

Polarizability effect in silatranes and related compounds

Mikhail G. Voronkov^a, Alexey N. Egorochkin^{b,*}, Olga V. Kuznetsova^b

^a A.E. Favorsky Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russia

^b G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 603950 Nizhny Novgorod, Russia

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Abstract

The dipole moments (μ) of the molecules, the dipole moments (μ_{DA}) and the length (d_{DA}) of the Si \leftarrow N bonds, and the electrochemical oxidation potentials (E_p) of Si-substituted silatranes, the dipole moments (μ^{hs}) of the molecules of Si-substituted 3-homosilatranes as well as the enthalpies of formation (ΔH^0) of the intermolecular complexes of SiF₄ with aniline derivatives depend not only on the inductive and resonance effects, but also on the polarizability of substituents which can be characterized by the σ_x constants.

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1. Introduction

Silatranes $X-Si(OCH_2CH_2)_3N$ (**1**) and their analogs such as 3-homosilatranes $XSi(OCH_2CH_2)_2N$ (**2**) are typical representatives of pentacoordinate organosilicon compounds [1]. By the present time the molecular structure, physical properties and reactivity as well as biological activity of silatranes and related compounds have been investigated in much detail [2]. All the structural studies of silatranes have unambiguously provided the evidence for the presence in their molecule of transannular Si \leftarrow N interaction and a specific electronic structure of the silatrane skeleton, Si(OCH₂CH₂)₃N (Sa) [1].

Systematic investigations of the silatranes using NMR, IR, UV, electron and photoelectron spectroscopy, mass-spectrometry, dielectrometry, electrochemistry, thermochemistry and quantum chemistry have shown that the electronic structure of silatranes and

their analogs essentially depends on the nature of substituent X bound to the silicon atom [1]. Even the earlier structural studies of silatranes by physical–chemical methods [1a] have brought into attempts of characterizing the influence of the substituents X on the silatrane group Sa basing on their inductive and resonance σ -parameters. At the present time we think that the mechanism of interaction of X and Sa fragments is not exhausted by the inductive and resonance effects of the substituent at the silicon atom.

Indeed, the transannular coordinate interaction in the heterocyclic system Sa brings the atoms of silicon and nitrogen closer to each other by a distance of ~ 2.00 – 2.25\AA (depending on the nature of the substituent X) and induces a partial negative charge (δ^-) on the silicon atom. This slightly lowers the positive charge on the silicon atom resulting from its interaction with more electronegative oxygen atoms and the axial substituent X. However, one cannot but mention unfavorable conditions for the above charge transfer since the silicon atom is a typical resonance acceptor with respect to atoms and groups containing lone electron pairs or carrying the negative charge (d,n-conjugation effect caused by mutual influence of vacant 3d-orbitals of the silicon

* Corresponding author. +7 831 2 127795; fax: +7 831 2 127497.
E-mail address: egor@iomc.ras.ru (A.N. Egorochkin).

atom and antibonding σ^* orbitals of the Si–X and Si–O bonds) [3]. In spite of this, delocalization of the negative charge from the nitrogen atom to the silicon (δ^-) and its surrounding (SiO_3) is beyond any doubt.

As it is known, in electron-deficient and electron-excess molecular systems a so-called polarizability effect operates alongside with the inductive and resonance interactions [4,5]. This effect, first observed in studying ionic gas-phase reactions, affects significantly the physical properties of individual compounds and complexes thereof (ionization potentials [6], electron affinity [7], spectroscopic and thermodynamical characteristics of charge-transfer complexes [8], hydrogen bond complexes [9] and other donor–acceptor complexes [10]). A distinctive feature of molecules and complexes of this type is a short distance between the reaction center R_C and the substituent R_S that can be shown schematically as R_S-R_C or R_S-Y-R_C , where Y is a mono- or two-carbon organic bridge.

A necessary condition for the occurrence of the polarizability effect is the appearance of excess charge q (δ^+ or δ^-) on R_C as a result of chemical reaction, complexation or electromagnetic impact: $R_S-R_C^q$ or $R_S-Y-R_C^q$.

