_b$	$S_c$	$S_Y$	$r$	$n$
$\Delta G^\ddagger$	(10)	$\sigma_R^-$	59.4	29.6	15.1	-	1.7	8.3	15.1	-	2.6	0.854	5
$\Delta G^\ddagger$	(11)	$\sigma_R^-$	61.7	33.3	18.6	6.2	0.4	1.4	1.3	0.7	0.4	0.996	5
$P(\text{SiN})$	(12)	$\sigma_R^-$	0.27	0.47	0.24	-	0.03	0.15	0.14	-	0.05	0.808	5
$P(\text{SiN})$	(13)	$\sigma_R^-$	0.31	0.53	0.30	0.11	0.02	0.09	0.08	0.05	0.03	0.944	5
$\delta(^1\text{H})$	(14)	$\sigma_R$	3.82	0.45	0.19	-	0.01	0.05	0.04	-	0.03	0.926	13
$\delta(^1\text{H})$	(15)	$\sigma_R$	3.80	0.44	0.16	-0.05	0.02	0.05	0.05	0.03	0.03	0.932	13
$\delta^{\text{cr}}(^{29}\text{Si})$	(16)	$\sigma_R$	-72.6	-56.4	14.4	-	1.1	5.1	4.9	-	2.0	0.983	8
$\delta^{\text{cr}}(^{29}\text{Si})$	(17)	$\sigma_R$	-68.5	-58.4	20.6	6.3	2.4	4.3	5.2	3.3	1.7	0.989	8
$\delta^{\text{c}}(^{29}\text{Si})$	(18)	$\sigma_R$	-68.4	-65.4	14.2	-	1.6	7.1	6.8	-	2.8	0.975	8
$\delta^{\text{c}}(^{29}\text{Si})$	(19)	$\sigma_R$	-62.4	-68.5	23.3	9.2	3.2	5.7	6.9	4.4	2.2	0.985	8
$\delta^{\text{cr}}(^{15}\text{N})$	(20)	$\sigma_R^-$	-353.6	13.8	1.0	-	1.1	5.1	4.0	-	1.6	0.799	6
$\delta^{\text{cr}}(^{15}\text{N})$	(21)	$\sigma_R^-$	-351.9	17.2	3.8	4.6	0.6	2.4	1.9	1.2	0.7	0.965	6
$\delta^{\text{d}}(^{15}\text{N})$	(22)	$\sigma_R^-$	-354.5	17.8	4.1	-	1.1	5.2	4.9	-	1.6	0.868	5
$\delta^{\text{d}}(^{15}\text{N})$	(23)	$\sigma_R^-$	-353.0	20.8	6.6	4.0	0.1	0.3	0.3	0.2	0.1	0.999	5
$\delta^{\text{c}}(^{15}\text{N})$	(24)	$\sigma_R^-$	-356.7	21.2	4.5	-	1.2	5.6	4.4	-	1.8	0.867	6
$\delta^{\text{c}}(^{15}\text{N})$	(25)	$\sigma_R^-$	-354.7	25.1	7.8	5.2	0.6	2.2	1.7	1.1	0.6	0.984	6
$\delta^{\text{c}}(^{15}\text{N})^{\text{a}}$	(26)	$\sigma_R^-$	-358.4	23.5	1.7	-	0.5	1.3	1.5	-	0.5	0.995	5
$\delta^{\text{c}}(^{15}\text{N})^{\text{a}}$	(27)	$\sigma_R^-$	-356.8	24.5	4.3	2.5	0.3	0.4	0.6	0.5	0.1	0.999	5
$\delta_{\text{Ge}}^{\text{c}}(^{15}\text{N})$	(28)	$\sigma_R^-$	-367.2	15.2	-1.0	-	0.8	2.3	2.8	-	0.9	0.960	5
$\delta_{\text{Ge}}^{\text{c}}(^{15}\text{N})$	(29)	$\sigma_R^-$	-364.1	16.9	3.9	4.7	0.3	0.3	0.5	0.4	0.1	0.999	5
