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Abstract

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DETERMINATION OF THE ENERGY OF FORMATION OF A QUASIAROMATIC RING WITH AN H BOND FROM IR SPECTRA OF MOLECULES

(Presented by Academician V. A. Kargin on 3 X 1962)

In works ($^{1-5}$) it was assumed that the formation of an H bond in molecules may lead to the appearance of a quasiaromatic (coplanar, six-membered) ring, owing to the delocalization of the six electrons of the system: four π-electrons of the $C = C$ and $C = O$ bonds, as well as two p-electrons of the oxygen atom of the $O—H$ group. In this treatment the hydrogen atom participates in the formation of the quasiaromatic ring not only with its valence electron, but also provides, in doing so, a modified p^*-orbit.

In the case of a quasiaromatic ring with an M bond, the delocalization (“delocalization”) of electrons is accomplished more effectively, owing to the presence of free, energetically favorable orbits at the metal atom. However, the nature of the phenomenon of formation of quasiaromatic rings with an H bond and an M bond is analogous (^{1}). In π-electron systems the H bond is formed through three types of interaction: dipole 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:

$$E''_{\mathrm{H}} = E_d + E_a(S) + E_\pi(p^*). \tag{1}$$

In the case under consideration the term $E_\pi(p^*)$ is decisive. The question arises of how to determine the energy of formation of the H bond E_{H} (or of the quasiaromatic ring) from vibrational spectra of molecules. A quantum-mechanical treatment of the three-atom model

$$\mathrm{X—H}\cdots\overset{x}{\mathrm{Z}}$$

without π-electrons, given by N. D. Sokolov (^{6}), shows that the energy of formation of the H bond is proportional to the relative displacement of the stretching-vibration band of the X—H group, i.e.,

$$E_{\mathrm{H}} = \frac{1}{k}\frac{\Delta\nu}{\nu_0} \text{ kcal.} \qquad (2)$$

The numerical value of k should be determined from experimental data for one or two compounds similar in their nature to the compounds of the series under consideration. The energy of formation of the H bond (with π-electron interaction) in a dimer of carboxylic acids, according to the experimental data of work (^{7}), is ≈ 8 kcal/mol ($\Delta\nu \cong 520$ cm^{-1}). Starting from these data, from formula (2) we obtain the value $k \approx 1.7 \cdot 10^{-2}$ kcal^{-1}. The energy of an intramolecular H bond with π-electron interaction can also be determined from experimental data for α-oxyanthraquinone. Using the equation for the maximum work of reaction $A = RT \ln K_p$ (K_p is the equilibrium constant), one can find the difference in the energies of the H bonds of α-oxyanthraquinone (intramolecular) and β-oxyanthraquinone (intermolecular O—$H \cdots O$—$H \cdots$), if their dissociation constants are known. The dissociation constant of α-oxyanthraquinone is $K_{p\alpha} = 3.2 \cdot 10^{-12}$, and for β-oxyanthraquinone it is $K_{p\beta} = 2.4 \cdot 10^{-8}$ (^{8}). The difference in the dissociation constants is determined by the dif-

Table 1

H-cycles with E''_H	ν_{OH}, cm^{-1}	$\Delta\nu$, cm^{-1}	E''_H, kcal	E_π, kcal	H-cycles with E'_H	$N_{\mathrm{C=C}}$
I(CCl_4 1 : 400)	3545	85	1.38	0	Ia	
II(CCl_4 1 : 400)	3620	0	0	0		
III(CCl_4 1 : 400)	3270($\nu_{\mathrm{OD}}-$2440)	345	5.61	4.23	IIIa	IIIb
IV(vapors 144°)	3610 (β) 3265 (α)	355	5.77	4.39	IVa	
V(CCl_4 1 : 400)	3230	39	6.35	4.97	Va	
VI(CCl_4 1 : 400)	3200	420	6.82	5.44	VIa	
VII(vapors 300°)	3150	470	7.64	6.26		
VIII(CCl_4 1 : 400)	3100($\nu_{\mathrm{OD}}-$2325)	515	8.41	7.03	VIIIa	VIIIb

H-cycles with E''_H	ν_{OH}, cm^{-1}	$\Delta\nu$, cm^{-1}	E''_H, kcal	E_π, kcal	H-cycles with E'_H	$N_{C=C}$
IX(vapors 290°)	3620 (β) 3100 (α)	520	8.46	7.08		
X(CCl_4 1 : 100)	3610	0				
XI(CCl_4 1 : 100)	∼ 3000(ν_{OD}− 2190)	610	9.93	8.55	XIa	XIb
XII(CCl_4 1 : 10)	2700(ν_{OD}− 2000)	920	14.9	13.71	XIIa	
XIII(CCl_4 1 : 400)	3640	0			XIIIa	
XIV(CCl_4 1 : 10)	2640	1000	16.15	14.77	XIVa	
XV(CCl_4 1 : 10)	2630	1010	16.35	14.97	XVa	
XVI(CCl_4 1 : 10)	∼ 2600	1020	16.46	15.08	XVIa	

Ia –structural formula shown; **or** IIIb –structural formula shown, 1.660.