The polarizability effect is an electrostatic attraction between the charge q and the dipole moment induced by the charge q in the substituents R_S [4–10]. The energy of electrostatic stabilization (E_{es}) of the charge q is expressed as follows:

$$E_{\text{es}} = -q^2\alpha/(2\epsilon r^4), \quad (1)$$

where α is the substituent polarizability, ϵ is the dielectric constant, and r is the distance between the charge q and the induced dipole.

From Eq. (1) it follows that the polarizability effect value depends strongly on the distance r .

It is believed that the polarizability effect operates not only in intermolecular, but also in intramolecular complexes, and the silatranes are typical example of this phenomenon.

Below we will try to prove this suggestion.

2. Results and discussion

One of possible approaches to the goal is correlation analysis.

In the system of Hammett–Taft correlation equations the chemical (logarithms of equilibrium and reaction rate constants) and physical properties (P) of classic objects of type 1,4- $\text{XC}_6\text{H}_4\text{Y}$ are described as follows:

$$P = P_{\text{H}} + a\sigma_{\text{I}} + b\sigma_{\text{R}}, \quad (2)$$

where σ_{I} and σ_{R} are the inductive and resonance constants of the substituents X, respectively, and P_{H} is P value when $\text{X} = \text{H}$. In the presence of a high positive or

negative charge on the reaction center Y the resonance constants σ_{R}^+ or σ_{R}^- , respectively, are used [3,5].

For non-classic reaction series distinguished from classic ones by lower r distance and the existence of the polarizability effect, Eq. (2) transforms [4–10] to

$$P = P_{\text{H}} + a\sigma_{\text{I}} + b\sigma_{\text{R}} + c\sigma_{\alpha}, \quad (3)$$

where σ_{α} is the polarizability constant of the substituent X. Like the σ_{I} and σ_{R} values which are measures of the inductive and resonance effects, respectively, the σ_{α} constants serve as quantitative characteristics of the polarizability effect and were calculated for a large number of substituents X by non-empirical quantum-chemical methods [4,5]. The use of σ_{α} values makes it possible to spare time-consuming calculations of the polarizability effect by the formula (1). Statistical significance of the polarizability contribution $c\sigma_{\alpha}$ to the P value is a rigorous criterion of the existence of the polarizability effect. In this case it is necessary that the reaction center R_C or fragment $Y-R_C$ in each of the reactions remains constant, whereas the inductive, resonance, and polarizability properties of the substituents R_S (X) vary in a wide range.

These requirements are met by the following physical properties of silatranes **XSa** (1): dipole moments (μ) and dipole moments (μ_{DA}) of the Si ← N bond [11], the Si ← N bond length (d_{DA}) [11], electrochemical oxidation potentials (E_{p}) [11], and dipole moments (μ^{hs}) of 3-homosilatranes (2) [11d] (Table 1). The enthalpy (ΔH_{AD}) of the Si ← N bond in 1-silatranes representing weak intramolecular complexes is, judging by different evaluations, 24–25 [11f], 5–15 [11d], 13–22 [11g] kcal mol⁻¹. According to exact thermochemical data the energy of the transannular Si ← N bond in 1-alkylsilatranes falls in the range 7.7–9.6 kcal mol⁻¹ (depending on the alkyl substituent nature) [11h,11i]. The silatranes were compared by us with strong intermolecular

Table 1

Dipole moments $\mu(\text{D})$ of molecules, dipole moments $\mu_{\text{DA}}(\text{D})$ and length $d_{\text{DA}}(\text{\AA})$ of Si ← N bonds, electrochemical oxidation peak potentials $E_{\text{p}}(\text{V})$ of Si-substituted silatranes (1); dipole moments $\mu^{\text{hs}}(\text{D})$ of Si-substituted 3-homosilatranes (2); σ -constants of X substituents