$\delta_{\text{Ge}}^{\text{d}}(^{15}\text{N})$	(30)	$\sigma_R^-$	-365.7	14.8	0.8	-	1.0	2.5	2.9	-	1.0	0.950	5
$\delta_{\text{Ge}}^{\text{d}}(^{15}\text{N})$	(31)	$\sigma_R^-$	-362.9	16.4	5.3	4.3	1.8	2.0	3.4	2.5	0.7	0.975	5
$^1J^{\text{d}}(^{15}\text{N}-^{29}\text{Si})$	(32)	$\sigma_R^-$	1.55	5.91	3.12	-	0.35	1.71	1.60	-	0.53	0.846	5
$^1J^{\text{d}}(^{15}\text{N}-^{29}\text{Si})$	(33)	$\sigma_R^-$	2.03	6.67	3.83	1.29	0.06	0.22	0.20	0.11	0.06	0.998	5
$^1J^{\text{c}}(^{15}\text{N}-^{29}\text{Si})$	(34)	$\sigma_R^-$	0.77	3.34	1.14	-	0.25	1.21	1.13	-	0.37	0.786	5
$^1J^{\text{c}}(^{15}\text{N}-^{29}\text{Si})$	(35)	$\sigma_R^-$	1.11	3.88	1.64	0.91	0.02	0.09	0.08	0.05	0.03	0.999	5
$^1J^{\text{d}}(^{15}\text{N}-^{13}\text{C})$	(36)	$\sigma_R^+$	6.87	-1.62	-0.44	-	0.10	0.44	0.21	-	0.15	0.866	5
$^1J^{\text{d}}(^{15}\text{N}-^{13}\text{C})$	(37)	$\sigma_R^+$	6.75	-1.76	-0.49	-0.35	0.01	0.02	0.01	0.01	0.01	0.999	5
$^1J^{\text{c}}(^{15}\text{N}-^{13}\text{C})$	(38)	$\sigma_R^-$	7.18	-1.69	-0.70	-	0.09	0.44	0.41	-	0.14	0.878	5
$^1J^{\text{c}}(^{15}\text{N}-^{13}\text{C})$	(39)	$\sigma_R^-$	7.07	-1.87	-0.87	-0.31	0.06	0.24	0.22	0.12	0.07	0.970	5
$^2J^{\text{d}}(^{15}\text{N}-\text{C}-^{13}\text{C})$	(40)	$\sigma_R^-$	1.16	-1.40	-0.66	-	0.04	0.19	0.18	-	0.06	0.964	5
$^2J^{\text{d}}(^{15}\text{N}-\text{C}-^{13}\text{C})$	(41)	$\sigma_R^-$	1.11	-1.47	-0.73	-0.13	0.03	0.12	0.11	0.06	0.03	0.988	5
$^2J^{\text{c}}(^{15}\text{N}-\text{C}-^{13}\text{C})$	(42)	$\sigma_R^+$	1.32	-1.70	-0.14	-	0.07	0.32	0.16	-	0.11	0.941	5
$^2J^{\text{c}}(^{15}\text{N}-\text{C}-^{13}\text{C})$	(43)	$\sigma_R^+$	1.23	-1.80	-0.18	-0.25	0.03	0.11	0.06	0.06	0.04	0.993	5
$^3J^{\text{d}}(^{15}\text{N}-\text{C}-\text{C}-^1\text{H})$	(44)	$\sigma_R^-$	2.19	-0.43	-0.18	-	0.03	0.14	0.13	-	0.04	0.813	5
$^3J^{\text{d}}(^{15}\text{N}-\text{C}-\text{C}-^1\text{H})$	(45)	$\sigma_R^-$	2.15	-0.49	-0.24	-0.10	0.01	0.02	0.02	0.01	0.01	0.996	5

