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1963

SovietRxiv

scheme 1

Figure 1: scheme 1

Abstract

Full Text

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H-Bonds in Excited Electronic States of Molecules with π-Electrons

(Presented by Academician A. N. Terenin, 23 I 1963)

In systems with π-electrons, the formation of an H-bond may lead to the appearance of a quasiaromatic (coplanar, six-membered) ring owing to the delocalization of its six electrons: four π-electrons of the C=C and –Y=Z bonds, and also two p-electrons of the atom of the $-\overset{\times\times}{X}-$group $-\overset{\times\times}{X}-$H···(scheme 1a, where M is a metal, $X = \mathrm{O, N}$, etc.; $Z = \mathrm{O, N}$, etc.; $-Y = \mathrm{C, N}$, etc.). In this treatment the hydrogen atom of the –X–H···group participates in the formation of the quasiaromatic ring by providing a p-orbital to the π-electron system.

A quasiaromatic ring with a hydrogen or metallo-element bond becomes similar to an aromatic ring of the benzene type because delocalization of six electrons takes place in it; these electrons can use six molecular orbitals: three bonding and three antibonding (scheme 1b). All six bonds of the ring acquire π-electronic character, i.e., become $\sigma\pi$-bonds, although not to the same extent. Apparently, for H-bonds formed in π-electron systems one may introduce the concept of σ- and π-hydrogen bonds (scheme 1b).

(1)

In the case under consideration (^{1,2}), the energy of the H-bond (the change in the energy of the system as a result of formation of the ring by means of the H-bond) in the ground state is equal to:
$E_{\mathrm{H}} = E_{\mathrm{d}} + E_{\mathrm{a}}(S) + E_{\pi}(P^{*})$
(E_{d} is the energy of dipole interaction, $E_{\mathrm{a}}(S)$ is that of acceptor-donor interaction, and $E_{\pi}(P^{*})$ is that of π-electronic interaction). In papers ($^{3-5}$), on the basis of luminescence spectra of α-derivatives of anthraquinone, o-oxyazo compounds, and o-oxyazomethine compounds, the conclusion was drawn that upon excitation of molecules the H-bond in a quasiaromatic ring is not destroyed and may even be strengthened due to an increase in the contribution of the energy of

π-electronic interaction, $E_\pi(P^*)$. It was noted that the H-bond in quasiaromatic rings stabilizes the system (lowers the electronic level) both in the ground and in the excited states. On the other hand, in the works of Weller (^{6}), as well as of Naboikin and Zadorozhnyi (^{7,8}), conclusions were drawn concerning rupture of the quasiaromatic ring upon excitation of molecules (of the methyl salicylate type and methyl esters—

of o-oxynaphthoic acids). These conclusions of the authors contradict the experimental data noted above and the nature of the H-bond in quasiaromatic rings (^{1,9}). The stability of a quasiaromatic ring is determined by the quantity $E_\pi(P^*)$, which depends (other conditions being equal) on the multiplicity of the $C = C$ bond (^{10,11}). Formation of an additional quasiaromatic ring with an H-bond is equivalent to lengthening a chain with conjugated bonds (^{1}), and this should lead to a long-wavelength shift in the electronic absorption and emission spectra (^{12}).