X	μ	μ_{DA}	d_{DA}	E_{p}	μ^{hs}	σ_{I}	σ_{R}	σ_{α}
H	–	–	–	1.70	–	0	0	0
Me	5.40	2.15	2.175	1.43	4.74	–0.05	–0.12	–0.35
Et	5.34	2.10	2.214	1.42	–	–0.05	–0.10	–0.49
Ph	5.76	2.14	–	1.55	5.23	0.12	–0.13	–0.81
H ₂ C=CH	5.88	2.63	2.150	1.52	5.18	0.13	–0.17	–0.50
HC≡C	–	–	–	1.80	–	0.22	0.01	–0.60
ClCH ₂	7.40	3.3	2.120	1.85	6.45	0.13	–0.01	–0.54
Cl ₂ CH	–	–	2.062	–	–	0.31	0.01	–0.62
MeO	–	–	–	1.53	–	0.29	–0.56	–0.17
EtO	5.88	1.52	2.152	1.53	4.71	0.26	–0.50	–0.23
PhO	7.08	2.5	–	–	–	0.37	–0.40	–0.38
F	–	–	2.042	–	–	0.45	–0.39	0.13
Cl	–	–	2.022	–	–	0.42	–0.19	–0.43

complexes (*p*-XC₆H₄NH₂)₂SiF₄ (**3a**) and (*o*-XC₆H₄NH₂)₂SiF₄ (**3b**) (Table 2), the enthalpy of formation of which (ΔH^0) exceeds 75 kcal mol⁻¹ [12].

Correlation equations of type (2) and (3) were calculated by standard programs “Statgraphics 3.0”. The least-square processing was performed at a confidence level of 95%. The previously used standard set of the substituent σ_I , σ_R , σ_R^+ and σ_x constants has been employed [5–10].

Let us consider the effect of substituents X on the dipole moments (μ) of silatranes and 3-homosilatranes (Table 1). As known [1], the high dipole moments of silatranes and their analogs provide one of the most convincing evidence for the presence of transannular Si ← N bond formed due to charge transfer from the nitrogen to the silicon atom (approximately 0.2e in 1-organylsilatranes [11]). Unfortunately, many compounds of type (1) and (2) are poorly soluble in non-polar organic solvents and this may impede measurement of their dipole moments. The most reliable μ and μ^{hs} values (benzene solutions, 25 °C), taken from [11d,11e], are given in Table 1 together with the calculated μ_{DA} values. According to [11e], calculation of the μ_{DA} values of

silatranes (1) by a vector scheme requires detailed data on their molecular geometry and dipole moments of individual bonds, which in principle depend on the nature of the substituent X in XSa. Due to this there appears to be some uncertainty in the μ and μ_{DA} values.

As follows from [11e], the most reliable data seem to be μ and μ_{DA} of silatranes (1), if X = Me, Et, Ph, EtO and PhO. In Eqs. (4) and (5) of type (2) standard deviations of the coefficients (S_a , S_b , S_c) as well as standard error of the approximation (S_Y) are high for these five compounds (Table 3). Correlation coefficients (r) are small and this do not allow consideration of (4) and (5) as even approximate. This indicates that the use of only the inductive effect and conjugation fails to give any idea concerning the influence of substituents X on the μ and μ_{DA} values.

On going from relationships (4) and (5) to three-parameter equations (6) and (7) of type (3) the correlation coefficients (r) sharply increase, whereas the S_a , S_b , S_c and especially S_Y values show a strong decrease (Table 3).

