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A SPECTROSCOPIC STUDY OF HYDROGEN BOND FORMATION BY SILATRANES AND THEIR ANALOGUES *

M.G. VORONKOV, E.I. BRODSKAYA, N.M. DERIGLAZÔV, V.P. BARYSHOK and V.V. BELYAEVA

Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, 664033 Irkutsk (U.S.S.R.)

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Summary

The IR absorption shifts of OH and OD stretching vibrations upon interaction of silatranes $XSi(OCH(CH_3)CH_2)_3N$ and their monocyclic analogues of the type $R_2(OCHR'CH_2)_2NR''$ with phenol and deuteromethanol, respectively, were measured. In the systems involving silatranes these values are higher than in systems with the corresponding ethoxysilanes. The equilibrium constants and thermodynamic parameters of the interaction of the compounds studied with phenol in n-heptane were measured by electronic spectroscopy. The interaction of phenol with the compounds studied shows two lines correlating with the thermodynamic parameters $\Delta H = f(\Delta S)$. One of the lines is plotted by alkoxysilanes, cyclic and acyclic ethers. The second line corresponds to the compounds having a O—C—C—N group. This enables a conclusion to be drawn that in a non-polar medium the basic centre of silatranes and their monocyclic analogues is different from the oxygen in ethers and alkoxysilanes.

Introduction

The formation of hydrogen bonds by compounds having several heteroatoms have been studied until now on a small number of substances [1,2]. Of special nterest in this respect are silatranes of the type $XSi(OCHRCH_2)_3N$ which have n their skeleton four potential basic centres, i.e., three oxygen atoms and a nitrogen atom [3].

The inability of the endocyclic nitrogen atom in silatranes to react with

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methyl iodide and perchloric acid led to the conclusion that this atom is chemically inert [4]. Some recent studies, however, have provoked critical revision of this point of view [5—8]. One of the items of evidence for a potential chemical activity of the nitrogen atom in silatranes is the dependence of the degree of Si←N transannular interaction on the solvent polarity [5,6], as well as a lengthening by more than 0.2 Å of the Si—N interatomic distance in the molecule of 1-methylsilatrane in going from the crystalline to the gaseous state [7]. The ability of 1,3,7,10-tetramethylsilatrane to form a labile hydrochloride with hydrogen chloride in a non-polar solvent offers strong evidence that the nitrogen atom in silatranes exhibits nucleophilic properties [8].

The base properties of silatranes and their monocyclic analogues of the type $R_2Si(OCHR'CH_2)_2NR''$ have not been studied much. To determine the basicity and the reaction centre of molecules of the type $XSi(OCH(CH_3)CH_2)_3N$, $(CH_3)_2Si(OCHRCH_2)_2Y$, R = H, CH_3; Y = NCH_3, O; $(CH_3)_{4-n}Si(OC_2H_5)_n$, n = 1—3, we have examined absorption spectra and stretching frequency shifts of the OH and OD groups upon the reaction of these compounds with phenol and deuteromethanol, respectively. The equilibrium constants and thermodynamic parameters for the interaction of the compounds studied with phenol have been determined using ultraviolet spectroscopy.

Experimental

Procedure

Electronic absorption spectra of the compounds in n-heptane and acetonitrile were recorded on a Specord UV VIS spectrophotometer in the 190—240 nm region in a nitrogen atmosphere. The equilibrium constants in n-heptane were determined on the same instrument equipped with a temperature regulated cell holder 1 cm thick. For each base, six solutions of various concentrations were examined at four temperatures spaced between 285—310 K (the test was repeated not less than twice). The temperature was kept constant to within ±0.5 K. Freshly prepared solutions were used and kept in the dark. The concentration of phenol was 4×10^{-4} mol/l. The equilibrium constants were calculated from the relation given by Baba and Suzuki [9].

The fact that the molecules studied have several nucleophilic centres made it necessary to check the conditions under which the Benesi-Hildebrand equations are met with greater probability for the complex composition of 1 : 1 :$C_D >> C_A$ (Table 1), the presence of clear isobestic points and the independence of K on the wavelength (the latter was checked for a long phenol wavelength, $'L_b$) [10]. Besides, it should be taken into consideration that the participation of one nucleophilic centre in complexation decreases the analogous reactivity of other centres [2].

