

ATRANES

XVII. Dipole Moments of Si-Substituted Silatranes*

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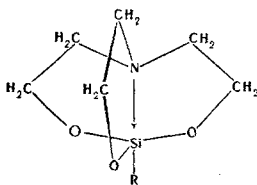
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The dipole moments of 12 Si-substituted silatranes have been determined in chloroform and ethyl acetate. We have followed the electronic influence of silicon atom substituents on the dipole moment of the silatranes, taking into account the presence of the Si←N transannular bond in them. A hypothesis has been put forward on the formation by chloroform of a hydrogen bond with the silatranes (the oxygen atoms act as the donor centers). A study of the IR spectra of the silatranes in paraffin oil and in chloroform has shown that in CHCl₃ the frequencies corresponding to the asymmetric stretching vibrations of the Si—O bond increase by 15–30 cm⁻¹.

The dipole moment method is widely used to study the structure of organosilicon compounds and to elucidate the valence state of the Si atoms in them and also the possibility of the participation of the vacant 3d orbitals of silicon in conjugation (see, for example, [2–7]).

Among organosilicon compounds particular interest is afforded by ethers of silanetriols and triethanolamine, the so-called silatranes [8, 9], with the general formula:



R=CH₃ (I), C₂H₅ (II), CH₂=CH (III), C₆H₅ (IV),
H (V), C₂H₅O (VI), C₆H₅O (VII), 3-CH₃C₆H₄O (VIII),
4-(CH₃)₃CC₆H₄O (IX), 5-CH₃-2-(CH₃)₂CHC₆H₃O (X),
4-ClC₆H₄O (XI), 3-O₂NC₆H₄O (XII).

According to the literature [2, 9, 10] the characteristic feature of the silatranes is the presence of a transannular donor-acceptor Si←N bond due to the predominant sp³d hybridization of the silicon atom. This determines the features of the chemical behavior of the silatranes and permits the high values of their dipole moments to be satisfactorily explained, and it also enables the changes in the values of the dipole moments (μ) of the silatranes to be connected with the electronic influence of the substituents on the silicon atom.

We have determined the dipole moments of 12-Si-substituted silatranes at 25° C in chloroform (Table 1) and in ethyl acetate (Table 2) (the dipole moments of some of the silatranes studied have previously been

determined in benzene [2]). The method of measurement has been described previously [11]. Calculation of the dipole moments in a polar solvent was carried out by means of Osipov's formula [12]. The refractive indices were determined by means of an RF-22 refractometer.

The dipole moments of the metalloatranes are determined mainly by the moment of the highly polar M←N coordination bond (where M is a metal) [13]. The contribution of this bond to the dipole moment is so considerable that for the silatranes ($\mu \approx 6$ D in C₆H₆ [2]), if it were absent, the calculated moment would have a far lower value of the order of 0.2–0.5 D [2, 9].

Two interconnected factors affect the dipole moments of the silatranes studied: 1) the increase in the dipole moment through the vectorial combination of the moments of the Si←N and Si—R bonds; 2) the change in the moment of the coordination bond due to the electronic effect of the substituent.

The results obtained show that the dipole moments of the silatranes containing an alkoxy or an aryloxy group on the silicon atom (R = Oalk or OAr) are always greater than the moments of the silatranes in which the Si atom is connected with the corresponding hydrocarbon substituent (R = Alk or Ar). Since in both cases the positive end of the dipole is directed toward the silicon atom [2, 3], the moment of the molecule is composed of the moment of the donor-acceptor bond and the moment of the Si—R bond.

As is well known, the dipole moment of the Si—O bond (1.36 D for R = Oalk, 1.86 D for R = OAr [7]) exceeds the moment of the Si—C bond (0.6 D) [14] which, assuming the constancy of the moment of the Si←N bond, satisfactorily explains the observed increased values of the dipole moments of the aryloxy- and alkoxy-silatranes. However, the moment of the Si←N bond cannot be considered constant, as is shown by the lack of correspondence between the increases in the dipole moments on passing from the alkyl- and arylsilatranes to the corresponding alkoxy and aryloxy derivatives and the vectorial sum of the moments. Since the 3d orbitals of the silicon atom participate in the formation of the donor-acceptor bond, the moment of the Si←N bond also obviously depends on the competing occupancy of the vacant Si orbitals by the electrons of the substituent R. Electron-donating substituents oppose the existence of the Si←N coordination bond and its dipole moment decreases, which leads to a fall in the moment of the molecule as a whole.