Thus, the high statistical characteristics of Eqs. (6) and (7) indicate a significant influence of the polarizability

Table 2

Enthalpies of formation ΔH^0 (*para*) (kcal mol⁻¹) for (**3a**) and ΔH^0 (*ortho*) (kcal mol⁻¹) for (**3b**) and sum $\sum \sigma$ of two σ -constants of X substituents

X	ΔH_c^0 (<i>para</i>) ^a	ΔH_{av}^0 (<i>para</i>) ^b	ΔH_{av}^0 (<i>ortho</i>) ^b	$\sum \sigma_I$	$\sum \sigma_R^+$	$\sum \sigma_x$
H	-77.8	-78.4	-78.4	0	0	0
Me	-81.0	-80.7	-77.2	-0.10	-0.52	-0.70
MeO	-81.3	-81.4	-76.6	0.58	-2.14	-0.34
Cl	-78.1	-78.0	-76.2	0.84	-0.62	-0.86
Br	-78.0	-78.2	-75.8	0.90	-0.60	-1.18

^a Calorimetric data [12].

^b Average values of the calorimetric and thermographic data [12].

Table 3

Coefficients (P_H , a , b , and c) of equations $P = P_H + a\sigma_I + b\sigma_R$ (or $\Delta H^0 = \Delta H_H^0 + a\sum \sigma_I + b\sum \sigma_R^+$) and $P = P_H + a\sigma_I + b\sigma_R + c\sigma_x$ (or $\Delta H^0 = \Delta H_H^0 + a\sum \sigma_I + b\sum \sigma_R^+ + c\sum \sigma_x$), 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	P_H or ΔH_H^0	a	b	c	S_P	S_a	S_b	S_c	S_Y	r	n
μ	(4)	5.72	5.09	1.97	–	0.32	1.82	1.82	–	0.34	0.873	5
μ_{DA}	(5)	2.48	2.66	3.00	–	0.28	1.59	1.60	–	0.30	0.527	5
μ	(6)	7.34	8.08	6.12	2.13	0.30	0.71	0.89	0.39	0.09	0.992	5
μ_{DA}	(7)	3.91	5.30	6.66	1.88	0.21	0.49	0.61	0.27	0.06	0.986	5
μ	(8)	7.51	8.56	6.76	2.40	0.51	1.13	1.21	0.80	0.26	0.949	7
μ_{DA}	(9)	3.68	4.74	5.92	1.60	0.21	0.48	0.51	0.34	0.11	0.981	7
μ^{hs}	(11)	5.47	5.58	4.67	–	0.26	2.15	1.27	–	0.36	0.861	5
μ^{hs}	(12)	6.27	6.88	6.18	1.38	0.55	1.85	1.38	0.89	0.28	0.921	5
d_{DA}	(13)	2.167	-0.378	-0.140	–	0.011	0.039	0.042	–	0.018	0.964	8
d_{DA}	(14)	2.130	-0.369	-0.202	-0.063	0.028	0.036	0.059	0.044	0.017	0.970	8
E_p	(16)	1.59	1.15	0.77	–	0.04	0.31	0.19	–	0.09	0.825	9
E_p	(17)	1.70	1.33	0.95	0.25	0.06	0.25	0.16	0.11	0.07	0.902	9
ΔH_c^0 (<i>para</i>)	(18)	-78.8	2.40	1.99	–	0.74	1.14	0.67	–	1.00	0.819	5
ΔH_c^0 (<i>para</i>)	(19)	-77.9	3.90	2.34	2.08	0.35	0.57	0.26	0.54	0.36	0.979	5
ΔH_{av}^0 (<i>para</i>)	(20)	-78.9	2.38	1.88	–	0.43	0.68	0.40	–	0.60	0.927	5
ΔH_{av}^0 (<i>para</i>)	(21)	-78.4	3.30	2.10	1.27	0.02	0.04	0.02	0.04	0.02	0.999	5
ΔH_{av}^0 (<i>ortho</i>)	(22)	-77.7	1.73	-0.14	–	0.52	0.81	0.47	–	0.71	0.696	5
ΔH_{av}^0 (<i>ortho</i>)	(23)	-78.4	0.64	-0.40	-1.52	0.10	0.19	0.09	0.18	0.12	0.992	5

effect on the dipole moments of silatranes. In this connection, it is likely that two possible factors responsible for the high μ values in the silatranes may be distinguished. These are:

