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MOLECULAR COMPLEXES OF CHLOROFORM WITH METHYL-SUBSTITUTED 1,3-DIOXANES

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The ^{1}H NMR method was used to study the relative electron donor capacity of a number of methyl-substituted 1,3-dioxanes in complex formation with chloroform. The spectral and thermodynamic parameters of 1:1 H-complexes were determined. The values of the chemical shifts from the hydrogen bond in the complexes vary in correlation with the charges on the oxygen atoms of the investigated bases, calculated by the CNDO/2 method.

In studies of acid-catalyzed conversions of 1,3-dioxacycloalkanes it is suggested that the reactivity is largely determined by the basicity of the acetal [1, 2]. A study of the spectral and thermodynamic characteristics of hydrogen bonds with H-acids permits an estimation of the donor properties of the compounds and a characterization of the influence of the electronic and geometrical structure of the molecules on these properties [3, 4]. Earlier the relative basicity of 1,3-dioxane and some of its derivatives was determined in the reaction of complex formation with iodine [5], deuteromethanol [6], and phenol [7, 8] by the method of IR spectroscopy.

In this work the electron donor properties of 1,3-dioxane and its derivatives were investigated by the ^{1}H NMR method as a function of the number and position of the methyl substituents in the ring. Chloroform was used as the standard CH acid. The selection was due to the weakness of the autoassociates of chloroform [9] and its rather high ability to form molecular complexes with various bases [10-18].

When chloroform is diluted with an inert solvent, cyclohexane, the signal of the chloroform proton is shifted by 0.13 ppm in the strong-field direction, which is explained by the presence of weak autoassociates in the solutions [9]. In the region of chloroform concentrations below 0.10 mole fraction, the chemical shift (CS) of the proton (δ_M = 7.06 ppm) is unchanged. This is evidence of the absence of association of the molecules in $CHCl_3$ at high dilutions. In solutions of compounds I-XIII the signal of the proton of chloroform is shifted in the weak-field direction with increasing concentration of the base (Fig. 1), which is an indication of the formation of intermolecular associates through a hydrogen bond. In the series of 1,3-dioxanes studied (Table 1), the least changes in the CS of the $CHCl_3$ proton due

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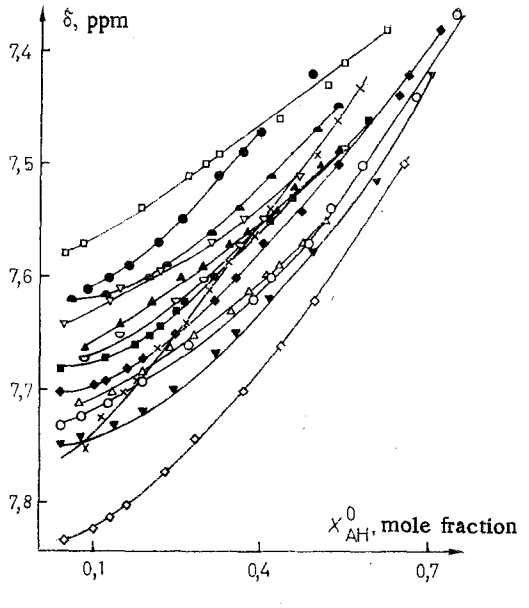


Fig. 1

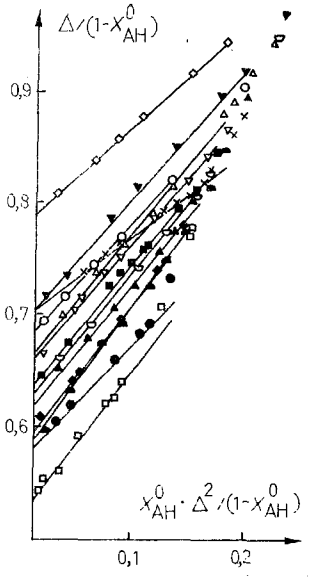


Fig. 2

Fig. 1. Concentration dependences of the chemical shifts of the proton of chloroform in binary mixtures with methyl-substituted 1,3-dioxanes. Notations: I) ▽, II) ○, III) ■, IV) ▼, V) ◓, VI) □, VII) ▲, VIII) ◡, IX) ◇, X) ◆, XI) △, XII) ×, XIII) ●.

Fig. 2. Dependence of the type of $y_p = f(x)$ for binary systems of chloroform–methyl-substituted 1,3-dioxanes. For notations, see Fig. 1.

to complex formation are observed in the system chloroform–5,5-dimethyl-1,3-dioxane (Δ_a = 0.52 ppm) and the greatest in the system chloroform–2,2-dimethyl-1,3-dioxane (Δ_a = 0.77 ppm).