The electronic influences of aryloxy and alkoxy groups are characterized by the -I and +M effects. It

*For part XVI, see [1].

Table 1
Dipole Moments of the Silatranes in Chloroform and Intermediate
Figures for Their Determination*

Com- pound	R	N	ϵ^{25}	d_4^{25}	n_D^{25}	P_{or}, cm^3		μ, D
						solu- tion	sub- stance	
I	CH ₃	0.00293	4.9940	1.4787	1.4430	35.10	1172	7.57
		0.00303	5.0051	1.4783	1.4431	35.23	1176	7.57
II	C ₂ H ₅	0.00300	4.9475	1.4790	1.4431	34.59	1030	7.09
		0.00434	5.0602	1.4784	1.4433	35.86	1014	7.04
III	CH ₂ =CH	0.00124	4.7812	1.4796	1.4435	32.70	1134	7.44
		0.00196	4.8471	1.4796	1.4437	33.42	1100	7.33
IV	C ₆ H ₅	0.00247	4.9408	1.4785	1.4437	34.52	1152	7.50
		0.00267	4.9648	1.4782	1.4439	34.79	1167	7.55
V	H	0.00159	4.9122	1.4791	1.4440	34.12	1649	8.97
		0.00165	4.9247	1.4791	1.4440	34.25	1674	9.04
VI	C ₂ H ₅ O	0.00208	4.9368	1.4794	1.4432	34.44	1403	8.27
		0.00278	5.0300	1.4794	1.4433	35.47	1429	8.35
VII	C ₆ H ₅ O	0.00251	5.0830	1.4793	1.4438	36.07	1751	9.24
		0.00352	5.2345	1.4787	1.4440	37.77	1740	9.21
VIII	3-CH ₃ C ₆ H ₄ O	0.00194	4.9927	1.4805	1.4439	35.03	1660	9.00
		0.00208	5.0147	1.4804	1.4439	35.28	1672	9.03
IX	4-(CH ₃) ₃ CC ₆ H ₄ O	0.00059	4.7608	1.4797	1.4431	32.49	1554	8.74
		0.00110	4.8241	1.4796	1.4431	33.22	1510	8.52
X	5-CH ₃ -2-(CH ₃) ₂ CHC ₆ H ₃ O	0.00127	4.8418	1.4793	1.4433	33.31	1387	8.22
		0.00191	4.9232	1.4790	1.4437	34.33	1468	8.47
XI	4-ClC ₆ H ₄ O	0.00107	4.8855	1.4813	1.4430	33.85	2056	10.02
		0.00113	4.9025	1.4816	1.4430	34.04	2116	10.16
XII	3-O ₂ NC ₆ H ₄ O	0.00079	4.8434	1.4803	1.4435	33.37	2619	11.31
		0.00134	4.9875	1.4800	1.4438	34.98	2754	11.60

*N, ϵ^{25} , d_4^{25} , n_D^{25} , P_{or} , and μ are, respectively, the molar fraction, the dielectric constant, the density, the refractive index of the solution, the orientation polarization, and the dipole moment.

Table 2
Dipole Moments of the Silatranes in Ethyl Acetate

Com- pound	R	N	ϵ^{25}	d_4^{25}	n_D^{25}	P_{or}, cm^3		μ, D	μ, D in C ₆ H ₆ *
						solu- tion	sub- stance		
I	CH ₃	0.00125	6.2085	0.8921	1.3700	62.74	656	5.66	5.30
		0.00160	6.2224	0.8922	1.3701	62.94	649	5.63	
III	CH ₂ =CH	0.00144	6.3390	0.8904	1.3700	64.58	734	5.99	5.88
		0.00201	6.3701	0.8907	1.3700	65.02	758	6.09	
VII	C ₆ H ₅ O	0.00025	6.0102	0.8935	1.3700	60.01	1046	7.14	7.13
		0.00031	6.0137	0.8936	1.3700	60.05	965	6.85	
XII	3-O ₂ NC ₆ H ₄ O	0.00072	6.3685	0.8903	1.3699	64.97	1943	9.74	9.69
		0.00087	6.3907	0.8906	1.3700	65.25	1926	9.69	

