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π_l,π^*-Absorption Bands as a Valuable Source of Information on the Structure of Tautomers and Conformers

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Abstract—The presence of several π_l,π^*-absorption bands in the electronic spectrum of hydroxyanthraquinones indicates the occurrence of tautomeric and conformational equilibria. The structure of tautomers and conformers can be determined from the correlation between $\lambda_{\max}$ and the sums of the constants σ^A of hydroxy and oxido groups, calculated for each isomer.

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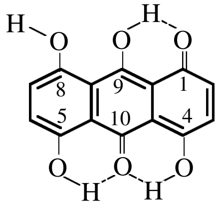
Using α-hydroxyanthraquinones as examples we showed that the long-wave π_l,π^*-absorption bands are valuable as a source of information on the tautomeric and conformational structure of organic compounds. Each hydroxy-substituted anthraquinone can exist in different forms resulting from tautomeric transformations and rotational isomerism. According to quantum-chemical calculations, each state is characterized by its unique π_l–π^* transition; therefore, the presence of several π_l,π^* bands in a single experimental spectrum indicates the existence of tautomeric and conformational equilibria.

In each state, the hydroxy group can be free (OH), intramolecularly H-bonded (OH*) or ionized (in alkaline medium, O^-). For example, 1,4,5,8-tetrahydroxyanthraquinone exists as four tautomers having 9,10-, 1,10-, 1,4-, and 1,5-quinoid structures. In the three latter, the hydroxy groups occupy different α- and *meso*-positions and are free or H-bonded, e.g., as shown below.



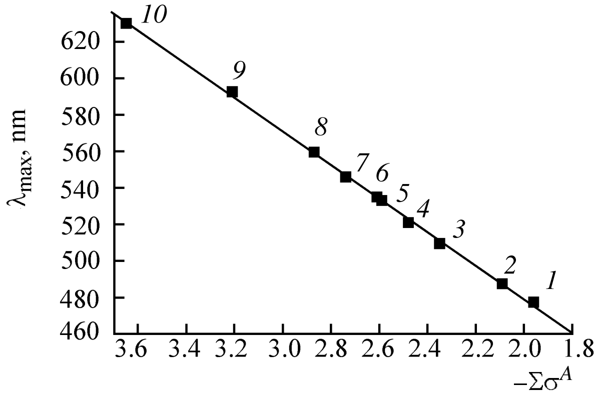
Each tautomer could give rise to several conformers as a result of rupture of intramolecular hydrogen bonds.

It was proposed to use correlations of $\lambda_{\max}$ with the sums of the constants σ^A of OH, OH*, and O^- groups for the assignment of experimental π_l,π^*-absorption bands to particular conformers. Spectroscopic constants σ^A [1] characterize the donor–acceptor power of a substituent X in intramolecular charge transfer along the conjugated bond sequence X–$(CH{=}CH)_n$–C=O; this charge transfer determines the position of long-wave absorption maxima of substituted 9,10-anthraquinones. Separate scales of constants σ^A for the α- and *meso*-positions of each tautomeric anthraquinone are necessary to ensure a correlation between the position of the π_l,π^* maximum of each conformer and the sum of σ^A within an isostructural series. Such constants were calculated both from the experimental values of $\lambda_{\max}$ for different α-hydroxyanthraquinones in various solvents and theoretically (by quantum-chemical methods; see table). The results were independent on the calculation method. Correlation analysis of several tens absorption spectra of different α-hydroxyanthraquinones, their substituted derivatives, and the corresponding anions in various solvents revealed no π_l,π^* band which could not be assigned to a particular tautomer and conformer; moreover, very high correlation coefficients suggest nonrandom character of the relations found.

As an example, let us consider the correlation between the π_l,π^* maxima of 1,4,5,8-tetrahydroxyan-

Constants σ^A of hydroxy and oxido groups in tautomeric anthraquinones

Constant	9,10	1,4	1,10	1,5
$-\sigma^A_{\alpha}$(OH)	0.49	0.66	0.67	0.85
$-\sigma^A_{\alpha}$(OH*)	0.62	0.81	0.81	1.00
$-\sigma^A_{\alpha}$(O^-)	1.01	1.25	1.23	1.45
$-\sigma^A_{meso}$(OH)	–	0.58	0.60	0.77
$-\sigma^A_{meso}$(OH*)	–	0.71	0.72	0.90
$-\sigma^A_{meso}$(O^-)	–	1.10	1.09	1.30



Correlation between the π_l,π^*-absorption maxima of 1,4,5,8-tetrahydroxyanthraquinone in heptane [2] and its anion [3] with the sum of the constants σ^A of hydroxy and oxido groups: (*1*) $(OH)_4$-9,10-, (*2*) $(OH)_3OH^*$-9,10-, (*3*) $OH(OH^*)_3$-9,10-, (*4*) $(OH^*)_4$-9,10-, (*5*) $(OH)_4$-1,10-, (*6*) 5,8,10-$(OH)_3$-9-OH^*-1,4-, (*7*) $(OH)_2(OH^*)_2$-1,4-, (*8*) $(OH)_2(OH^*)_2$-1,10-, (*9*) $(OH)_3OH^*$-1,5-, and (*10*) 1-OH^*-4,5,8-$(O^-)_3$-9,10-anthraquinones.

thraquinone and its anion with $\Sigma\sigma^A$. This correlation made it possible to assign each π_l,π^* band and propose a structure for the only reported anion of this compound, for which even the degree of ionization was unknown. The correlation is decribed by the following equation (see figure):

$$\lambda_{max} = (296.7 \pm 2.2) - (91.21 \pm 0.80)\Sigma\sigma^A, \text{ nm}; \quad r = 0.9997, \; s = 1.2 \text{ nm}.$$

This results, as well as other analogous data, indicates that the generally accepted views implying exclusively 9,10-quinoid structure of anthraquinones and obligatory intramolecular hydrogen bond between the carbonyl oxygen atom and hydroxy group in the *peri* position should be revised. The molecular structure of many hydroxyanthraquinones cannot be given by a single formula, for these compounds exist in different states occurring in a dynamic equilibrium with each other. The composition of such a mixture of different forms may change depending on the conditions, e.g., solvent nature.

Hydroxyanthraquinone structure is inherent to a vast number of naturally occurring compounds [3] whose color and biological activity are determined by the number of α-hydroxy group and their mutual arrangement. Our concepts made it possible not only to rationalize for the first time the presence of a set of π_l,π^* bands in the electronic absorption spectra of hydroxyanthraquinones but also to predict their position. It might be expected that our concepts on the presence of several π_l,π^* bands in the electronic absorption spectra as a result of existence of tautomeric and conformational equilibria would be general for organic chemistry.

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