The IR spectra of phenol and deuteromethanol in CCl_4 (c = 0.005—0.01 and 0.05 mol/l, respectively) and the compounds studied (c = 0.05—0.1 mol/l) were recorded on a Specord 75 IR spectrometer in the 3700—3100 and 2750—2400 cm^{-1} regions, respectively. The cell thickness was 0.5 cm. The hydrogen bond shift, $\Delta\nu$, was determined as the difference between stretching frequencies of monomeric and associated OH and OD groups.

aterials

The silatranes studied (VII—XI) were prepared by the method described 'eviously [4] and further purified by double sublimation in vacuum. 2,2'-Diethyl-1,3,6-dioxo-2-silacyclooctane (IV) was obtained by a reported method .1]. 2,2-Dimethyl-1,3-dioxo-6-methylaza-2-silacyclooctane (V) and its 4,8-diethyl derivative (VI, b.p. 77°C/15 mmHg) were synthesized in an analogous anner [12]. Methylethoxysilanes, $(CH_3)_{4-n}Si(OC_2H_5)_n$, ($n$ = 1—3) were prepared cording to reported methods [13,14]. Methylbis(2-trimethylsiloxypropyl)nine (XII, b.p. 230°C/720 mmHg) was obtained by the reaction of methylbis-:-oxypropyl)amine with excess hexamethyldisilazane.

Carbon tetrachloride, n-heptane, acetonitrile, phenol, deuteromethanol were ırified by standard methods.

esults and discussion

In the electronic spectra of amines the absorption in the 200 nm region is ıe to the $n \rightarrow \sigma^*$ transition with participation of the lone electron pair of the trogen atom [15]. (The $n \rightarrow \sigma^*$ transition in compounds having C—O—C, —O—Si and Si—O—Si groups occurs in the far UV region.) In the absorption ıectra of methyl(2-trimethylsiloxypropyl)amine (XII) and tris(3-hydroxy-'opyl)amine (XIV) a hypsochromic shift and hypochromic effect as compared ı that of triethylamine (XV) are observed [16] (Fig. 1), which are probably .used by the electron withdrawing influence of the hydroxy and trimethyl-.oxy groups. This shows that the nitrogen atom in these molecules is less basic .an in triethylamine. The maximum position and intensity in the spectra of onocyclic (V, VI) and acyclic (XII) silatrane analogues are similar. The entical absorption of these compounds indicates that the transannular Si←N teraction in molecules of V and VI is either absent or weak in a non-polar lvent. The greater hypsochromic shift in the spectra of silatranes VII—XI is dicative of a marked Si←N transannular interaction, which is favoured by the olecular structure (the more intense absorption of compound IX is likely to : due to overlapping of intense $\pi \rightarrow \pi^*$ transition of the vinyl group [15]). This teraction increases with the increase in the electron withdrawing effect of e substituent at the silicon atom and the solvent polarity. In fact, if the spectra : solutions of monocyclic silatrane analogues V, VI in acetonitrile show a ght hypsochromic shift and hypochromic effect, as is the case with acyclic ımpounds XII and tris(2-oxypropyl)amine XIV, the spectra of silatranes splay only a long wavelength absorption edge (Fig. 1b). This is in agreement ith the previously observed enhancement of the Si←N transannular interaction ith increasing solvent polarity [5]. The silatranes with X = CH_3, $ClCH_2$ and $\overline{CHCH_2CH}$ and R = H in an acetonitrile solution exhibit almost the same ısorption as the corresponding 3,7,10-trimethyl-substituted compounds (R = H_3) do. Consequently, the Si←N transannular interaction in C-substituted atranes does not differ much from that in 3,7,10-trimethyl-substituted derivatives.