<sup>a</sup> X = Me, Ph, EtO, Cl, Br ( $n = 5$ ).

Table 6  
Contributions Ind, Res, and Pol (%) to the overall change in  $P$  properties due to the influence of substituents X

Property $P$	Equation	Ind	Res	Pol
$\Delta G^\ddagger$	(11)	51 ± 2	33 ± 2	16 ± 2
$P(\text{SiN})$	(13)	50 ± 8	32 ± 9	18 ± 8
$\delta(^1\text{H})$	(15)	58 ± 7	29 ± 9	13 ± 7
$\delta^{\text{cr}}(^{29}\text{Si})$	(17)	64 ± 5	23 ± 6	13 ± 7
$\delta^{\text{c}}(^{29}\text{Si})$	(19)	62 ± 5	22 ± 6	16 ± 8
$\delta^{\text{cr}}(^{15}\text{N})$	(21)	56 ± 8	19 ± 9	25 ± 7
$\delta^{\text{d}}(^{15}\text{N})$	(23)	59 ± 1	22 ± 1	19 ± 1
$\delta^{\text{c}}(^{15}\text{N})$	(25)	58 ± 5	21 ± 5	21 ± 4
$\delta^{\text{c}}(^{15}\text{N})$	(27)	80 ± 1	12 ± 2	8 ± 2
$\delta_{\text{Ge}}^{\text{c}}(^{15}\text{N})$	(29)	69 ± 1	14 ± 2	17 ± 2
$\delta_{\text{Ge}}^{\text{d}}(^{15}\text{N})$	(31)	65 ± 8	19 ± 12	16 ± 9
$^1J^{\text{d}}(^{15}\text{N}-^{29}\text{Si})$	(33)	50 ± 2	34 ± 2	16 ± 1
$^1J^{\text{c}}(^{15}\text{N}-^{29}\text{Si})$	(35)	53 ± 1	26 ± 1	21 ± 1
$^1J^{\text{d}}(^{15}\text{N}-^{13}\text{C})$	(37)	51 ± 1	32 ± 1	17 ± 1
$^1J^{\text{c}}(^{15}\text{N}-^{13}\text{C})$	(39)	55 ± 7	30 ± 8	15 ± 6
$^2J^{\text{d}}(^{15}\text{N}-\text{C}-^{13}\text{C})$	(41)	58 ± 5	34 ± 5	8 ± 4
$^2J^{\text{c}}(^{15}\text{N}-\text{C}-^{13}\text{C})$	(43)	69 ± 4	15 ± 5	16 ± 4
$^3J^{\text{d}}(^{15}\text{N}-\text{C}-\text{C}-^1\text{H})$	(45)	52 ± 2	30 ± 2	18 ± 2

tials of Si-substituted silatranes [2], the free energy of dissociation and the order of the Si ← N bonds, the NMR chemical shifts and the spin–spin coupling constants.

- Polarizability effect of substituents X also influences the  $\delta(^{15}\text{N})$  chemical shifts of germatranes  $\text{XGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$ .
- Polarizability effect of substituents X affects the properties  $P$  of silatranes both in solid state and in solution. In the latter case the value of this effect depends on the nature of solvent.
- The value of polarizability contribution Pol as well as the ratio of contributions Ind, Res and Pol depends on sample size  $n$ , i.e. nature of the X substituents in narrow series of silatranes. Thus, if  $n = 6$  (X = H, Me, Ph, EtO, Cl, Br; Eq. (25)) contribution Pol = 21%, while if  $n = 5$  (X = Me, Ph, EtO, Cl, Br; Eq. (27)) Pol = 8%.

Let us compare the influence of polarizability effect on chemical shifts in NMR spectra  $\delta(^{15}\text{N})$  for silatrane and germatranes at constant sample size  $n = 5$  (Eqs. (27), (29) and (31)). From Table 6 it follows that contributions Pol to the overall change of properties  $\delta_{\text{Ge}}^{\text{c}}(^{15}\text{N})$  and  $\delta_{\text{Ge}}^{\text{d}}(^{15}\text{N})$  in germatrane spectra are almost identical. Probably, the influence of polarizability effect on chemical shifts  $\delta(^{15}\text{N})$  of germatranes does not depend on solvent. At the same time, the influence of polarizability effect on  $\delta(^{15}\text{N})$  in germatranes is higher than in silatranes.

From the values of the spin–spin coupling constants  $J$  (Table 2) it follows that intramolecular interaction in silatranes, involving the nitrogen atom, is not limited by the Si ← N and C–N bonds but includes also the N–C–C–H moiety and depends on solvent. In addition, the nature of solvent affects the contribution Pol to the overall change of the coupling constants  $J$  due to the influence of substituents X (Table 6).

Consequently, in silatranes  $\text{XSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$  substituents X affect all the atoms of  $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$  group including the oxygen ones [1k,17]. According to Tables 5 and 6 and the data reported in [2], the properties  $P$  of silatranes change under the influence of inductive, resonance and polarizability effects of substituents X. At the same time, the elucidation of the relationships between the properties  $P$  and contribution ratio of Ind, Res and Pol is a complicated problem.

