ELECTRONIC ABSORPTION SPECTRA OF SOME
o-BENZOQUINONE DERIVATIVES

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Compounds belonging to the quinone class are widely distributed in nature. Many of them are biologically active: they take part in processes of metabolism of materials [1], and they are used as medicinal preparations [2]. The presence of carbonyl groups in the quinone molecules makes it possible for compounds of this class to enter into oxidation−reduction reactions [3]. However, both the oxidation−reduction potentials and also the spectral characteristics of these substances depend greatly on the substituents on the quinoid ring. A study of structure, basic physicochemical properties, and biological activity requires a reliable interpretation of the absorption bands in the electronic spectra of quinones. While a number of works [4-6] have been devoted to a study of the electronic absorption spectra of p-benzoquinones, the absorption spectra of o-benzoquinones have been inadequately studied, since it is known that unsubstituted o-benzoquinone is extremely unstable.

The objective of the present work was the assignment of electronic absorption bands of five o-benzoquinone derivatives (see Table 1). In this work we have investigated the absorption spectra of solutions of these compounds as a function of solvent polarity and pH of the medium, and we have also studied the absorption of the reduced and oxidized forms. Together with this, with the objective of unequivocally assigning absorption bands to definite electronic transitions, we have studied the polarization of the absorption bands and have calculated the oscillator forces of the long-wavelength band.

Spectra of the indicated compounds were recorded on a Specord UV VIS spectrophotometer in the 210-700-nm region. Polarized spectra of the o-benzoquinones, oriented in stretched films of polyvinyl alcohol (PVA), were recorded on SF-4A and Specord UV VIS spectrophotometers equipped with a polaroid. The spectral shape of the dichroism of partially oriented molecules was calculated by the formula

$$d = \frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + D_{\perp}} \cdot 100\,\%,$$

where $D_{\parallel}$ is the parallel component of optical density in polarized light whose electrical vector coincides with the direction of stretch of the film and $D_{\perp}$ is the perpendicular component of optical density, with an electrical vector perpendicular to the direction of stretch. Reduction of the o-benzoquinone derivatives was performed with molecular hydrogen in the presence of PtO_2 catalyst in 0.02 N HCl.

Spectra of the compounds studied are shown in Fig. 1. In the visible and near-UV regions, compounds I, II, IV, and V have three clearly expressed absorption maxima. In the spectra of compound III, two sharp bands are observed in the 250-350-nm region, one of which (at about 270 nm) has a diffuse fine structure which is displayed more clearly in weakly polar solvents (in dioxane, for example). On change in the acidity of the solution in the direction of lower pH values, in addition to changing its position, this band decreases in intensity. Moreover, a bathochromic shift of this band is observed on transition to nonpolar solvents. To all appearances, this pertains to an $n \rightarrow \pi^*$ transition of a disubstituted benzene ring [7]. This conclusion is supported by the fact that the 280-nm band which we observed in the absorption spectrum of the H_2N- ⟨⟩ −

COONa molecule undergoes similar changes with respect to shift and intensity as a function of the pH of the medium and the polarity of the solvent. In all the compounds we studied, the absorption band in the 200-nm region pertains to electronic transitions of the conjugated bond system of a quinoid ring. A detailed study of this

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No.	Structural formula	Solvent	Band C		Band B		Band A		f
			λ	$\varkappa\cdot10^{-4}$	λ	$\varkappa\cdot10^{-4}$	λ	$\varkappa\cdot10^{-4}$	
I	O=⟨⟩—OCH₃ / O=⟨⟩—OCH₃	Water			290	1,3	430	0,055	0,028
		Methanol			285	1,3	411	0,055	
		Chloroform			283	1,3	407	0,055	
		Dioxane			280	1,3	400	0,055	
			Shoulder						
II	O=⟨⟩—OCH₃ / O=⟨⟩—NH—⟨=⟩	Water	292	0,8	328	1,36	510	0,32	0,14
		Methanol	292	0,8	322	1,36	488	0,32	
		Chloroform	292	0,8	321	1,36	476	0,32	
		Dioxane	292	0,8	307	1,36	460	0,32	
III	O=⟨⟩—OCH₃ / O=⟨⟩—NH—⟨⟩—COONa	Water	270	2,5	335	1,5	509	0,264	0,10
		Methanol	279	2,5	334	1,5	490	0,264	
		Dioxane	280	2,5	328	1,5	476	0,264	
IV	O=⟨⟩—OCH₃ / O=⟨⟩—NH—CH₂—COONa	Water			312	1,55	494	0,18	0,082
		Methanol			305	1,55	475	0,18	
		Dioxane			294	1,55	471	0,18	
V	O=⟨⟩—OCH₃ / O=⟨⟩—N(CH₃)₂	Water			330	1,6	516	0,36	0,15
		Methanol			325	1,6	495	0,36	
		Chloroform			323	1,6	484	0,36	
		Dioxane			320	1,6	472	0,36	

band was not conducted, due to the limited spectral sensitivity of the instruments used. The shoulder in the 240-nm region, which is observed only in amino derivatives, corresponds to a band which arises due to p–π conjugation on interaction of the nitrogen atom with the quinoid ring [7].