To interpret the results obtained we have assumed that the absorption inten-;y in the electronic spectra of the compounds studied is, at a certain wave-ngth, proportional to the absorption intensity in the band maximum, and

(Continued on p. 198)

TABLE 1

ENTHALPY AND ENTROPY CHANGES AND OH AND OD STRETCHING FREQUENCY SHIFTS ON COMPLEXATION IN THE DONOR—ACCEPTOR SYSTEM

No.	Electron donors	Concentration range (mol/l)	Proton donor (solvent)				
			Phenol (n-C_7H_{16})			Phenol (CCl_4) $\Delta\nu(OH)$ (cm^{-1})	Deutero-methanol $\Delta\nu(OD)$ (cm^{-1})
			$-\Delta H$ (kJ mol^{-1})	$P(\Delta H)$ [a]	$-\Delta S$ (J K^{-1} mol^{-1})		
I	$(CH_3)_3SiOC_2H_5$ [b]	2×10^{-1}—2×10^{-2}	28.03	1.05	78.3	266	99
II	$(CH_3)_2Si(OC_2H_5)_2$	2×10^{-1}—2×10^{-2}	26.57	0.42	72.0	257 [20]	94
III	$CH_3Si(OC_2H_5)_3$	1×10^{-1}—1×10^{-2}	23.51	0.17	60.4	246	78
						237 [20]	
IV	$(CH_3)_2Si(OCH_2CH_2)_2O$	2×10^{-1}—3×10^{-2}	25.02	0.50	64.9	250	90
V	$(CH_3)_2Si(OCH_2CH_2)_2NCH_3$	8×10^{-2}—9×10^{-3}	29.92	1.26	79.1	286	112
VI	$(CH_3)_2Si(OCH(CH_3)CH_2)_2NCH_3$	1×10^{-1}—6×10^{-2}	35.10	0.67	100.8	270	95
VII	$CH_3Si(OCH(CH_3)CH_2)_3N$	4×10^{-2}—5×10^{-3}	32.43	2.05	86.3	275	98
VIII	$Cl(CH_2)_4Si(OCH(CH_3)CH_2)_3N$	2×10^{-2}—3×10^{-3}	32.01	2.09	82.7	276	100
IX	$CH_2{=}CHSi(OCH(CH_3)CH_2)_3N$	4×10^{-2}—5×10^{-3}	28.03	2.09	67.0	250	93
X	$ClCH_2Si(OCH(CH_3)CH_2)_3N$ [c]					238, 116	81, 54
XI	$Cl\overline{CHCH_2C}HSi(OCH(CH_3)CH_2)_3N$ [c]					250	89
XII	$CH_3N(CH_2CH(CH_3)OSi(CH_3)_3)_2$	5×10^{-2}—9×10^{-3}	27.91	0.92	62.9	295	117
XIII	$HN(CH_2CH_2)_2O$	2×10^{-2}—3×10^{-3}	27.74	1.21	60.1	—	—

[a] Standard deviation. [b] in CCl_4 $\Delta H = -24.1$ kJ mol^{-1}, $\Delta S = 68.6$ J K^{-1} mol^{-1} [21]. [c] Solubility in n-heptane is less than 0.005 mol/l.

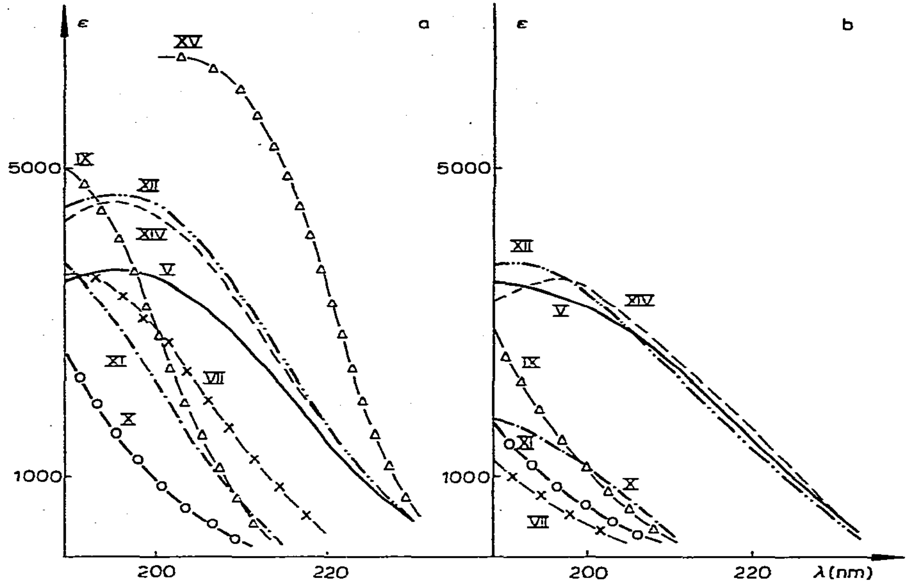


Fig. 1. Absorption spectra of organosilicon compounds IV—XII, tris(2-oxypropyl)amine (XIV) and triethylamine (XV) [16] in n-heptane (a) and acetonitrile (b). Numbers of the compounds are the same as in Table 1.