For instance, Si and N atoms as well as H atom in  $\text{OCH}_2$  moiety are in different distance from substituent X. However, the contributions of Ind, Res and Pol to the overall change of properties  $\delta^{\text{c}}(^{29}\text{Si})$ ,  $\delta^{\text{c}}(^{15}\text{N})$  and  $\delta(^1\text{H})$  differ little in value (Table 6). Another example is almost equal contribution ratios of Ind, Res and Pol, calculated by Eqs. (33) and (45) (Table 6) that describe the influence of substituent X on coupling constants  $^1J^{\text{d}}(^{15}\text{N}-^{29}\text{Si})$  and  $^3J^{\text{d}}(^{15}\text{N}-\text{C}-\text{C}-^1\text{H})$ . At the same time, the Si ← N fragment is close whereas the N–C–C–H fragment is far from substituent X.

Difficulties emerge when we consider the signs of resonance constant  $\sigma_{\text{R}}$ ,  $\sigma_{\text{R}}^+$  and  $\sigma_{\text{R}}^-$  in Eqs. (10)–(45) (Table 5). It is easily comprehended that resonance influence of substituent X on properties  $\delta(^{29}\text{Si})$  (Eqs. (16)–(19)) is characterized by the constants  $\sigma_{\text{R}}$ . As noted above, the constants  $\sigma_{\text{R}}$  are used when small charge  $q$  is presented on the reaction centre (Si atom in our case). It is not easy to explain the influence of substituents X on properties  $P$  of silatranes which are caused by the molecular fragments located in large distance from substituents X. In our opinion, to understand this fact one should take into account the conjugation in the O–CH<sub>2</sub>–CH<sub>2</sub>–N moiety.

In this connection let us consider the M ← N bond lengths in atranes  $\text{XM}(\text{OCH}_2\text{CH}_2)_3\text{N}$  (M = C, Si, Ge, Sn, Pb) (Table 7). Geometries of atranes have been determined using density functional theory [18].

From Table 7 it follows that the M ← N bond lengths change under the influence of substituents X. According to the calculations made by the least squares method, statistical characteristics of the three-parameter equation (9) are better than these of the two-parameter equation (8).

On going from Eq. (8) to Eq. (9) the correlation coefficients  $r$  increase, whereas the standard errors of approximation  $S_Y$  decrease (Table 8).

It follows that the polarizability effect markedly affects the M ← N bond lengths, calculated by quantum chemistry method [18]. The contributions of Ind, Res and Pol were calculated by Eq. (46) and given in Table 9.

Eq. (48) for carbatranes (M = C) is of special interest. Minkin et al. have published the quantum chemistry study of carbatranes, silatranes and germatranes using ab initio [MP2(full)/6-31G\*\*] and density functional theory (B3LYP/6-311+G\*\*) methods [19]. Donor–acceptor interaction M ← N in atranes is explained by the donation of lone electron pair of nitrogen atom on the antibonding orbital  $\sigma_{\text{MX}}^*$ . The energy of  $n_{\text{N}} \rightarrow \sigma_{\text{MX}}^*$  interaction in carbatranes (M = C) seems not to exceed 1 kcal mol<sup>−1</sup>, while

Table 7  
M ← N bond lengths (Å) for atranes  $\text{XM}(\text{OCH}_2\text{CH}_2)_3\text{N}^{\text{a}}$

X	M = C $d(\text{C} \leftarrow \text{N})$	M = Si $d(\text{Si} \leftarrow \text{N})$	M = Ge $d(\text{Ge} \leftarrow \text{N})$	M = Sn $d(\text{Sn} \leftarrow \text{N})$	M = Pb $d(\text{Pb} \leftarrow \text{N})$
H	3.115	2.301	2.335	2.401	2.480
Me	3.159	2.400	2.376	2.412	2.488
Me <sub>2</sub> N	3.161	2.452	2.370	2.399	2.474
HO	3.129	2.329	2.314	2.379	2.461
F	3.066	2.244	2.268	2.358	2.445
Cl	3.033	2.262	2.289	2.370	2.453
Br	3.009	2.254	2.289	2.371	2.455

<sup>a</sup> Ref. [18].