All the o-benzoquinone derivatives have a coloring which is bright yellow for dimethoxy-o-benzoquinone (1) and dark red (with shadings) for the amino derivatives; i.e., in the visible region of the spectrum (430–520 nm) the compounds of this series have a typical absorption (band A). Moreover, all the derivatives which we studied display absorption in the 280–340-nm region (band B). The presence of these bands in the electronic absorption spectrum, just like the absorption at 1680–1645 cm^{-1} in the IR region [8], indicates the presence of a quinoid type of structure in these compounds. Bands A and B disappear in the absorption spectrum of the reduced form of the quinones (Fig. 1), which supports the correctness of this statement. The bands in the 220- and 295-nm regions, which are displayed in the spectra of the phenolic forms, pertain to the absorption of a substituted benzene ring [7].

With the objective of assigning bands A and B to a definite type of transition, we studied their positions as a function of the polarity of the solvent. As is evident from Table 1, both bands undergo a hypsochromic shift on transition from polar to nonpolar solvents; that is, they behave as $\pi \rightarrow \pi^*$ transitions. While the B band from all three criteria (position, coefficient of molar extinction $\varkappa_{max}$ of the order of $1.5\cdot10^4$, and "blue" shift on transition from a polar solvent to a nonpolar one) satisfies the $\pi \rightarrow \pi^*$ transition settled on, the assignment of band A requires a more detailed examination.

Some workers [9] assign the long-wavelength band of o-quinones to an n $\rightarrow \pi^*$ transition; others [10] indicate the possibility of forming a charge-transfer complex. In assigning the long-wavelength absorption band of anthraquinone derivatives, the authors of [11] indicate the possibility of an intramolecular charge transfer. As was noted above, the A band of o-benzoquinone derivatives cannot be assigned to an n $\rightarrow \pi^*$ transition, since it undergoes a hypsochromic shift on transition to nonpolar solvents. We have also eliminated correspondence of the long-wavelength to a charge-transfer complex, since neither sublimation, heating a solution in solvents with different dielectric permittivites (5–80) to high temperatures, nor pH change in the range 1–13 leads to a disappearance of this band.
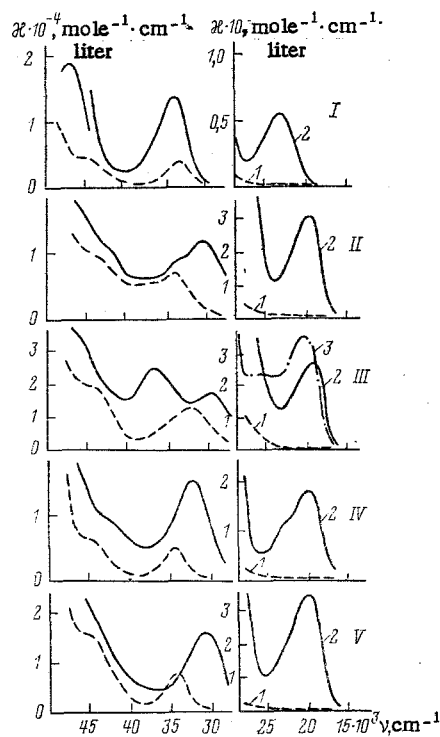
Fig. 1. Electronic absorption spectra of o-benzoquinone derivatives in water: 1) reduced form; 2) oxidized at pH 7.0; 3) oxidized at pH 10.0. I-V correspond to the numbers of the compounds in Table 1.
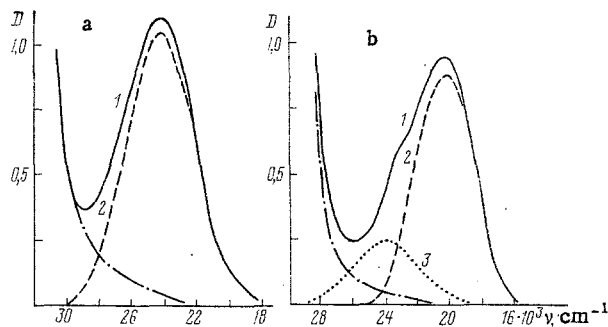

Fig. 2. Contours of separated absorption bands of compounds I (a) and IV (b). Experimental curve (1) and separated contours of the A_1 (2) and A_2 bands (3).

To prove that the A band has the character of a $\pi \rightarrow \pi^*$ transition, we performed a calculation of the oscillator forces of this band using the Kravets integral, with allowance for a correction for the effect of the internal field of a dilute solution and the chaotic distribution of the absorbing dipoles [12]:

$$f = \frac{1,17 \cdot 10^{-7} n}{(n^2 + 2)^2} \int \varkappa_\nu d\nu,$$

where n is the refractive index of the solvent and $\varkappa_\nu$ is the decimal molar absorption coefficient.