IIIa –structural formula shown.

IVa; Va; VIa –structural formula shown.
IVb; Vb; VIb –structural formula shown, 1.667.

VIIIa –structural formula shown.
VIIIb –structural formula shown, 1.700.

XIa –structural formula shown.
XIb –structural formula shown, 1.733.

XIIa; XIIIa; XIVa; XVa; XVIa –structural formula shown.
XIIb; XIIIb; XIVb; XVb; XVIb –structural formula shown, 1.850.

Structural formulas I–XVI are shown below the table:

I –structural formula shown.
II –structural formula shown.
III –structural formula shown.
IV –structural formula shown, with OH (β) and H-bond (α).
V –structural formula shown.
VI –structural formula shown.
VII –structural formula shown.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

VIII –structural formula shown.
IX –structural formula shown, with (α) and (β) positions indicated.
X –structural formula shown.
XI –structural formula shown.
XII –structural formula shown.
XIII –structural formula shown.
XIV –structural formula shown.
XV –structural formula shown.
XVI –structural formula shown.

lower energy of H-bonds (all other conditions being equal), namely: $-\Delta A = E_{\mathrm{H}\alpha} - E_{\mathrm{H}\beta} = -RT \ln K_{p\alpha}/K_{p\beta} \approx 5$ kcal/mole. The energy of the intermolecular H-bond ($-\mathrm{O}-\mathrm{H} \cdots \mathrm{O}-\mathrm{H} \cdots$) of β-oxyanthraquinone (analogously to phenol, naphthol, etc.), according to experimental data, is ≈ 3.5 kcal. Thus, the energy of the intramolecular hydrogen bond of α-oxyanthraquinone is ≈ 8.5 kcal/mole. If one takes into account that for α-oxyanthraquinone $\Delta\nu = 520$ cm^{-1}, and $\nu_0 = 3620$ cm^{-1}, then from formula (2) we obtain $k \approx 1.7 \cdot 10^{-2}$ kcal^{-1}.

Fig. 1

Fig. 2

Thus, for the compounds of the series we are considering we obtain $k = 1.7 \cdot 10^{-2}$ kcal^{-1}, and the H-bond energy can be determined from the equation

$$E_{\mathrm{H}} = 1/1.7 \cdot 10^{-2} \frac{\nu_0 - \nu}{\nu_0} \text{ kcal.} \tag{3}$$

Such a choice of k makes it possible to obtain values of E_{H} close to the experimental values. Experimental determination of the energy of formation of an intramolecular H-bond in systems with π-electrons on the basis of studying thermal dissociation (by the equation of the reaction isochore $\frac{d \ln k}{dT} = \frac{Q}{RT^2}$) does not appear possible because of its high thermal stability. Thus, in the case of α-oxyanthraquinones the H-bond is retained at $t^\circ = 300^\circ$C (^{2}). It was noted above that in systems with π-electrons the term $E_\pi(p^*)$ in equation (1) is of decisive importance. The question arises of how to estimate $E_\pi(p^*)$–the energy of π-electron interaction in the formation of a quasiaromatic ring. The quantity $E_\pi(p^*)$ characterizes the increase in the H-bond energy on going from a ring without conjugated bonds to a ring with conjugated bonds.

Table 1 gives several cases illustrating changes in the structural elements of molecules in which a quasiaromatic ring with an H-bond arises. From Table 1 it is seen that in the present series of compounds the sum $E_a(S) + E_d = E'_{\mathrm{H}}$ should be an approximately constant quantity. Then the energy of π-electron interaction in the formation of the H-bond in the quasiaromatic ring is equal to $E_\pi(p^*) = E''_{\mathrm{H}} - E'_{\mathrm{H}}$ (see Table 1). It follows from what has been said that one of the compounds without conjugated bonds may be taken as a standard. In the present work, diacetone alcohol (solution in $\mathrm{CCl_4}$; 1:400) was adopted as the standard substance.

The H-bond energies E''_{H} and E'_{H} (standard) are determined from vibrational-spectra data by formula (3). Table 1 gives the H-bond formation energies calculated by the indicated method and the values of $E_\pi(p^*)$.

The change in the stretching-vibration frequency of the group $\mathrm{O-H}\cdots$, equal to $\Delta\nu = \nu_0 - \nu$, can be represented as two terms: $\Delta\nu_{a+d}$, determined by the magnitude of the energy of dipole and acceptor-donor interaction, and $\Delta\nu_\pi(E_\pi)$, dependent on the energy of π-electron interaction. As already noted, in the present series of compounds $E_a + E_d$

changes little, and therefore $\Delta\nu_{a+d}$ remains approximately constant, whereas $\Delta\nu_\pi(E_\pi)$ changes as E_π changes. Therefore we may write the relation

$$\Delta\nu = \Delta\nu_{a+d} + \Delta\nu_\pi(E_\pi), \tag{4}$$

which is well confirmed by the experimental data (Table 1, Fig. 1).