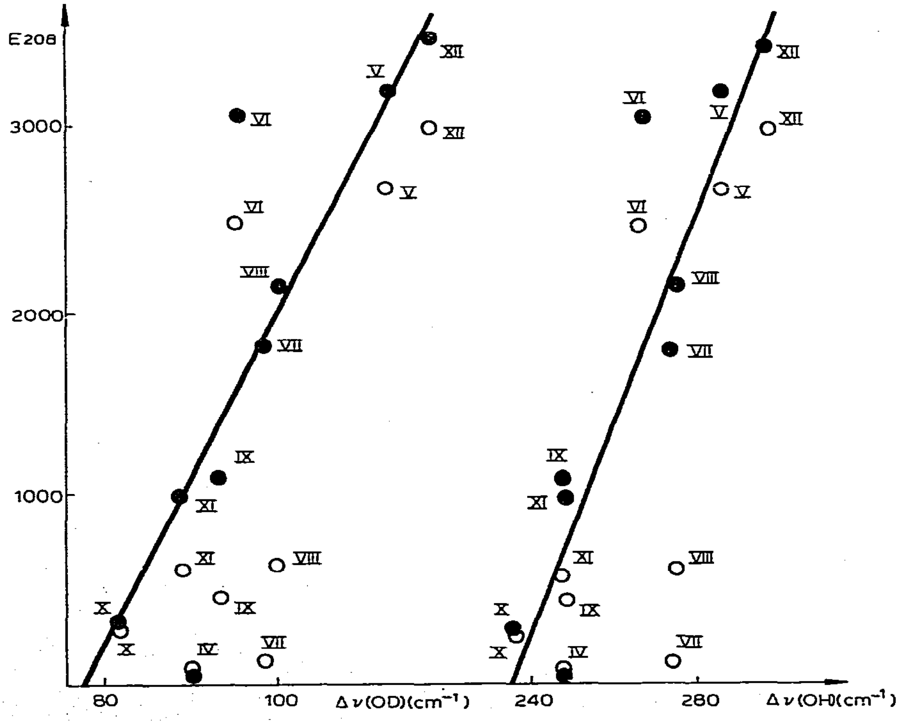


Fig. 2. $n \to \sigma^*$ Transition intensity at λ = 208 nm in absorption spectra of compounds IV—XII in n-heptane (●●●●) and acetonitrile (○○○○) against OH and OD stretching frequency shifts on complexation with the above compounds.

an attempt has been made to correlate the ϵ_λ and $\Delta\nu$ values (Fig. 2). It turned out that a satisfactory linear dependence is observed between the absorption intensity at λ = 208 nm in a non-polar solvent (n-heptane) and the relative basicity upon the interaction with phenol or deuteromethanol (in CCl_4), where r = 0.996 and 0.974, respectively. It is natural that methylethoxysilanes displaying no absorption in the UV region (I—IV) fall out of this dependence. At the same time, when a more polar solvent is used (CH_3CN) such a correlation fails to be a satisfactory one (r = 0.871 and 0.744, respectively, Fig. 2). Silatranes having electron-donor substituents, X = CH_3, $Cl(CH_2)_4$ (VII, VIII) deviate most from the above relationship. The absorption of 1-chloromethyl-3,7,10-trimethylsilatrane solutions in n-heptane and acetonitrile is almost the same. This indicates that the transannular interaction is most clearly expressed in this molecule.