If the group $-Y = Z$ $(> C = O,\ > C = N,\ -N = N-$, etc.$)$ of the quasiaromatic ring, which forms the H-bond, is at the same time responsible for the long-wavelength absorption ($n \to \pi^*$-transition) and luminescence of the compound, then upon excitation of the molecules the energy of the acceptor–donor interaction, $-E_a(S)$, may decrease and even become equal to zero. Therefore the energy of the H-bond in the excited state will be equal to: $E^*_H = E^*_d + E^*_\pi(P^*)$ (where E^*_d and $E^*_\pi(P^*)$ are, respectively, the energies of dipole and π-electron interaction in the excited state). Consequently, the difference between the H-bond energies in the ground and excited states $\Delta E = E^*_H - E_H$ will be determined mainly by the change in the energy of the π-electron interaction: $\Delta E = E^*_\pi - E_\pi - E_a$. In the quasiaromatic ring, upon excitation of the molecule, the following changes will occur: the π-bond in the group $-Y = Z$ will be sharply weakened (as a result of the $n \to \pi^*$-transition and especially upon transition of the system into the triplet state), and the interatomic distances will be changed accordingly. These changes should lead to more effective delocalization (“delocalization”) of the six electrons of the ring, increasing the probability of participation of the altered (“hybridized”) P^*-orbital of the hydrogen atom in the π-electron interaction of the system. Thus, in the excited state the value E^*_π must increase, and therefore the difference $E^*_\pi - E_\pi > 0$. If one takes into account that in the formation of the H-bond of a quasiaromatic ring in the ground state $E_a(S)$ amounts to only 10-15% of the total energy (^{10,11}), then one may expect an increase of E_H in the excited state of the molecule: $E^*_H - E_H > 0$. The first experimental proof of the reality of the changes occurring in the quasiaromatic ring upon excitation of the molecule is the fact that fine vibrational structure is absent in the luminescence spectrum of α-oxyanthraquinone, $\tau \approx 10^{-8}$ sec, and present in the spectrum of α-methoxyanthraquinone, $\tau \approx 10^{-5}$ sec (^{2}). The energy difference $E^*_H - E_H \approx \Delta\nu_{0-0}$ is determined as the shift of the frequency of the purely electronic 0–0 transition of the molecule arising upon formation of the quasiaromatic ring (see Scheme II). The frequencies of the 0–0 transitions of the corresponding compounds

Scheme II: energy-level diagram comparing the quasiaromatic H-bonded compound and the methoxy compound

Figure 2: Scheme II: energy-level diagram comparing the quasiaromatic H-bonded compound and the methoxy compound

(a and b, Scheme II) were determined from the intersection points of the absorption and emission spectra (^{13}). The luminescence spectra of hexane solutions of the compounds were obtained at $T = 77°$K, and the absorption spectra at $T = 293°$K. Table 1 gives the experimental values of the H-bond energies for the excited state of the molecules.

The data of Table 1 show that the energy of the H bond in quasiaromatic cycles, when the molecules pass into an excited electronic state, increases strongly (almost twofold). Strengthening of the quasiaromatic cycle with an H bond upon excitation of the molecule can be observed under certain conditions: in the presence of coplanarity and a sufficiently large energy of π-electronic interaction.

Table 1

Compound	$E_H^{(11)}$, kcal	$\nu_{\mathrm{O—O}}$, cm^{-1}	$\Delta\nu_{\mathrm{O—O}}$, cm^{-1}	$E_H^* = E_H + \frac{\Delta\nu_{\mathrm{O—O}}}{352}$, kcal
1,5-dioxyanthraquinone	8	20050	2710	15.7 ± 1.5
1,5-dimethoxyanthraquinone	–	22760		
1-oxyanthraquinone	8.5	20480	2380	15.3 ± 1.5
1-methoxyanthraquinone	–	22860		
1,4-dioxyanthraquinone	8	19050	1830	13.2 ± 1
1,4-dimethoxyanthraquinone	–	20880		

In this connection we studied the luminescence spectra of 1,4-naphthoquinone and its α-hydroxy derivatives (Fig. 1). If 1,4-naphthoquinone in hexane solutions at $T = 77°$K gives a luminescence spectrum with a pronounced vibrational structure, characterized by frequencies of valence vibrations of the $C = O$ groups (n electrons, which carry out the $n \to \pi^*$ transition), then α-oxy-1,4-naphthoquinone exhibits weak and decaying luminescence.

If in the systems an intermolecular H bond is formed with participation of the chromophoric group ($> C = O$; $> C = N$, etc.), which is responsible for long-

Scheme III

Figure 3: Scheme III

wavelength absorption and luminescence (the $n \to \pi^*$ transition), then upon their excitation rupture of the original hydrogen bond may occur, owing to disruption of the acceptor–donor interaction which in this case determines the bond energy. This may lead to a decrease in the luminescence yield. Indeed, our results$^{(14)}$ show that 1,4-anthraquinonedicarboxylic acid has bright-green but rapidly and reversibly decaying luminescence, whereas the luminescence spectrum of a powder of β-anthraquinonecarboxylic acid has the structure of four intense bands shifted to the long-wavelength side and does not undergo self-quenching. IR measurements established that the intermolecular H bonds in β-anthraquinonecarboxylic acid are effected through the carboxyl groups (dimerization), while association of the molecules of 1,4-anthraquinonedicarboxylic acid proceeds with participation of the carbonyl (chromophoric) group of anthraquinone and the OH of the carboxyl group. In dioxane solution the association is destroyed, and the solution of 1,4-anthraquinonedicarboxylic acid acquires stable green luminescence.

