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Electronic Effects of 2-Azasilatran-3-one Groups

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Abstract—1-Phenyl-2-azasilatran-3-ones have been studied by multinuclear NMR spectroscopy. The π-accepting ability of 2-azasilatran-3-one groups is substantially lower and their σ-donating ability is higher than those of (acetamido)diethoxysilyl groups of the model tetracoordinated compounds.

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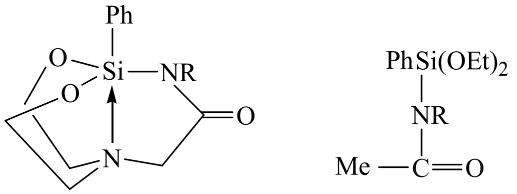
One of the fundamental problems of modern organic and organoelement chemistry is investigation of the effect of the stereoelectronic structure of molecules on their reactivity. These studies include both experimental and theoretical investigation of the nature of intramolecular stereoelectronic interactions and elucidation of the key factors determining the interaction of the functional groups as well as quantitative determination of the substituent effects on the reaction center [1–10]. The Hammett–Taft equations are successfully used for quantitative assessment of electron donating properties of organosilicon substituents [1, 3, 11–14], including those containing pentacoordinated silicon. This way, the Taft inductive constants of the silatranyl group $Si(OCH_2CH_2)_3N$ have been determined taking advantage of various spectral methods [15, 16]. The silatranyl group possesses a strong electron donating ability resulting in unique physico-chemical properties of silatranes [16, 17]. The most vivid manifestation of this effect has been observed in the series of 1-aminomethylsilatranes $R^1R^2NCH_2Si(OCH_2CH_2)_3N$. Introduction of the silatranyl group in the geminal position with respect to nitrogen atom has increased the N atom basicity and, con-sequently, has led to sharp increase of reactivity of α-silatranylamines as compared with organic amines [18–22]. Recently, we have synthesized a series of new silatranes analogues – 1-organyl-2-azasilatran-3-ones [23–25]. The present study aimed at quantitative assessment of the 2-azasilatran-3-one groups electronic effects in those compounds.

The ^{13}C NMR chemical shifts of the *meta*- and *para*-carbon atoms of the monosubstituted benzenes C_6H_5X phenyl ring are determined by inductive and resonance effects of the substituent X [26]. The procedure for quantitative assessment of the silyl groups electronic effects using the ^{13}C chemical shifts in the NMR spectra of 1-phenylsilatrane and the model phenyltrialkoxysilanes has been suggested in [27]. Table 1 summarizes the data of the NMR spectra of 1-phenyl-2-azasilatran-3-ones (**I, II**) and the model *N*-[phenyl(diethoxy)silyl]acetamides (**III, IV**).



R = H (**I, III**); R = Me (**II, IV**).

NMR spectra of the studied compounds (20 wt % solutions in $CDCl_3$) were recorded using Bruker DPX-400 spectrometer [100.6 (^{13}C), 79.5 MHz (^{29}Si)] with TMS as internal standard. The enhanced shielding of the silicon atom in compounds **I** and **II** (reflected in the chemical shift change by 36.4 and 36.8 ppm, respectively, as compared to the model tetracoordinated compounds **III** and **IV**) was due to the presence of the intramolecular N→Si coordination bond. The coordination-induced shift in the cases of 1-phenyl-2-azasilatran-3-ones was intermediate as compared with those in the cases of 1-phenylsilatrane (23.3 ppm [28]) and 1-phenyl-2,8,9-triazasilatrane (44.2 ppm [29]); that was indicative of the N→Si hypervalent interaction strengthening upon replacement of the oxygen atoms

Table 1. ^{13}C, ^{29}Si, ^{15}N NMR parameters (δ, ppm) for compounds **I–IV** in $CDCl_3$

