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Abstract

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The Influence of the Position and Nature of the Substituent on the Fluorescence Spectra of Anthraquinone Derivatives in Frozen Solutions

(Presented by Academician A. N. Terenin, 27 III 1958)

The fluorescence spectra of vapors and adsorbates of anthraquinone and its derivatives were investigated by A. V. Karyakin and A. N. Terenin (^{1}). In works (^{2}), using the method of infrared spectroscopy, it was shown that in α-hydroxy and amino derivatives of anthraquinone a strong intramolecular hydrogen bond is formed, which is retained at temperatures of 280–300°C. It was established that such an H-bond has a strong influence on the vibrational spectra of the molecules.

In the electronic spectra, something analogous is observed: a hydrogen bond included in a system with π-electrons affects the position of the electronic level of the molecules and in many cases greatly lowers it (^{3}). In the electronic absorption spectra of α-derivatives of anthraquinone, the bands are not only strongly shifted toward longer wavelengths, but are also considerably more diffuse in comparison with the β-derivatives.

The nature of the α-substituent also has some influence on the position of the electronic level, even if it is not capable of forming a hydrogen bond. In this case the substituent and the group $C = O$ can substantially influence one another through π-electron interaction, since they simultaneously interact with one and the same carbon atom. At the same time, for β-substituents this influence will be many times weaker, because the substituent and the $C = O$ group are not linked to one another by direct interaction.

The greater diffuseness of the electronic absorption bands in α-derivatives as compared with β-derivatives is also connected with differences in their structure, which is directly reflected in the acceleration of the process of conversion of electronic energy into vibrational energy in the former more than in the latter.

It should be noted that, in studying the electronic spectra of molecules, we are dealing with the excited state of the π-electron system. It is also necessary to take into account that a large share of the "responsibility" for the position of the electronic level of the anthraquinone molecule and its derivatives in the excited state falls on the $C = O$ group. Upon excitation of the molecule, the π-bond $C = O$ is sharply weakened ($n \to \pi^*$ transition), with a possible subsequent transition of the molecule into the triplet state (^{1}, ^{4}).

Fig. 1. Fluorescence of anthraquinone and its β-derivatives in n-hydrocarbons at 77°K.
1a, 1b, 1c —anthraquinone; *2a, 2b, 2c* —β-chloroanthraquinone; *3a, 3b, 3c* —β-methylanthraquinone; *4b* —β-aminoanthraquinone; *a* —in hexane, *b* —in heptane, *c* —in octane

Fig. 2. Fluorescence spectra of certain anthraquinone derivatives in hexane.
1 —α-hydroxyanthraquinone (5558 Å); 2 —1,8-dihydroxyanthraquinone (5410 Å); 3 —1,4-dihydroxyanthraquinone (5248 Å); 4 —α-chloroanthraquinone (5200 Å); 5 —1,5-dichloroanthraquinone (5220 Å); 6 —β-hydroxyanthraquinone (5140 Å); 7 —1,5-dihydroxyanthraquinone (5680 Å) (the positions of the initial bands are indicated in parentheses)

(Figure: Figure 1)

Fig. 1

(Figure: Figure 2)

Fig. 2

quinone in hexane, the principal bands are split into 4 components. The weakest component is the short-wavelength one; the most intense is the 2nd component; the 3rd and 4th components have approximately equal intensities. In octane, however, for β-chloroanthraquinone only 3 components remain, with the long-wavelength component being the most intense. In all spectra, a tendency is observed toward equalization of the intensities among the components within a band upon moving into the long-wavelength region.

In the spectra of all compounds that give a fine structure, the basic form of the spectrum is preserved and has the appearance of a threefold repeated pattern, as indicated above, in the regions between the intense bands. The corresponding components of these intense bands, as well as all correspondingly taken weaker bands, are separated from one another by a distance averaging 1664 cm^{-1}, which corresponds to the totally symmetric CO vibration in the ground electronic state (see Table 1), and this difference,

Table 1

Compound	λ_{init}	λ_1	λ_2	λ_3	$\nu_{\text{init}} - \nu_1$	$\nu_1 - \nu_2$	$\nu_2 - \nu_3$
	Position of one of the components in the principal bands (Å)	Frequency differences (cm^{-1})					
Anthraquinone: in hexane	4591	4972	5419.7	5947.5	1668	1662	1638
in heptane	4571	4950.6	5390	5914	1677	1647	1644
in octane	—	4948.5	5392	5914	—	1662	1637
β-Cl-anthraquinone: in hexane	4580	4960	5405.7	5928	1673	1661	1632
in heptane	4573	4952	5398	5925.3	1673	1668	1649
in octane	—	4953	5399	5930	—	1667	1660
β-methylanthraquinone: in hexane	4573*	4946	5390	5913	—	1666	1641
in heptane	4562	4939	5380	5895	1672	1660	1623
in octane	4573*	4942	5385.3	5906	—	1666	1639

Compound	λ_{init}	λ_1	λ_2	λ_3	$\nu_{\text{init}} - \nu_1$	$\nu_1 - \nu_2$	$\nu_2 - \nu_3$
β-aminoanthraquinone: in heptane	–	4970	5418	5946.3	–	1663	1640

* Diffuse line.

somewhat larger between the bands in the short-wavelength part, decreases monotonically upon moving into the red region of the spectrum. The latter indicates the anharmonicity of the C=O vibrations. It is precisely this vibration that is manifested most actively in the electronic-vibrational spectrum, both in pure form (principal bands) and in superposition with all the other frequencies that appear. Upon transition from the violet to the red region of the spectrum, the intensity of the indicated bands first increases and, after reaching a certain maximum, decreases again; this is explained, in accordance with the Franck-Condon principle, by an increase in the internuclear equilibrium distance for the excited electronic level (6). As a result, the $0''$—$0'$ transition is unlikely, and frequencies corresponding not to transitions to the first vibrational sublevels of the ground state but to higher ones appear more intensely in the spectrum; in this case the number of the most intense bands is rather large. The question of the nature of the splitting of the electronic-vibrational level has not been studied in detail. Apparently, the nature of this splitting is connected with the orientation of the fluorescing molecules in the crystal lattice of the solvent.

The α-derivatives of anthraquinone that we studied gave spectra sharply different from those considered above. First of all, they proved to be strongly shifted into the red region and had the form of rather diffuse bands. These bands, even in broad outline, did not repeat the form of the spectrum of anthraquinone,

and some α-derivatives gave no visible fluorescence at all upon excitation by the mercury line λ 365 mμ (α-aminoanthraquinone).

The spectra of the α-derivatives studied—α-hydroxyanthraquinone, α-chloroanthraquinone, 1,5-dihydroxyanthraquinone, 1,8-dihydroxyanthraquinone, and 1,4-dihydroxyanthraquinone—are presented in Fig. 2.

Special attention should be given to the spectrum of β-hydroxyanthraquinone that we investigated. For it, a spectrum is observed that is broadened into bands and shifted into the red region. This can apparently be explained by the preservation, for this molecule, even in neutral solvents and at low concentrations, of intermolecular hydrogen bonds. Evidently, the β-hydroxyanthraquinone molecule is present in the solvent in the form of associates: dimers or polymers. The presence of intermolecular interaction affects the π-electron system of the molecules and leads to a strong increase in the probability of energy redistribution between vibrational sublevels (7).

Thus, the experimental results obtained confirm the assumptions put forward concerning the influence of the position of the substituent and its nature on the fluorescence spectra of molecules.

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