The most important characteristic of the hydrogen bond is its energy [19]. Generalization of a large number of experimental data on the thermodynamics of hydrogen bonds and their spectral manifestations in NMR has made it possible to establish [20-24] that for complex formation of the type

$$A_iH + B_j \rightleftarrows A_iH \ldots B_j \pm \Delta H_{ij} \qquad (1)$$

in most cases a correlation between the chemical shift ($\Delta_C = \delta_C - \delta_M$) and the energies of the H-bond in the complexes (in an approximation that does not consider the anisotropy of the base B_j), of the following type, is fulfilled:

$$-\Delta H\,[\text{kcal/mole}] = k \cdot \Delta_C\,[\text{ppm.}], \qquad (2)$$

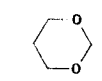
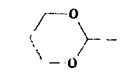
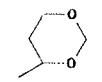
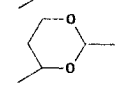
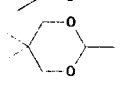
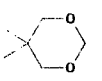
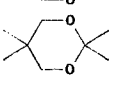
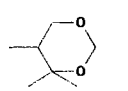
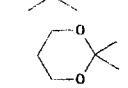
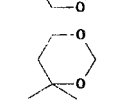
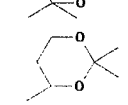
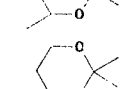
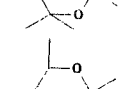
where k is a coefficient of proportionality, the accuracy of the finding of which is determined by the accuracy of the finding of δ_M. For weak molecular complexes of α-acetylenes and mercaptans, k = 1.15 [24, 26]. According to the data of [24], this ratio is also rather well fulfilled for complexes of phenols, alcohols, hydroperoxides, chloroform, and acids with various bases. When there is no precise values of Δ_C available, in a first approximation we can use the value of Δ_a obtained by extrapolation of the CS of the proton participating in the formation of a hydrogen bond to infinite dilution in a solution of the given base [25].

To determine the equilibrium constants of the complex formation of chloroform with bases we used the graphical method of Lin et al. [18] for binary complexes. The method suggests that for the equilibrium of binary association, the constant expressed in mole fractions is set by the equation:

$$K = \frac{X_{AH\ldots B}}{X_{AH}\cdot X_B} = \frac{N_{AH\ldots B}\,(N_{AH}^0 + N_B^0 - N_{AH\ldots B})}{(N_{AH}^0 - N_{AH\ldots B})\,(N_B^0 - N_{AH\ldots B})}, \qquad (3)$$

where X represents the mole fractions of the complex A–H...B, the acid A–H, and the base B; N_o is the initial number of moles; $N_{AH\ldots B}$ is the number of moles of the complex at equilibrium.

TABLE 1. Characteristics of the Electron Donor Centers of Methyl-Substitued 1,3-Dioxanes and Their Complexes with Chloroform

Compound	Base	Δ_a, ppm.	Complex (1:1)			First ionization potential, eV	Charge, e		p
			Δ_c ppm.	$-\Delta H$, kcal/mole	K, mole fraction		$O_{(1)}$	$O_{(3)}$	
I		0,58	0,71	0,82	4,33	10,12	0,242	0,242	0,50
II		0,67	0,90	1,04	3,17	10,03	0,262	0,262	0,50
III		0,62	0,80	0,92	4,00	10,04	0,242	0,250	0,00
IV		0,69	0,90	1,04	3,76	9,80	0,262	0,269	0,85
V		0,56	0,75	0,86	3,63	—	0,245	0,245	0,50
VI		0,52	0,73	0,84	2,70	—	0,243	0,243	0,50
VII		0,60	0,83	0,95	3,00	—	0,247	0,247	0,50
VIII		0,61	0,80	0,92	3,76	—	—	—	—
IX		0,72	0,91	1,04	4,00	9,90	0,261	0,261	0,50
X		0,64	0,83	0,95	4,00	9,84	0,242	0,272	0,57
XI		0,65	0,88	1,01	3,17	9,63	0,262	0,269	1,00
XII		0,69	1,28	1,47	1,47	—	0,262	0,278	0,00
XIII		0,55	0,96	1,10	1,56	—	0,270	0,278	0,98

In the case of the ^{1}H-NMR spectrum, averaged for the bound and free protons of the acid A–H:

$$N_{AH\ldots B} = [(\delta_o - \delta_m)/(\delta_c - \delta_m)]N_{AH}^0, \quad (4)$$

where δ_o, δ_m, and δ_c are the CS of the observed signal, the signal of the chloroform proton, and the signal of the chloroform proton entirely bound in a complex with the base B, respectively.

Simultaneous solution of Eqs. (3) and (4) gives an equation of the type

$$\frac{\Delta}{1-X_{AH}^0} = \frac{1}{\Delta_c} \cdot \frac{X_{AH}^0 \cdot \Delta^2}{1-X_{AH}^0} + \Delta_c \frac{1}{1+(1/K)}, \quad (5)$$

where $\Delta = \delta_o - \delta_m$.