1. Charge transfer from the nitrogen to the silicon atom leading to the formation of the transannular Si \leftarrow N bond. The coefficients of Eq. (6) are positive. This points to the fact that with strengthening the inductive and resonance acceptor (donor) properties of the substituents X, i.e., with growing the positive (negative) σ_I and σ_R values, the dipole moments (μ and μ_{DA}) increase (decrease). Consequently, the charge transfer from N to Si increases or decreases, respectively.
2. Polarizability effect. The charge q , transferred from the nitrogen atom to the silicon and, seemingly, delocalized along the Sa silatrane skeleton induces the dipole moment in the substituent X. The induced dipole, on the one hand, electrostatically interacts with the charge q (polarizability effect; see Eq. (1)) and becomes one of the components of the μ and μ_{DA} values, on the other hand.

With increasing the sample size (n) of the substituents X from 5 to 7, Eqs. (6) and (7) become (8) and (9) (Table 3).

The influence of the polarizability effect on the μ values and other properties P of silatranes can be evaluated quantitatively if Eq. (3) is depicted in the form

$$P = P_H + \text{Ind} + \text{Res} + \text{Pol}, \quad (10)$$

where $\text{Ind} = a\sigma_I$, $\text{Res} = b\sigma_R$ and $\text{Pol} = c\sigma_\alpha$, i.e., the inductive, resonance and polarizability contributions, respectively, to the overall change in P properties caused by the effect of the substituents X. The results of calculations of these contributions are tabulated in Table 4. From Table 3 it follows that a change in the μ and μ_{DA} values of the Si \leftarrow N bond in silatranes XSa when X varies from 16% to 18% is due to the polarizability effect of these substituents bound to the silicon atom.

Table 4

Contributions Ind, Res, and Pol (%) to the overall change in P properties of molecules (1), (2), and (3) due to the influence of substituents X

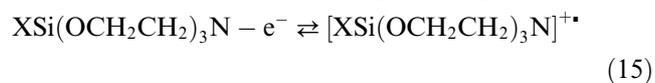
Property P	Equation	Sample size n	Ind	Res	Pol
μ	(6)	5	48 \pm 4	35 \pm 5	17 \pm 3
μ_{DA}	(7)	5	37 \pm 3	45 \pm 4	18 \pm 3
μ	(8)	7	43 \pm 6	40 \pm 7	17 \pm 6
μ_{DA}	(9)	7	34 \pm 4	50 \pm 4	16 \pm 3
μ^{hs}	(12)	5	36 \pm 10	51 \pm 11	13 \pm 9
d_{DA}	(14)	8	56 \pm 6	31 \pm 9	13 \pm 9
E_p	(17)	9	38 \pm 7	45 \pm 8	17 \pm 8
$\Delta H_c^0(\text{para})$	(19)	5	34 \pm 5	44 \pm 5	22 \pm 6
$\Delta H_{av}^0(\text{para})$	(21)	5	36 \pm 1	48 \pm 1	16 \pm 1
$\Delta H_{av}^0(\text{ortho})$	(23)	5	17 \pm 5	23 \pm 5	60 \pm 7

The polarizability effect influences the μ^{hs} value of Si-substituted 3-homosilatranes (2) (Table 1). Therefore, on going from two-parameter equation (11) to three-parameter one (12) the correlation coefficient (r) increases greatly, whereas the standard error of approximation (S_Y) decreases (Table 3). The polarizability contributions to (1) and (2) (Eqs. (6), (8) and (12)) are of similar value (Table 4).

Evidently, the polarizability effect, which influences significantly the transannular Si \leftarrow N bond polarity (i.e., the μ_{DA} value), changes also the bond length, d_{DA} (Table 1) in XSa molecules. This suggestion is supported by the X-ray diffraction d_{DA} data for eight crystalline silatranes [11] (the Si \leftarrow N bond lengths in the crystalline and gaseous XSa differ appreciably [11,13]). An increase of the correlation coefficient (r) on going from Eq. (13) to three-parameter equation (14) testifies that in silatranes the length of the transannular Si \leftarrow N bond depends not only on the inductive and resonance effects, but also on the polarizability effect of the substituent X. The contribution of the polarizability effect is 13 \pm 9% (Table 4).