*According to the literature [2]

may be assumed that in the 1-aryloxysilatrane the aryloxy group exhibits predominantly electron-accepting properties, which lead to an increase in the moment of the Si←N bond and, correspondingly, of the dipole moment of the compound. To a considerable extent this explains the increase in the values of μ of compounds XI and XII, which contain electronegative substituents in the aromatic nucleus, and the decrease in the moments of compounds VIII, IX, and X, containing electron-donating groups in the phenyl radical. From this point of view it is also possible to understand the decrease in the dipole moments of the silatrane on passing from alkoxy and aryloxy to alkyl substituents, which, in this case, apparently exhibit electron-donating properties. Thus, the treatment of the results obtained is in good agreement with ideas on the presence in the silatrane of a transannular donor-acceptor Si←N bond.

The dipole moments of some silatrane determined in ethyl acetate (Table 2) are considerably lower than the moments of the corresponding compounds in chloroform (by 1.3–2.4 D) but are identical with the values of the moments in benzene [2]. Since to calculate the dipole moments of the silatrane in CHCl_3 and $\text{CH}_3\text{COOC}_2\text{H}_5$ an equation [12] was used which largely takes into account the influence of a polar solvent, as is shown by the values of μ in ethyl acetate, in this case some other factors probably affect the value of μ .

We assume that this is explained by the formation by chloroform of a hydrogen bond with the silatrane molecule. As is well known, the protonated hydrogen atom of the C—H bond of chloroform is capable of taking part in the formation of a hydrogen bond with electron-donating atoms [15]. Chloroform does not form a hydrogen bond with the nitrogen atom of a silatrane since this would necessarily lead to a weakening of the Si←N coordination bond and this, as mentioned above, would cause not an increase but a decrease in the dipole moment of the molecule. This shows the relative strength of the Si←N coordination bond in which the unshared pair of electrons of the nitrogen atom participates.

The increase in the dipole moments of the silatrane in chloroform can apparently be explained by the formation of a hydrogen bond between the CHCl_3 and the oxygen atoms of the silatrane skeleton. (The existence of such an interaction has been shown by V. A. Pestunovich, M. G. Voronkov, and G. I. Zelchan in a study of the PMR spectra of systems of silatrane with chloroform.) In this case, the unshared pair of electrons of an oxygen atom participates in donor-acceptor interaction with the hydrogen atom of the chloroform, which leads to a weakening of the p_π — d_π conjugation of the silicon with the oxygen, in consequence of which the 3d orbitals of the silicon are partially freed. This, in its turn, leads to an increase in the moment of the Si←N bond and to a corresponding rise in the dipole moment of the silatrane in chloroform. However, the influence of the hydrogen bonds of the oxygen atoms with CHCl_3 may also have a purely inductive nature.

Some confirmation of the formation of hydrogen bonds is given by the IR spectra that we obtained of

the silatrane under consideration in paraffin oil and in chloroform. These spectra were taken on an IKS-14A double-beam spectrometer in the range of a NaCl prism (700 – 1800 cm^{-1}). The assignment of the absorption bands was carried out in accordance with published data [16]. Without dwelling on a detailed analysis of the spectra of the silatrane, which has been given previously [16], we may note that the spectra of solutions of the silatrane in chloroform and in the condensed phase scarcely differ from one another, with the exception of the bands corresponding to the antisymmetric stretching vibrations of the Si—O bond in the 760 – 800 cm^{-1} region. There is a considerable increase in the frequency of this bond (by 15 – 30 cm^{-1}) in the IR spectra of solutions of all the compounds in CHCl_3 as compared with the spectra of the condensed phase.

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