Comp. no.	δ_C									δ_{Si}	δ_N
	CH_2N	CCH_2N	CH_2O	C^{ipso}	C^o	C^p	C^m	C=O	CH_3N		
I	53.28	55.29	58.08	139.12	134.29	128.64	127.38	168.19	–	–80.9	–256.9 –346.0
II	53.14	55.89	57.55	141.92	135.03	128.17	127.41	172.55	32.13	–79.0	–257.2 –344.9
III				122.35	134.81	131.45	128.16	172.10		–44.5	–275.9
IV				130.31	134.38	131.03	128.20	175.91	31.00	–42.2	–277.3

Table 2. σ_I Constants for silatranes, their analogues and model compounds of the general formula PhX

X	σ_I	σ_R	σ_R^0	σ_R^+	σ_R^-	σ*
$Si(OEt)_3$	–0.08	0.10	0.08	0.21	0.17	–0.18 [27]
$Si(OCH_2CH_2)_3N$	–0.40	0.02	0.02	–0.09	0.17	–0.89 [27]
$Si(NHPr)_3$	–0.01	0.03	0.02	0.12	0.08	–0.03 [29]
$Si(NHCH_2CH_2)_3N$	–0.17	–0.04	–0.03	–0.08	0.05	–0.38 [29]
$Si(OEt)_2NHC(O)Me$	0.09	0.14	0.10	0.34	0.16	0.20
$Si(OEt)_2N(Me)C(O)Me$	0.09	0.11	0.08	0.22	0.18	0.20
$Si(OCH_2CH_2)_2NCH_2C(O)NMe$	–0.23	0.02	0.01	0.00	0.13	–0.51
$Si(OCH_2CH_2)_2NCH_2C(O)NH$	–0.22	0.05	0.04	0.05	0.15	–0.49

in the equatorial plane of the atrane backbone by nitrogen atoms.

Taking advantage of the two-parameter linear equation: $\sigma_I = a_0 + a_1\delta(C^m) + a_2\delta(C^n)$ [27], the σ_I constants for 2-azasilatran-3-one groups $Si(OCH_2CH_2)_2\cdot[NRC(O)CH_2]N$ (R = H, Me) in compounds **I, II** were calculated (Table 2). The regression parameters a_0, a_1 and a_2 were taken from [27]. For comparison, in Table 2 the σ_I constants for 1-phenylsilatrane, 1-phenyltriazasilatrane and their model compounds are given [27, 29].

Similarly to the case of silatranes, the π-accepting ability of the 2-azasilatran-3-one groups was notably smaller [σ_R = 0.05 and 0.02 for **I** and **II**, respectively], than that of the (acetamido)diethoxysilyl groups of the model compounds [σ_R = 0.14 and 0.11 for compounds **III** and **IV**, respectively]. The σ-donating ability of the 2-azasilatran-3-one group of the model compounds **III**, **IV** was strongly increased as compared with that of 1-phenyl-2-azasilatran-3-ones (**I, II**), the Δσ* value being 0.69 and 0.71 for compounds **I** and **II**, respectively. Those values coincided with the Δσ* value of in the case of 1-phenylsilatrane (0.71) and were almost twice larger than that in the case of 1-phenyl-2,8,9-triazasilatrane (Δσ* = 0.36) [29]. No direct correlation was revealed between the change of the coordination shift, taken as a measure of the N→Si intramolecular interaction strength, and change of the atrane group σ-donating ability in the following series: 1-phenylsilatrane, 1-phenyl-2-azasilatran-3-one, and 1-phenyl-2,8,9-triazasilatrane. 1-Phenyl-2-azasilatran-3-ones contained two oxygen atoms and one nitrogen atom in the equatorial plane, but that nitrogen atom was a part of the amide fragment bearing special structural features. To understand the relationship between the electronic effects of the atrane groups and the extent of the N→Si intramolecular coordination interaction, expressed via spectral parameters, a comprehensive study of 1-phenylsilatranes with varied structure of the atrane cycle should be performed. Such a study goes beyond the scope of this paper and will be reported separately. The results reported in this paper showed that 2-azasilatran-3-one groups as well as the silatranyl group were strong σ-donors. Therefore, the reactivity of the functional groups X (Hlg, RO, RS, R^1R^2N) of α-carbofunctional 2-azasilatran-3-ones XCH_2SiAtr could be assumed notably different from that of their organic analogues XCH_2R.

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