Table 8  
Coefficients ( $P_{\text{H}}$ ,  $a$ ,  $b$ , and  $c$ ) of equations  $P = P_{\text{H}} + a\sigma_{\text{R}}^+ + b\sigma_{\text{R}}^-$  and  $P = P_{\text{H}} + a\sigma_{\text{I}} + b\sigma_{\text{R}}(\sigma_{\text{R}}^+, \sigma_{\text{R}}^-) + c\sigma_{\text{z}}$ , standard deviations ( $S_{\text{P}}$ ,  $S_{\text{a}}$ ,  $S_{\text{b}}$ , and  $S_{\text{c}}$ ), standard errors of approximation ( $S_{\text{Y}}$ ), correlation coefficients ( $r$ ), and sample size ( $n$ )

Property $P$	Equation	Resonance constant	$P_{\text{H}}$	$a$	$b$	$c$	$S_{\text{P}}$	$S_{\text{a}}$	$S_{\text{b}}$	$S_{\text{c}}$	$S_{\text{Y}}$	$r$	$n$
$d(\text{C} \leftarrow \text{N})$	(47)	$\sigma_{\text{R}}^+$	3.122	-0.231	-0.049	-	0.016	0.044	0.014	-	0.023	0.926	7
$d(\text{C} \leftarrow \text{N})$	(48)	$\sigma_{\text{R}}^+$	3.133	-0.228	-0.051	0.052	0.014	0.033	0.011	0.026	0.018	0.957	7
$d(\text{Si} \leftarrow \text{N})$	(49)	$\sigma_{\text{R}}$	2.337	-0.294	-0.152	-	0.021	0.058	0.036	-	0.030	0.925	7
$d(\text{Si} \leftarrow \text{N})$	(50)	$\sigma_{\text{R}}$	2.320	-0.298	-0.150	-0.077	0.014	0.035	0.022	0.028	0.018	0.973	7
$d(\text{Ge} \leftarrow \text{N})$	(51)	$\sigma_{\text{R}}$	2.350	-0.184	-0.044	-	0.010	0.029	0.018	-	0.015	0.934	7
$d(\text{Ge} \leftarrow \text{N})$	(52)	$\sigma_{\text{R}}$	2.341	-0.187	-0.043	-0.042	0.004	0.011	0.007	0.008	0.006	0.991	7
$d(\text{Sn} \leftarrow \text{N})$	(53)	$\sigma_{\text{R}}^-$	2.407	-0.088	0.002	-	0.004	0.014	0.013	-	0.006	0.949	7
$d(\text{Sn} \leftarrow \text{N})$	(54)	$\sigma_{\text{R}}^-$	2.400	-0.099	-0.014	-0.021	0.002	0.004	0.004	0.003	0.002	0.996	7
$d(\text{Pb} \leftarrow \text{N})$	(55)	$\sigma_{\text{R}}^-$	2.483	-0.071	0.001	-	0.003	0.009	0.009	-	0.004	0.965	7
$d(\text{Pb} \leftarrow \text{N})$	(56)	$\sigma_{\text{R}}^-$	2.479	-0.078	-0.008	-0.013	0.002	0.004	0.004	0.003	0.002	0.993	7

Table 9  
Contributions Ind, Res, and Pol (%) to the overall change in  $P$  properties due to the influence of substituents X

Property $P$	Equation	Ind	Res	Pol	$\frac{\text{Ind}}{\text{Res}}$
$d(\text{C} \leftarrow \text{N})$	(48)	47 ± 7	38 ± 8	15 ± 8	1.2
$d(\text{Si} \leftarrow \text{N})$	(50)	42 ± 5	42 ± 6	16 ± 6	1.0
$d(\text{Ge} \leftarrow \text{N})$	(52)	57 ± 3	25 ± 4	18 ± 4	2.3
$d(\text{Sn} \leftarrow \text{N})$	(54)	67 ± 3	13 ± 4	20 ± 3	5.2
$d(\text{Pb} \leftarrow \text{N})$	(56)	72 ± 4	11 ± 5	17 ± 4	6.5

in silatranes ( $M = \text{Si}$ ) and in germatranes ( $M = \text{Ge}$ ) this value is 5–10 times higher [19]. The occurrence of the  $n_{\text{N}} \rightarrow \sigma_{\text{MX}}^*$  interaction suggests that qualitative regularities of the substituent influence on the properties  $P$  are common to all the atranes ( $M = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ). This suggestion is verified by data given in Tables 8 and 9. The contribution Pol in the  $\text{XM}(\text{OCH}_2\text{CH}_2)_3\text{N}$  ( $M = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ) atranes depends almost not at all on the nature of  $M$  atom (Table 9). Besides, on going from  $M = \text{C}$  and  $\text{Si}$  to  $M = \text{Ge}, \text{Sn}, \text{Pb}$  the inductive effect of substituents  $X$  increases and conjugation weakens. Therefore the  $\frac{\text{Ind}}{\text{Res}}$  value grows.

