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scheme 1

Figure 1: scheme 1

Abstract

Full Text

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THE NATURE OF THE H-BOND IN SYSTEMS WITH π-ELECTRONS AND ITS INFLUENCE ON PROTON MAGNETIC RESONANCE

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It is known that the method of nuclear magnetic resonance (n.m.r.) is sensitive to the formation of an H-bond ([1,2]). The chemical shift in n.m.r. is a relative quantity defined by the expression $\delta = \frac{H_{\text{ref}} - H_{\text{st}}}{H_{\text{st}}} \cdot 10^6$ (H_{ref} and H_{st} are the resonance values of the strength of the constant magnetic field for the sample under investigation and for the standard sample).

Of particular interest is the study by n.m.r. of the H-bond in systems with π-electrons. In a number of works by one of us ([2,3–6]), on the basis of a study of the electronic and vibrational spectra of molecules with π-electrons, it was concluded that the energy of the H-bond, the magnitudes of the shift, broadening, and intensity of the bands of valence vibrations of the groups participating in its formation depend on changes in the parameters of the entire system.

In systems with π-electrons, formation of an H-bond often leads to the emergence of a quasiaromatic (coplanar, six-membered) ring, owing to the delocalization of six electrons of the system, including the valence electrons of the group –X–H (scheme 1)

In this treatment, the hydrogen atom participates in the formation of the quasiaromatic ring not only by means of its valence electron, but at the same time represents a modified p^*-orbit.

In π-electron systems the H-bond is formed through three types of interaction: dipolar $-E_d$, acceptor-donor $-E_a(s)$, and π-electron interaction $E_\pi(p^*)$, i.e., the energy of the H-bond is equal to: $E_H = E_d + E_a(s) + E_\pi(p^*)$.

In the case under consideration, the term $E_\pi(p^*)$ is the determining one. The magnitude $E_\pi(p^*)$ characterizes the increase in the energy of the H-bond as a result of the formation of a quasiaromatic ring with participation of π-electrons.

The energy of the hydrogen bond and the magnitude of the energy of the π-electron interaction $E_\pi = E_H - [E_d + E_a(s)]$ can be approximately calculated (for a given series of compounds) by the method described in works (^{3,5}). The results of the calculation are given in Table 1.

With the aid of the proposed model of the H-bond with a predominant value of the π-electron interaction (in the quasiaromatic ring), it is possible to explain, in particular, the sharp decrease in the frequency ($\Delta\nu = \nu_0 - \nu$ of the standard) of the valence vibration of the O–H group, as well as the large chemical shift ($\Delta\delta = \delta - \delta$ of the standard) of the signal from the proton O–H . . . toward smaller values of the magnetic-field strength.

Table 1

Compound No.	δ_{OH}	$\Delta\delta$	ν_{OH}, cm^{-1}	$\Delta\nu$, cm^{-1}	E_π, kcal	$N_{C=O}$
I	0	0	3630	0		
II standard substance	1.48	1.48	3545	85	0	1
III	3.26	0	3615	0	–	–
IV	8.68	5.42	3270; $\nu_{OD} =$ 2440	345	4.23	1.660
V	3.06	0	3620	0	–	–
VI	9.32	6.26	3200	420	5.44	1.667
VII	10.82	7.56	3100; $\nu_{OD} =$ 2325	515	7.03	1.700
VIII	3.50	0	3610			
IX	12.15	8.65	3000; $\nu_{OD} =$ 2174	610	8.55	1.733
X	14.2	13.44	2700; $\nu_{OD} =$ 2000	920	13.57	1.850
XI	0.83	0	3640	0		
XII	15.15	14.32	2640	1000	14.77	
XIII	15.4	14.63	2630	1010	14.97	

Structural formulas of compounds I–XIII are shown on the page (labels I–XIII).

The main reason for the increase in $\Delta\sigma_{\mathrm{O-H}}$ in this case will apparently be the appearance of ring paramagnetism, which considerably reduces $\sigma_{\mathrm{O-H}}$ (7), as well as a decrease in the electron density on the hydrogen atom

Fig. 1. Dependence of the chemical shift on the magnitude of the displacement of the frequency of the stretching vibration of the group O—H···(Roman numerals correspond to the compound numbers in Table 2)

Fig. 2. Dependence on δ of the energy of π-electron interaction (the designations are the same)

(compared with the O—H group . . . in a ring without π-electron interaction) owing to the direct participation of its electron in the formation of bonds of the quasiaromatic ring.

On the other hand, the delocalized closed electron cloud of the quasiaromatic ring, placed in a magnetic field, as a result of the "circulation" of electrons around the ring, will create a local magnetic field directed perpendicular to the plane of the ring and opposite to the direction of H_0. This leads to a chemical shift of the protons of the $= \underset{|}{\mathrm{C}} - \mathrm{H}$ groups of the quasiaromatic ring toward weak magnetic fields.

The experimental data obtained by us, presented in Table 1, confirm the assumptions made. The NMR spectra of the compounds were obtained on a Trüb—Täuber spectrometer; cyclohexane was used as the reference sample; the measurements were carried out in $\mathrm{CCl_4}$ solutions at molar ratios of $1 : 100$ (substance : solvent). At the indicated solution concentrations, infrared absorption spectra were measured in the region of the OH and OD groups. Analysis of the experimental data shows that there is a parallelism between the shifts $\Delta\delta$ and $\Delta\nu$ (Table 1 and Fig. 1), $\Delta\delta = k\Delta\nu$ for the given series of compounds.

