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A Quantum-Chemical Study of Prototropic Tautomerism in 1-Hydroxy-9,10-anthraquinones

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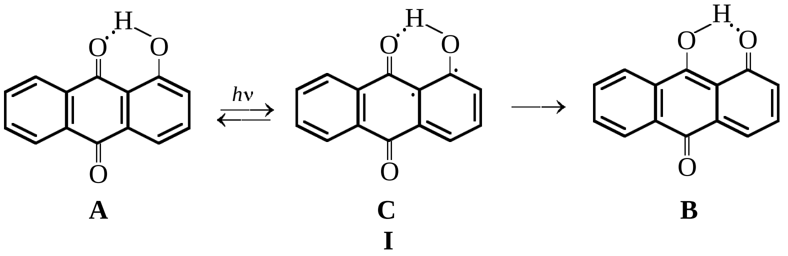
Abstract — The effect of substituents R on the tautomerism and electronic absorption spectra of 1-hydroxy-*x*-R-9,10-anthraquinones and 9-hydroxy-*x*-R-1,10-anthraquinones was studied by quantum-chemical and correlation methods. The former compounds ($x \neq 2$) are more sensitive to substituent effects than the latter compounds. Examination of the fine structure of long-wave absorption showed that the experimental spectra of 1-hydroxy-*x*-R-9,10-anthraquinones contain no bands assignable to *ana*-quinoid forms.

α-Hydroxyanthraquinones are important natural and manmade compounds, widely used as drugs, biologically active agents, intermediates in syntheses of dyes, analytical reagents, and indicators; they are also used in media for data recording, storage, and imaging, etc. [1]. Therefore, the structural features and physicochemical properties of these compounds are being actively studied.

The concept of prototropic tautomerism in a keto–hydroxy cell [2] was recently developed as applied to α-hydroxyanthraquinones [3–6]. The proton transfer in the excited state of 1-hydroxy-9,10-anthraquinone **I** (structure **A**) with the formation of 9-hydroxy-1,10-anthraquinone (structure **B**) was studied in detail by fluorescence excitation, electronic emission, and resonance Raman spectroscopy, and also by transformation analysis [6].

Compound **I** in the excited singlet state has structure **C** with two unpaired electrons whose delocalization favors stabilization of *ana*-quinoid structure **B** [5].



In the excited state, the zero energy level of structure **B** is lower than that of **I** by 10 kJ mol^{-1} [7], whereas in the ground state it is higher [5, 6]. The enthalpy of **A** → **B** isomerization calculated by the AM1 method is high (55.7 kJ mol^{-1}), suggesting that, in the ground state, the tautomeric equlibrium is essentially shifted toward form **A** [8].

The electronic absorption spectroscopy is an efficient tool in studying tautomeric equilibria, since each tautomer has its own π_l,π^* absorption band [9]. The goal of this study was to examine theoretically the effect of substituents on the prototropic tautomerism of **I** and to determine how it is manifested in the electronic absorption spectra.

To reveal the effect of the nature and position of substituent on the relative stability and electronic absorption spectra of **I** in the *p*-quinoid (**A**) and *ana*-quinoid (**B**) forms, we performed quantum-chemical calculations using the Dewar version of the π-electonic PPP method [10] in the approximation of varied β [11]. The atomization energies per electron $\Delta H/\bar{e}$(**A**) and $\Delta H/\bar{e}$(**B**) (eV mol^{-1}), differences between atomization energies of the two forms $\Delta\Delta H$ (eV mol^{-1}), solvation coefficients M(**A**) and M(**B**) and differences