At the same time it is impossible to characterize the conjugation in  $\text{XM}(\text{OCH}_2\text{CH}_2)_3\text{N}$  by universal set of resonance parameters of the substituents  $X$ . The  $M$  atoms and resonance parameters (in parentheses) are as follows:  $\text{C}$  ( $\sigma_{\text{R}}^+$ );  $\text{Si}, \text{Ge}$  ( $\sigma_{\text{R}}$ );  $\text{Sn}, \text{Pb}$  ( $\sigma_{\text{R}}^-$ ). Thus, the charge sign on the reaction centre depends strongly on nature of the  $M$  atom. Let us consider briefly the electronic interactions in the

$\text{O}-M \leftarrow \text{N}$  ( $M = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ) fragments, which determine the conjugation between  $X$  and  $M$  affecting the  $M \leftarrow \text{N}$  bond lengths.

As one might expect, in the  $\text{O}-\text{C} \leftarrow \text{N}$  fragment of carbatranes, the  $\text{C} \leftarrow \text{N}$  interaction (or, more precisely,  $n_{\text{N}} \rightarrow \sigma_{\text{CX}}^*$ ) is weak [19] and small charge  $q^-$  of the  $\text{C}$  atom is shifted to the  $\text{O}$  atom. Hence,  $\text{C}$  atom is likely to be positively charged and the influence of conjugation between  $X$  and the  $\text{C}(\text{OCH}_2\text{CH}_2)_3\text{N}$  fragment on the  $\text{C} \leftarrow \text{N}$  bond length is described by constants  $\sigma_{\text{R}}^+$  (Eq. (48)).

The interaction  $\text{Si} \leftarrow \text{N}$  in silatranes (the  $\text{O}-\text{Si} \leftarrow \text{N}$  fragment) is stronger and charge  $q^-$  is higher than in carbatranes. As discussed above, due to high electronegativity of the  $\text{O}$  atom and d,n-conjugation effect the charge  $q^-$  is delocalized in the  $\text{SiO}_3$  moiety. Due to small charge of the  $\text{Si}$  atom the influence of conjugation between  $X$  and the  $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$  fragment on the  $\text{Si} \leftarrow \text{N}$  bond length is described by constants  $\sigma_{\text{R}}$  (Eq. (50)). This regularity seems to be also true for germatranes (Eq. (52)).

It is well known that, the d,n-conjugation effect, which causes the shift of electron density from the  $\text{O}$  atom to the  $M$  atom in the  $\text{MO}_3$  group, weakens with the change of  $M$  in a  $\text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$  series [3]. This seemingly will lead to increase of the shift of the charge  $q^-$  from the  $M$  atom to the  $\text{I}$  atom when increasing the atomic number of  $M$ . But in opposite direction ( $\text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$ ) another strong electronic effect increases, namely, the  $M \leftarrow \text{N}$  interaction [18,19]. The end result is probably an

induction of negative charges on the M atoms (Sn, Pb) in atranes  $\text{X}^{\text{M}}\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ . As a consequence conjugation of the substituent X with atrane skeleton is described by the constants  $\sigma_{\text{R}}^-$  (Eqs. (54) and (56)).

The complexity of resonance interaction between the substituents X and atrane skeleton affects not only the M ← N bond lengths (M = C, Si, Ge, Sn, Pb) (Table 8). As discussed above, the influence of conjugation on NMR chemical shifts  $\delta$  and coupling constants  $J$  in silatranes  $\text{X}^{\text{Si}}\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$  is impossible to describe by a universal resonance parameter of the substituents X. To get a rough idea of conjugation in the O–CH<sub>2</sub>–CH<sub>2</sub>–N fragment of silatranes it is appropriate to mention briefly the hyperconjugative interactions in substituted ethanes.