The magnitude of the chemical shift of the proton (of the $\mathrm{O-H}\ldots$ group) increases linearly as the energy of the π-electron interaction E_π increases (Fig. 2). The change in the chemical shift $\Delta\delta$ may be represented as two terms: $\Delta\delta_{d+a}$, determined by the magnitude of the energy of the dipole and acceptor-donor interaction, and $\Delta\delta_\pi(E_\pi)$, dependent on the energy of the π-electron interaction. In the given series of compounds $E_d + E_a$ changes little, and therefore $\Delta\delta_{d+a}$ remains approximately constant, whereas $\Delta\delta_\pi$ changes as E_π changes. Therefore we may write the relation $\Delta\delta_{\mathrm{O-H}} = \Delta\delta_{d+d} + \Delta\delta_\pi(E_\pi)$, which is well confirmed by the experimental data (Table 1, Fig. 2).

The magnitude of the energy E_π, all other conditions being equal, is determined by the magnitude of the electron density or bond order ("double-bond character" $N_{\sigma+\pi}$) of the $\mathrm{C=C}$ bond directly adjoining the quasiaromatic ring. Therefore, a parallelism should be observed between E_π, $N_{\sigma+\pi}$, and $\Delta\delta_{\mathrm{O-H}}$. The values of $N_{\sigma+\pi}$ (the double-bond character of $\mathrm{C=C}$ before formation of the ring) were calculated from the equation

Fig. 3. Dependence of δ on the index of the $C = C$ bond (designations the same)

Figure 2: Fig. 3. Dependence of δ on the index of the $C = C$ bond (designations the same)

$$N_{\sigma+\pi} = N_0 - \Delta N \cdot n + \frac{\Delta N}{6} \cdot n_1 - \frac{\Delta N}{72} \cdot n_2,$$

based on the rule of the number of neighbors (^{8,9}). In this equation $N_0 = 2$, $\Delta N = 0.2$, and n, n_1, n_2 are, respectively, the numbers of nearest, next-nearest, and more distant neighbors of the bond. As was shown in work (^{6}), this method gives results in good agreement with the data of the molecular-orbital method, although it proceeds from different ideas about molecular orbitals in complex molecules.

Fig. 3. Dependence of δ on the index of the $C = C$ bond (designations the same)

The experimental data show the existence of a linear dependence between $\Delta\delta$ and $N_{\sigma+\pi}$ of the $C = C$ bond (Fig. 3, Table 1).

The magnitudes of the chemical shifts of some compounds (Table 1) are close to the data obtained in work (^{9}). However, the authors of the cited work carried out measurements in CCl_4 at higher concentrations and compared the values of $\Delta\delta$ with $\Delta\nu$ of the carbonyl group participating in formation of the H-bond.

The largest chemical shift ($\Delta\delta = 13$-15) of the proton and $\Delta\nu = 900$–1000 cm^{-1} of the $O - H \ldots$ group is observed for the enol forms of acetylacetone and dibenzoylmethane, in which, upon formation of the quasiaromatic

of the cycle, also reaches a large value of E_π (13-15 kcal). The formation of a quasiaromatic cycle in the enol isomers of the indicated compounds is also confirmed by the magnitude of the chemical shift δ of the proton of the group

$$= C - H$$

toward lower fields; for example, for acetylacetone $\delta = -4$, and for benzoylmethane $\delta = -5.3$ (for benzene $\delta = -6.10$).

On the basis of IR-spectral data, one of us $^{(10)}$ concluded that proton transfer in enol isomers (quasiaromatic cycles) from one oxygen atom to another is possible. The potential barrier which the hydrogen atom overcomes in passing from one well to another must be lowered owing to the proximity and equality of the potential wells.

The study of the NMR spectra of liquid acetylacetone $^{(1)}$ and of its solutions in CCl_4 (our data) confirms the presence of proton exchange in the indicated quasiaromatic cycles. The existence of proton exchange, in which the $O-H$ group of the enol isomer participates, follows from the equality of the chemical shifts of the protons of both methyl groups of the enol form of acetylacetone, and also from the broadening of the $O-H$ signal in the NMR spectrum. This question requires further study.

Thus, the experimental results obtained by us and the analysis of some literature data confirm the possibility of formation of a quasiaromatic cycle with an H bond, in which the π-electron interaction is of decisive importance.

The magnitude of the chemical shift $\Delta\delta$ of the proton of the $O-H\ldots$ group increases with an increase in the fraction of the energy of π-electron interaction in the formation of the quasiaromatic cycle, which, apparently, is explained by an increase in the value of the van Vleck paramagnetism of the system $(O-H\ldots)$, causing a decrease in $\sigma_{O-H\ldots}$ in the series of compounds studied. This conclusion is consistent with the fact that disruption of the quasiaromatic cycle by electron-donor solvents leads to a sharp decrease in the chemical shift (at 10 mole % acetylacetone in acetone $\Delta\delta_{O-H} = 8$; a similar picture is observed in triethylamine). In the latter case the π-electron interaction in the formation of the H bond is substantially disturbed (the van Vleck paramagnetism of the $O-H$ group is weakened), and donor–acceptor interaction plays a noticeable role, also leading to a relative increase in the electron density on the hydrogen atom of the hydroxyl group.

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Note: Figure translations are in progress. See original paper for figures.