The observed $\Delta\nu$(OH) and $\Delta\nu$(OD) values of acyclic and cyclic organosilicon ethers of aminoalcohol (V—XII) are of the same order as those of acyclic and cyclic alkoxysilanes containing no nitrogen (I—IV) (Table 1). As shown above, the nitrogen atom in methylbis(2-trimethylsiloxypropyl)amine (XII) is less basic than that in triethylamine (Fig. 1). The same follows from the relative basicities of the two compounds ($\Delta\nu$(OH) = 295 and 553 cm^{-1} [17], respectively) and the pK_a values (9.34 and 10.9 [18], respectively). Furthermore the shifts of the OH stretching frequencies in the phenol involved in systems with silatranes (VII, IX, X) are higher than in systems with the corresponding organyltriethoxysilanes, $XSi(OC_2H_5)_3$. Thus, for example, with X = CH_3 these shifts

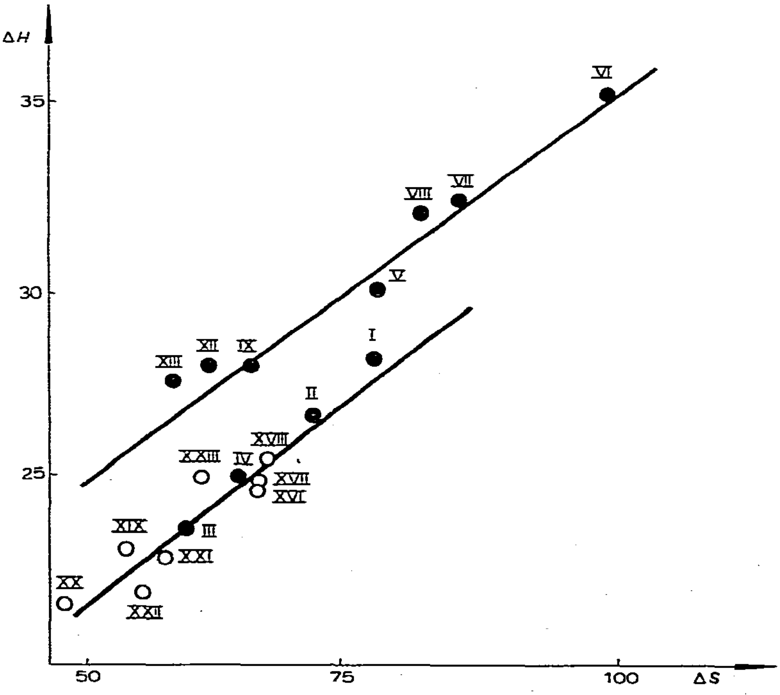
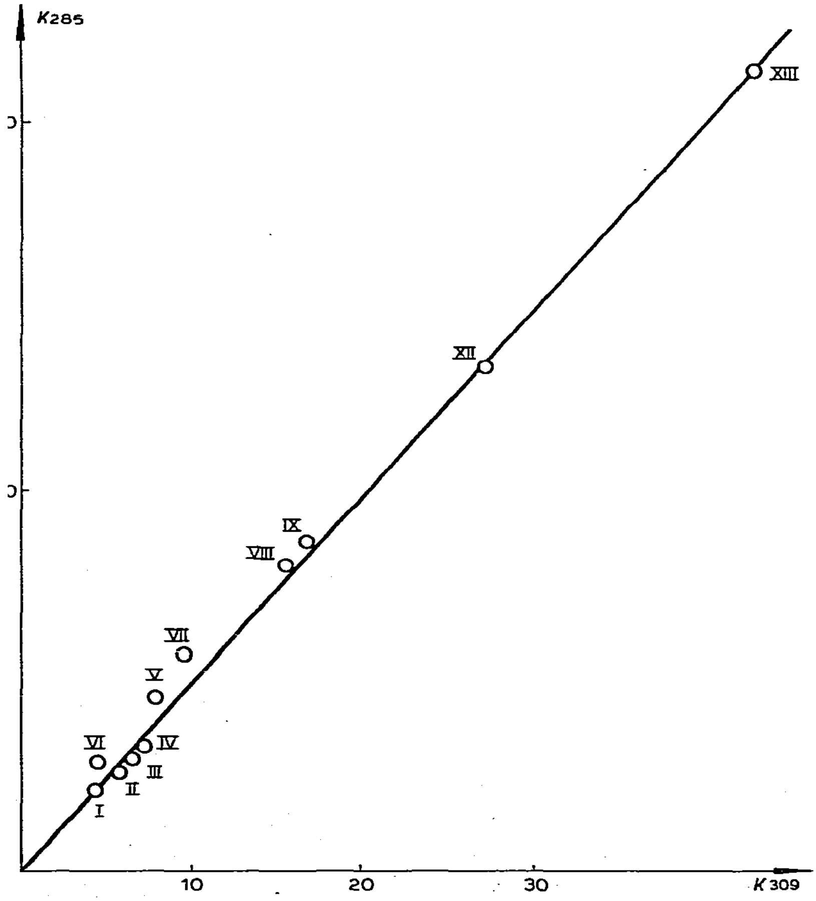