The quantum chemical study of molecules CH<sub>3</sub>CH<sub>2</sub>Y using density functional theory (B3LYP/6-31G\*\*) method and “natural” bond orbitals (NBO) analysis has made it possible to reveal the peculiarities of hyperconjugative  $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C-Y}}^*$  interaction between the vicinal orbitals [20]. For instance, the energies of interactions  $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C-OH}}^*$ ,  $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C-NH}_2}^*$  and  $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C-N}^+}^*$  are 4.7, 4.5, and 7.6 kcal mol<sup>-1</sup>, respectively. These values are close to the energies of interactions  $n_{\text{N}} \rightarrow \sigma_{\text{Si-H}}^*$  (3.3 kcal mol<sup>-1</sup>) and  $n_{\text{N}} \rightarrow \sigma_{\text{Si-F}}^*$  (mol<sup>-1</sup>) in silatranes [19].

The interaction  $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C-Y}}^*$  is accompanied by charge transfer from the hydrogen to the Y atom and represents a stereoelectronic effect, which value depends on relative positions of orbitals  $\sigma$  and  $\sigma^*$  [20]. Similarly the interactions  $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C-O}}^*$  and  $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C-N}}^*$  in silatranes influence the charges of the O and N atoms. In silatranes “... five-membered rings of... skeleton possess ‘twist’-like conformation” [18]. Because of this the orbitals  $\sigma$  and  $\sigma^*$ , probably, interact under unfavourable conditions.

Furthermore, in the molecules of silatranes the hyperconjugative interaction of the orbitals  $\sigma_{\text{C-O}}$  and  $\sigma_{\text{C-N}}$  is quite possible. However, it is not clear, which of these orbitals is an acceptor one. The substituents X also affect the hyperconjugative interactions in silatranes, because under the influence of the substituents X the energies of the orbitals  $\sigma$  and  $\sigma^*$  change.

The complex pattern of resonance interactions in silatranes is as yet imperfectly understood. Nevertheless, it is apparent that the charges on silatrane skeleton atoms are essentially different and the influence of the substituents X is propagated over all Si(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N fragment. This agrees well with the correlation analysis data (Tables 5 and 6).

### 3. Conclusions

A new approach to investigation of the substituent effects on various properties of atranes  $\text{X}^{\text{M}}\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$  (M = C, Si, Ge, Sn, Pb) has been developed. It is based on a consideration of electrostatic interaction (polarizability effect) due to the intramolecular charge transfer M ← N from the nitrogen atom to the M atom. The

occurrence of the polarizability effect is easily proved from the correlation analysis. A large body of literature data on X substituent influence on the experimental NMR chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) of silatranes and germatranes, as well as M ← N bond lengths ( $d$ ) in atranes obtained from quantum chemical calculation have been examined. Properties  $\delta$ ,  $J$  and  $d$  obey the linear free energy relationship. From the correlation analysis it follows that  $\delta$ ,  $J$  and  $d$  values depend not only joint influence of the inductive, resonance, and polarizability effects of substituents X. The polarizability contribution is variable from 8% to 25%. In silatranes substituents X affect all the atoms of Si(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N group. It is due to hyperconjugative interactions of the orbitals  $\sigma$  and  $\sigma^*$  in the O–CH<sub>2</sub>–CH<sub>2</sub>–N fragments of atranes. The qualitative regularities of the substituent influence are common to all the atranes. At the same time, the electronic interaction in the O–M ← N (M = C, Si, Ge, Sn, Pb) fragments, affecting the M ← N bond lengths, depend strongly on nature of the M atom. Therefore, it is impossible to characterize the conjugation in the molecules of atranes by the universal set of resonance parameters of X substituents.