Under the condition of formation of a (1:1) complex, a linear dependence of $[\Delta/(1 - X_{AH}^0)]$ on $[X_{AH}^0 \cdot \Delta^2/(1 - X_{AH}^0)]$ is observed. The values of Δ_c and K are determined according to the slope of this function and the segment that it intercepts on the y axis. An advantage of this method is its sensitivity to a change in the composition of the complex.

An analysis of the functions of the type of $y_p = f(x)$ for complexes of chloroform with the bases I-XIII (Fig. 2) shows that 1:1 complexes are formed only at low chloroform concen-

trations. In the region corresponding to 0.40-0.44 mole fraction of chloroform, on the straight lines $y_p = f(x)$, a distinct point of inflection is observed, indicating the formation of complexes with a more complicated composition than 1:1. Evidently at higher chloroform concentrations complexes with a 2:1 composition and autoassociates of chloroform are also formed.

In the series of 1,3-dioxanes studied (Table 1), at close values of K (3-4 mole fraction^{-1}), in addition to XII and XIII, the greatest influence on the value of Δ_C is exerted by the methyl substituents at the acetal carbon atom, and the least by the substituents of $C_{(5)}$. The effect of substituents at $C_{(4)}$ on the electron donor properties of 1,3-dioxanes is intermediate in value. The low stability of the complexes XII and XIII formed (K = 1.2-1.5 mole fraction^{-1}), despite the formation of the strongest of the investigated H-bonds, is evidently determined by the pecularities of the stereochemical structure of these compounds. As is well known [27], compounds I-XI are in a predominant chair conformation. A 2,5-twist form is characteristic of the molecules of XIII, while the molecules of XII undergo inversion between 2,5- and 1,4-twist forms [28]. Evidently the conformational differences determine the peculiarities of the stereoelectronic structure of these bases.

Earlier it was shown [29] that the first ionization potential for ethers can serve as a measure of their basicity. With increasing degree of substitution of the ether, the ionization potential decreases, while the basicity increases. However, for systems I-XIII no linear correlation is observed between the ionization potentials, measured by the method of photoelectronic spectroscopy [30], and Δ_C of K. This is evidently due to the fact that the ionization potential determine the PES for molecules of the gas phase. Moreover, in the formation of a hydrogen bond, a definite influence on its strength is also exerted by purely steric effects.

We used the CNDO/2 method to calculate the distribution of charges in compounds I-XIII (Table 1). For compounds I, II, V-VII, and IX a linear relationship is observed between Δ_C and the charge on the oxygen atoms:

$$\Delta_C = -1.322 - 8.446Q, \quad (6)$$

where Q is taken in fractions of the charge of the electron.

The values of the coefficient of correlation between Δ_C and Q is 0.985, which is evidence of statistical significance of the dependence.

Replacement of the H atom at $C_{(4)}$ by a CH_3 group, on the one hand, increases the charge on the $C_{(3)}$ atom, which should promote an increase in Δ_C; on the other hand, the presence of a methyl group hinders the formation of a complex at this atom. Equation (6) permits an estimation of the probabilities of formation of a complex at the atoms $O_{(1)}$ and $O_{(3)}$ in nonsymmetrically substituted compounds III, IV, X-XIII. For this purpose the following expression is substituted into Eq. (6) instead of the charge: $pQ^1 + (1 - p)Q^3$, where Q^1 and Q^3 are the charges on the $O_{(1)}$ and $O_{(3)}$ atoms, respectively; p is the probability of formation of a complex at $O_{(1)}$. The values obtained for p are cited in Table 1.

It should be noted that the ratio of the values of the charge on the atom and the steric hindrances is ambiguous and depends on the presence and number of substituents at $C_{(2)}$. For example, for compound III, p = 0. When one hydrogen at $C_{(2)}$ is replaced by a method group (IV), p = 0.85, while when two H atoms are replaced, the probability already becomes close to one (compound XI).

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Tesla BS-497 NMR spectrometer, working frequency 100 MHz. Hexamethyldisiloxane was used as the internal standard. The chemical shifts were measured in the δ scale with an accuracy of ±1 Hz. In the recording of the spectra, the temperature of the sample was maintaned equal to +(24 ± 0.5)°C.

Chloroform was thoroughly freed of ethanol and water [29].

Compounds I-XIV were synthesized according to the well known methods [1]. The purity of the compounds after redistillation over Na was monitored by the methods of gas–liquid chromatography and IR spectroscopy.

Calculations of the charges on the oxygen atoms were performed by the CNDO/2 method in the standard parametrization. The values of the valence angles and bond lengths were obtained

by partial optimization according to the minimum total energy. For 1,3-dioxane, the experimental values of [30] were taken as the initial data. The accuracy of the optimization for the bond lengths is 0.01 Å, and for the valence angles 0.1°. The bond lengths obtained as a result of optimization are in satisfactory agreement with the standard values.

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