Fig. 3. Entropy of hydrogen bonding on complexation of phenol with compounds I—XIII and acyclic and cyclic ethers: XVI, $(C_2H_5)_2O$: XVII, $(i\text{-}C_3H_7)_2O$; XVIII, $(C_4H_9)_2O$; XIX, $CH_3O(CH_2)_2OCH_3$; XX, $(CH_2)_3O$; XXI, $(CH_2)_4O$; XXII, $(CH_2)_5O$; XXIII, $O(CH_2CH_2)_2O$ [25,26] vs. enthalpy.

e 276 and 246 cm^{-1} for VII and III, respectively; with X = $CH{=}CH_2$ these lues are 250 and 227 cm^{-1} [19], and with X = $ClCH_2$ these values are 238 and 14 cm^{-1} [19]. Thus, the basicity of the two classes of compounds drops with creasing electronegativity of the substituent X.

The higher basicity of silatranes and the fact that $ClCH_2$-3,7,10-trimethylsila- ane (VII) is not titrated by acids [8] suggests one of oxygen atoms to be e basic centre in compounds VII—XI as well as in alkoxysilanes I—IV. (Kinetic nitations in the titration of silatranes are caused by steric inaccessibility of e nitrogen lone electron pair localized within the silatrane skeleton and volved in Si←N transannular interaction.) This is consistent also with the ν(OH) value (276 cm^{-1}) for the 1-methyl-4-ethylsilatrane containing an hyl group at the carbon atom attached to the nitrogen atom.

At the same time, acyclic and monocyclic organosilicon ethers of 2-oxyalkyl- nines (V, VI, XII) which possess a sterically available lone electron pair, are adily titrated by perchloric acid in methanol (pK_a = 7.84, 7.58 and 9.34, spectively). Consecutive insertion of CH_3 groups into the 3,7,10-silatrane



g. 4. Plot of equilibrium constants on complexation of phenol with compounds I—XIII at 285 K vs. ose at 309 K.

skeleton does not affect the $\Delta\nu$ value. Thus, in the series $CH_3Si(OCH_2CH_2)_n\cdot(OCH(CH_3)CH_2)_{3-n}N$ the $\Delta\nu$ values with $n = 0$, 2, and 3 are 275, 276 and 274 cm^{-1}, respectively.

The $\nu(Si—H)$ values for the corresponding methyl-substituted silatranes $HSi(OCH_2CH_2)_n(OCH(CH_3)CH_2)_{3-n}N$ ($n = 0, 3$) in CCl_4 are, however, far from similar, attaining 2166 and 2175 cm^{-1}, respectivily. This shows that the insertion of methyl groups into the 3,7,10-silatrane skeleton increases the electron density at the silicon atom by the inductive mechanism and should, consequently, change the basicity of the oxygen atoms involved.

Thus, the data obtained indicate that the problem of the proton-accepting site in compounds V—XIII is unresolved.

The interaction of phenol and *p*-fluorophenol with different types of bases (ethers, carboxylic compounds, amines, amides, nitriles, etc.) exhibits a linear correlation between thermodynamic parameters, $\Delta H = f(\Delta S)$ for each type [22—24]. We have attempted to use such a subdivision of types of bases according to the thermodynamic parameter ratio for the determination of the basic centre in the compounds studied (V—XIII). It turned out that all the alkoxysilanes (I—IV) lie on the first correlation line which corresponds to acyclic and cyclic ethers (Fig. 3). At the same time, acyclic, mono- and bicyclic organosilicon ethers of 2-oxyalkylamines (V—XIII) correspond to another correlation line common to all compounds containing an O—C—C—N group.

It is characteristic that the compounds on the second line are significantly different in both the composition and molecular structure. Taking into consideration that the $K^{T_1} = f(K^{T_2})$ linear dependence reflects the homogeneity of molecular interaction upon the formation of the hydrogen bonds [27,28] (Fig. 4), it should be assumed that in a non-polar medium the basic centre of compounds V—XIII lying on the second line is different from the oxygen in ethers and alkoxysilanes.

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