It follows from equation (4) that $\Delta\nu$ must depend linearly not only on E_π, but also on the multiplicity (the index $N_{\mathrm{C=C}}$) of the C=C bond on the basis of which the quasiaromatic ring is built, i.e. $\Delta\nu = \Delta\nu_{a+d} + \Delta\nu_\pi(N_{\mathrm{C=C}})$.

This is explained by the fact that, all other conditions being equal, the value of the energy E_π is determined by the magnitude of the electron density or multiplicity ($N_{\mathrm{C=C}}$) of the C=C bond, which determines the effectiveness of delocalization of the electrons of the quasiaromatic ring. Therefore a symbatic relation should be observed between E_π, $N_{\mathrm{C=C}}$, and $\Delta\nu_{\mathrm{O-H\cdots}}$. The values $N_{\mathrm{C=C}}$ were calculated from the equation $N_{\sigma+\pi} = N_0 - \Delta N n + \frac{\Delta N}{6} n_1 - \frac{\Delta N}{72} n_2$, based on the rule of the number of neighbors $^{(9)}$. In this equation $N_0 = 2$, $\Delta N = 0.200$; n, n_1, n_2 are, respectively, the numbers of nearest, next-nearest, and more distant bond neighbors. The experimental data do indeed show the presence of a linear dependence between E_π and $N_{\mathrm{C=C}}$, as well as between $\Delta\nu_{\mathrm{O-H}}$ and $N_{\mathrm{C=C}}$ (Table 1, Fig. 2). These dependences make it possible to solve the inverse problem, namely: from $\Delta\nu_{\mathrm{O-H}}$ or E_π, to find the multiplicity of the C=C bond in an aromatic ring. For this it is necessary to "attach" a bridge with an H bond, determine $\Delta\nu$, E, or $\Delta\delta$ (chemical shift of the NMR), and on this basis one can analyze the change in electron density in the molecule under the influence of various substituents. In work $^{(10)}$ the authors compared the change in $\Delta\nu_{\mathrm{C=O}}$ participating in the formation of the H bond and $N_{\mathrm{C=C}}$ of the compounds. The proposed model of the H bond (1–5) with π-electron interaction, containing at its basis the phenomenon of formation of a quasiaromatic ring (in which the π-electrons of the system use the p-orbital of the hydrogen atom), provides a reliable basis for further study of various manifestations of the H bond both in the ground and in excited states. The point of view considered here makes it possible to give a quantitative justification of the keto-enol transformation (11).

From the data of Table 1 it is seen that the largest shift of the valence vibration of the $\mathrm{O-H}\ldots$ group, $\Delta\nu = 920$-$1020\ \mathrm{cm}^{-1}$, is observed for the enolic forms of acetylacetone and its derivatives. The energy of formation of a quasiaromatic ring with an H bond is 15-17 kcal/mole, and the energy $E_\pi = 14$-15 kcal ($\sim 90\%$ of the total H-bond energy).

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REFERENCES

1. D. N. Shigorin, *Izv. AN SSSR, ser. fiz.*, **14**, 395 (1953); D. N. Shygorin, *Spectrochim. Acta*, **14**, 198 (1959).
2. D. N. Shigorin, N. S. Dokunikhin, *ZhFKh*, **29**, 1958 (1955).
3. D. N. Shigorin, M. M. Shemyakin et al., *DAN*, **108**, 672 (1956).
4. D. N. Shigorin, N. N. Shapetko et al., *DAN*, **148**, No. 5 (1963).
5. D. N. Shigorin, N. A. Shcheglova et al., *DAN*, **132**, 1372 (1960).
6. N. D. Sokolov, *Usp. fiz. nauk*, **57**, 205 (1955).
7. A. A. Shubin, *Izv. AN SSSR, ser. fiz.*, **14**, 442 (1950).
8. G. F. Huttig, *Zs. Phys. Chem.*, **87**, 129 (1914).
9. D. N. Shigorin, *ZhFKh*, **30**, 2753 (1956); *ZhFKh*, **32**, 1739 (1958).
10. J. M. Hunsberger, H. S. Gutowsky et al., *J. Am. Chem. Soc.*, **80**, 3294 (1958).
11. D. N. Shigorin, *ZhFKh*, **23**, 505 (1949).
12. D. N. Shigorin, Ya. K. Syrkin, *ZhFKh*, **23**, 241 (1949).

13. A. Kornberg, *Contemporary Problems of Biophysics*, **1**, IL, 1961, p. 257.

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