To establish the mechanism of the phenomenon of reversible quenching of luminescence, the EPR spectra of powders of 1,4-anthraquinonedicarboxylic and β-anthraquinonecarboxylic acids were studied in the course of their excitation ($\lambda_{\mathrm{Hg}} = 365\,\mu$). The first of these gave a strong singlet signal ($\Delta H = 20 \pm 1$ G, $g \simeq 2$), and the second a very weak one. On dissolution in pyridine (the association was destroyed), EPR was not observed. Upon excitation of the system, disruption of the original H bond occurs, apparently accompanied by transfer of a hydrogen atom with formation of radicals (see Scheme III):

(III)

For the article by D. N. Shigorina, N. A. Shchelova, A. K. Piskunova, G. A. Ozerova,
N. S. Dokunikhina, p. 862.

[spectra figure]

Fig. 1. Luminescence spectra (a) and absorption spectra (b) of certain quinones in solutions at 77° K, $C \simeq 10^{-4}$—10^{-5} mol/l.
1 –1,4-dioxyanthraquinone (in octane), 2 –naphthoquinone-1,4,
3 –3-oxynaphthoquinone-1,4 (in hexane)

For the article by L. M. Rozanova, I. Ya. Barskii, E. M. Brumberg, p. 907

[microphotographs figure]

Fig. 1. Microphotographs of lymphocytes in human peripheral blood, obtained in ultraviolet fluorescence rays.
a –healthy person; b –patient with lymphadenosis with a normal course of the

disease; *c* –patient with lymphadenosis with sharp exacerbation of the process (terminal stage). Objective –quartz-fluorite achromat 58$×$0.80, water immersion

[microphotographs figure]

Fig. 2. Microphotographs of human myeloblasts, obtained in ultraviolet fluorescence rays.
a –myeloblasts in the bone marrow of a healthy person; *b* –myeloblasts in the peripheral blood of a patient with myeloblastosis. Objective –quartz-fluorite achromat 58$×$0.80, water immersion

This becomes possible owing to the transition of the carbonyl group of anthraquinone (via an $n \rightarrow \pi^*$ electronic transition) into the triplet state (T). The formation of radicals may be regarded as the result of deactivation or reaction of the triplet state of molecules (Scheme III). In turn, the radicals that arise are capable of suppressing the luminescence of the molecules surrounding them ([15,16]). Processes of deactivation of triplet, and sometimes singlet (S^*), excited (pre-triplet) states with formation of radicals or ion radicals may proceed both by intramolecular ([17]) and by intermolecular mechanisms (through H-bonds or π-complexes).

In molecules (triphenylmethane, toluene, etc.) that are in the triplet state, substantial changes in interatomic distances occur, as well as enhanced interaction of the π-electronic and σ-electronic levels, which should favor the most effective conversion of electronic energy into the vibrational energy of the nuclei; moreover, the possibility appears for the transition $T \rightarrow T^*$ (the process becomes a two-photon one) ([18]). The probability of the two-quantum process $S \xrightarrow{h\nu_1} S^* \rightsquigarrow T \xrightarrow{h\nu_2} T^*$ will apparently be the greater, the larger $\tau_{\text{phosph.}}$ is. All this may ultimately lead to rupture of chemical bonds ($\equiv$ C—H) with formation of radicals. In the presence of intermolecular interaction, the unpaired electron of the triplet molecule, occupying an excited molecular orbital, may with a certain probability use the hybridized p^*-orbital of a hydrogen atom of another molecule participating in the formation of an H-bond or a π-complex between the particles. This apparently may lead to detachment of a hydrogen atom from another molecule with formation of the corresponding radicals (Scheme III). Similarly, an H-bond may participate in processes of radical transformation

$$\mathrm{R_1Y + H{-}X{-}R_2 \longrightarrow R_1Y \cdots H{-}X{-}R_2 \longrightarrow R_1YH + \uparrow XR_2}$$

where X and Y are atoms with n-electrons. From this point of view, certain oxidative processes may be regarded as the result of reaction of the triplet state of the oxygen molecule (with all the consequences following from this). If triplet molecules appear in any system, then under certain conditions the emergence of radicals is possible in that system.

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Received
11 I 1963

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