In Eq. (14) the a , b and c coefficients are negative. From this it follows that an increase in the inductive and resonance acceptor (donor) properties of the substituent X, i.e., in positive (negative) σ_I and σ_R values, decreases (increases) and, consequently, strengthens (weakens) the Si \leftarrow N bond length. A growth of the negative values of the polarizability σ_α constants, i.e., an increase in the polarizability (α) of the substituent X (if the q and r variables in Eq. (1) are conventionally regarded to be constant values) weakens the Si \leftarrow N bond.

Now let us consider the substituent X effect on the values of the electrochemical oxidation peak potentials (E_p) of Si-substituted silatranes XSa [11] (Table 1). Electrochemical oxidation of silatranes in carefully dried MeCN on a glassy-carbon electrode proceeds with the formation of radical cations as primary products



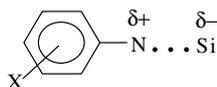
in which the Si \leftarrow N distance is longer than in the initial neutral XSa molecules [11]. Process (15) does not seem to be accompanied by Si \leftarrow N bond cleavage. This is supported by improvement in statistical characteristics (increased r , decreased S_Y) on going from Eq. (16) to three-parameter equation (17) (Table 3).

It is unlikely that a considerable contribution Pol (17 \pm 8%, Table 4) could occur in the absence of transannular Si \leftarrow N bond, when the distance between the radical cation center (nitrogen atom) and the substituent X is very large.

Thus, owing to the presence of the intramolecular Si \leftarrow N bond and the appearance of the charge q on the SiO₃ fragment, it is not only the inductive and resonance effects, but also the polarizability effect of the

substituent X occur in silatranes. It should be mentioned that some additional information on the polarizability effect can be derived by comparison of silatranes (mostly weak intramolecular complexes) containing the transannular Si—N bond with strong intermolecular complexes (3) bearing N...Si...N fragments (Table 2).

In complexes (3) one can observe a significant charge transfer from the nitrogen atom to the silicon. This leads to the appearing of a large positive charge δ^+ on the nitrogen atom.



In this case the conjugation between the substituent X and the reaction center $N^{\delta+}$ is characterized by the σ_R^+ constants [3,5], rather than the σ_R ones used with a small charge on the reaction center.

For the enthalpies of formation, ΔH^0 (*para*), of complexes of SiF_4 with *para*-substituted anilines (3a), Eqs. (18)–(21) are valid (Table 3).

Comparison of Eqs. (18) and (19), as well as (20) and (21) shows that in spite of the large distance (r) between R_C (nitrogen atom) and the substituent X, the polarizability effect in complexes (3a) plays an important part (Table 4). This is conditioned by a large q charge on R_C in strong complexes (3a) that, according to Eq. (1), increases the polarizability contribution.

The coefficients of equations (19) and (21) show plus sign, whereas absolute terms are negative. Therefore, strengthening of the inductive and resonance donor or acceptor properties of the substituent X, i.e., a decrease or increase in the σ_1 and σ_R^+ constants, as well as the corresponding change of the substituent X polarizability, i.e., a decrease or increase in the σ_α constants, leads to growth or lowering of the $-\Delta H^0$ (*para*) values and, consequently, to strengthening or weakening of complexes (3a).

Eqs. (22) and (23) (Table 3) are valid for the complexes of SiF_4 with *ortho*-substituted anilines (3b).

In complexes (3b) R_C and the substituent X are at a shorter distance (r) than in (3a). Therefore, according to Eq. (1), the contribution Pol should be expected to increase on going from (3a) to (3b). This is confirmed by the data tabulated in Table 4. Nevertheless, the interaction between R_C and the substituent X in complexes involving *ortho*-substituted anilines is a complicated problem, which invites further investigation.

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