The outlines of the long-wavelength absorption bands of the quinones were separated out by the procedure described below. Values of the oscillator forces for the A_1 band are given in Table 1. On the basis of their values it is possible to state that the long-wavelength band has the character of a resolved $\pi \rightarrow \pi^*$ transition.
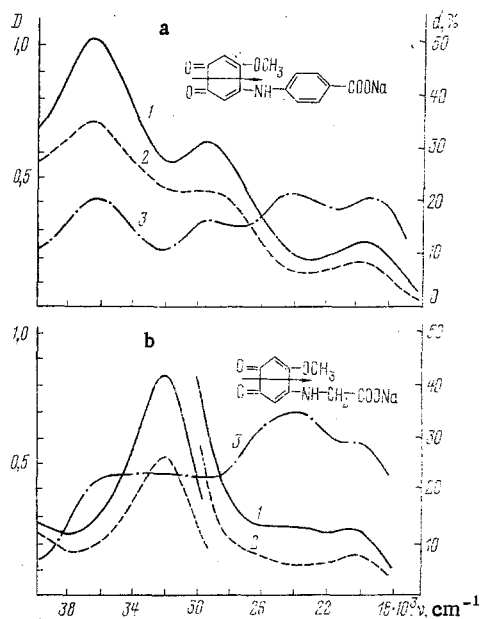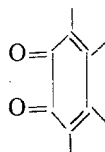
Fig. 3. Absorption spectra of compounds III (a) and IV (b) in stretched PVA film: 1) $D_\parallel$; 2) $D_\perp$; 3) d.

Attention is drawn to the fact that when a more electron-donating substituent than $-OCH_3$ is introduced into the 5-position, the B band undergoes a bathochromic shift and an increase in molecular extinction (see Table 1). To all appearances, this band pertains to the quinoid chromophore

It is known that additional introduction of electron-donor substituents into conjugated systems (benzene, for example) leads to a bathochromic shift of their long-wavelength absorption band due to an increase in the proportion of charge transfer in the excited electronic state [13]. By this same mechanism one can explain the bathochromic shift and increase in intensity of this band when the $-OCH_3$ group is replaced by an amino substituent, and the long-wavelength band of the o-benzoquinone derivatives may be considered as an internal charge-transfer (ICT) band.

Assuming that the A pertains to an ICT band, in the spectra of compounds II-V we should expect the appearance of two maxima: transfer along the system α O= $\diagdown\!\!\!/\!\!-\!N-$ (band A_1) and along the system β O= $\diagup\!\!\!\diagdown -OCH_3$

(band A_2). Transfer along the indicated α and β systems is possible, since in the molecules of amino derivatives of o-benzoquinone there are two electron-donor groups, $-OCH_3$ and $-NH-$ [or $-N(CH_3)_2$ for compound V] and the carbonyl groups of the quinoid ring, which show up as electron-acceptors with respect to them.

While the A band in the spectra of compounds II, III, and V displays only a strong asymmetry, in the spectrum of IV, in the short wavelength arm an inflection is observed (Fig. 1, curve 2) which, to all appearances, is caused by the presence of an A_2 band. In compound I, where an amino substituent is absent, a symmetrical band appears in the 430-nm region, which, in its extinction, is three times smaller than the A band in the spectrum of IV and six times smaller than the analogous band in the spectra of compounds II, III, and V. The observed difference in molar extinctions masks the A_2 band on a background of the A_1 and B bands in the spectra of II-V. The small difference in band intensities in compound IV makes it possible to separate these bands positively. If one assumes that the true outline of the absorption band has a symmetrical form (a Gaussian one, for example) and bears in mind that its long-wavelength arm is not distorted, then by the successive approximation method one can construct the individual A_1 and A_2 bands for compound IV (Fig. 2) and also for compounds II, III, and V. The presence of the A_2 band in the spectra of II-V is also confirmed by a study of the

absorption of o-benzoquinones in alkaline medium (Fig. 1). At pH 10 the B band undergoes a hypsochromic shift, and a clearly defined shoulder is detected on the short-wavelength arm of band A.

Polarization measurements of the absorption spectra of o-benzoquinones oriented in PVA films may serve as a confirmation of the fact that the electronic transitions corresponding to absorption bands A_1 and A_2 are actually effected along the conjugation systems α and β. From geometric considerations, the orientation axis should be considered as approximately coincident with the long molecular axis passing through the substituent in position 5 and the center of the benzene ring. In this case the dipole moments of the transitions should lie parallel to the direction singled out and one may expect a positive value of the dichroism in the 390–520-nm region. Actually, two maxima on the dichroism curve are observed in this region (Fig. 3). Since both electronic transitions are identically polarized, have closely similar numerical dichroism values, and behave as $\pi \rightarrow \pi^*$ transitions, it may be stated that the charge transfer in the excitation process is effected via the conjugation systems α and β.

The positive value of the dichroism in the B band permits one to state that the electronic transition of the quinoid chromophore is effected along the direction indicated.

Thus, in addition to the absorption of the quinoid chromophore in the visible region of the spectra, aminosubstituted o-benzoquinone derivatives display two absorption bands which bear a charge-transfer character.

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