### References

- [1] (a) M.G. Voronkov, Pure Appl. Chem. 13 (1966) 35; (b) M.G. Voronkov, Pure Appl. Chem. 19 (1969) 399; (c) M.G. Voronkov, V.M. Dyakov, S.V. Kirpichenko, J. Organomet. Chem. 233 (1982) 1; (d) P. Hencsei, L. Parkanyi, Rev. Silicon Germanium Tin Lead Comp. 8 (1985) 191; (e) S.N. Tandura, M.G. Voronkov, N.V. Alekseev, Top. Curr. Chem. 131 (1986) 99; (f) W.S. Sheldrick, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Part 1, Wiley, Chichester, 1989, p. 227; (g) R.J.P. Corriu, J.C. Young, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Part 2, Wiley, Chichester, 1989, p. 1241; (h) R.J.C. Corriu, J. Organomet. Chem. 400 (1990) 81; (i) J.D. Verkade, Coord. Chem. Rev. 137 (1994) 233; (j) P. Hencsei, Kemiai Koze 83 (1996) 165; (k) V. Pestunovich, S. Kirpichenko, M. Voronkov, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, Chichester, 1998, p. 1447; (l) M.G. Voronkov, V.P. Baryshok, Silatranes in Medicine and Agriculture, Publishing House of the SB RAS, Novosibirsk, 2005 (in Russian).
- [2] M.G. Voronkov, A.N. Egorochkin, O.V. Kuznetsova, J. Organomet. Chem. 691 (2006) 159.
- [3] M.G. Voronkov, A.N. Egorochkin, in: Z. Rappoport (Ed.), The Chemistry of Organic Germanium, Tin and Lead Compounds, Part 1, vol. 2, Wiley, Chichester, 2002, p. 131.
- [4] O.V. Kuznetsova, A.N. Egorochkin, O.V. Novikova, Russ. J. Gen. Chem. 76 (2006) 554.
- [5] P.D. Pacey, Q.-T.N. Tan, J. Phys. Chem. 99 (1995) 17729.
- [6] E. Kupce, E. Liepins, A. Lapsina, I. Urtane, G. Zalcans, E. Lukevics, J. Organomet. Chem. 279 (1985) 343.
- [7] S.N. Tandura, V.A. Pestunovich, G.I. Zelchan, V.P. Baryshok, Yu.A. Lukina, M.S. Sorokin, M.G. Voronkov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 30 (1981) 223.

- [8] M.Ya. Myagi, A.V. Samoson, E.T. Lippmaa, V.A. Pestunovich, S.N. Tandura, B.Z. Shterenberg, M.G. Voronkov, Dokl. Akad. Nauk SSSR 252 (1980) 140 (in Russian).
- [9] V.A. Pestunovich, S.N. Tandura, M.G. Voronkov, G. Engelhardt, E. Lippmaa, T. Pehk, V.F. Sidorkin, G.I. Zelchan, V.P. Baryshok, Dokl. Akad. Nauk SSSR 240 (1978) 914 (in Russian).
- [10] V.A. Pestunovich, B.Z. Shterenberg, E.T. Lippmaa, M.Ya. Myagi, M.A. Alla, V.P. Baryshok, L.P. Petukhov, M.G. Voronkov, Dokl. Phys. Chem. 258 (1981) 587.
- [11] V.A. Pestunovich, B.Z. Shterenberg, L.P. Petukhov, V.I. Rakhlin, V.P. Baryshok, R.G. Mirskov, M.G. Voronkov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 34 (1985) 1790.
- [12] V.A. Pestunovich, B.Z. Shterenberg, S.N. Tandura, V.P. Baryshok, M.G. Voronkov, N.V. Alexeev, N.Yu. Khromova, T.K. Gar, Izv. Akad. Nauk SSSR, Ser. Khim. (1980) 2179 (in Russian).
- [13] E. Liepins, I. Birgele, P. Tomsons, E. Lukevics, Magn. Res. Chem. 23 (1985) 485.
- [14] E. Kupce, E. Liepins, O. Pudova, E. Lukevics, J. Chem. Soc., Chem. Commun. (1984) 581.
- [15] (a) O. Exner, Correlation Analysis of Chemical Data, Plenum Press, New York, 1988;  
(b) A.N. Egorochkin, Russ. Chem. Rev. 61 (1992) 600;  
(c) T.M. Krygowski, B.T. Stepien, Chem. Rev. 105 (2005) 3482.
- [16] (a) W.J. Hehre, C.-F. Pau, A.D. Headley, R.W. Taft, J. Am. Chem. Soc. 108 (1986) 1711;  
(b) C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165.
- [17] E.E. Liepinsh, I.A. Zitsmane, G.I. Zelchan, E. Lukevits, J. Gen. Chem. USSR 53 (1983) 215.
- [18] S.E. Karlov, D.A. Tyurin, M.V. Zabalov, A.V. Churakov, G.S. Zaitseva, J. Mol. Struct. (THEOCHEM) 724 (2005) 31.
- [19] A.A. Milov, R.M. Minyaev, V.I. Minkin, Russ. J. Organ. Chem. 39 (2003) 340.
- [20] I.V. Alabugin, T.A. Zeidan, J. Am. Chem. Soc. 124 (2002) 3175.