Table 1. Parameters of 1-hydroxy-*x*-R-9,10- (**A**) and 9-hydroxy-*x*-R-1,10-anthraquinones (**B**) (PPP calculations)[a]

x-R	$\Delta H/\bar{e}(\mathbf{A})$, eV mol^{-1}	$\Delta H/\bar{e}(\mathbf{B})$, eV mol^{-1}	$\Delta\Delta H$, eV mol^{-1}	$M(\mathbf{A})$, eV mol^{-1}	$M(\mathbf{B})$, eV mol^{-1}	ΔM, eV mol^{-1}	$\lambda_{max}(\mathbf{A})$, nm	$\lambda_{max}(\mathbf{B})$, nm
H	1.859	1.851	0.58	2.40	3.10	–0.70	404	471
2-COOH	1.839	1.835	0.37	4.30	5.20	–0.90	400	479
3-COOH	1.839	1.833	0.54	4.25	5.03	–0.78	404	475
4-COOH	1.837	1.831	0.56	4.11	4.80	–0.69	422*	477
5-COOH	1.842	1.835	0.57	4.53	5.24	–0.71	415	483
6-COOH	1.840	1.833	0.58	4.34	5.03	–0.69	408	473*
7-COOH	1.840	1.833	0.54	4.20	5.04	–0.84	409	479
8-COOH	1.837	1.836	0.04	4.06	5.38	–1.32	406	476*
2-CH_3	1.849	1.844	0.40	2.49	3.27	–0.78	411	477*
3-CH_3	1.852	1.844	0.60	2.67	3.34	–0.67	410	478
4-CH_3	1.852	1.845	0.49	2.58	3.32	–0.74	448	477*
5-CH_3	1.853	1.846	0.56	2.64	3.37	–0.73	401	472
6-CH_3	1.851	1.844	0.56	2.58	3.32	–0.74	400	480
7-CH_3	1.851	1.844	0.58	2.59	3.31	–0.72	397	464
8-CH_3	1.852	1.843	0.70	2.64	3.29	–0.65	406	482
2-NO_2	1.768	1.759	0.71	6.23	6.62	–0.39	404*	473*
3-NO_2	1.765	1.757	0.59	5.56	6.34	–0.78	404*	472*
4-NO_2	1.765	1.758	0.53	5.76	6.46	–0.70	418	473*
5-NO_2	1.763	1.755	0.63	5.49	6.08	–0.59	–	–
6-NO_2	1.764	1.757	0.61	5.65	6.25	–0.60	–	473*
7-NO_2	1.764	1.757	0.60	5.64	6.28	–0.64	–	–
8-NO_2	1.763	1.760	0.22	5.50	6.54	–1.04	402*	474*
2-OH	1.830	1.826	0.30	2.74	3.63	–0.89	424	505
3-OH	1.832	1.825	0.59	2.96	3.61	–0.65	421	478
4-OH	1.833	1.828	0.41	2.96	3.78	–0.82	479	507
5-OH	1.834	1.827	0.54	3.02	3.76	–0.74	411	476
6-OH	1.832	1.825	0.55	2.86	3.62	–0.76	405	487
7-OH	1.832	1.824	0.58	2.87	3.58	–0.71	396	464
8-OH	1.834	1.824	0.76	3.00	3.53	–0.53	422	491
2-NH_2	1.830	1.826	0.22	3.02	4.06	–1.04	453	544
3-NH_2	1.832	1.825	0.60	3.27	3.93	–0.66	444	509
4-NH_2	1.833	1.828	0.35	3.38	4.26	–0.88	520	532
5-NH_2	1.834	1.827	0.53	3.42	3.17	–0.75	458	489
6-NH_2	1.832	1.825	0.53	3.16	3.94	–0.78	425	502
7-NH_2	1.832	1.824	0.58	3.17	3.88	–0.71	407	463
8-NH_2	1.834	1.824	0.82	3.38	3.83	–0.45	467	516

[a] For the meaning of the parameters, see text. The values corrected using Eq. (4) are marked with asterisks.

between them ΔM (eV mol^{-1}), and the wavelengths of the π_l,π^* absorption bands λ (nm) are listed in Table 1.

The difference between the atomization energies $\Delta\Delta H = \Delta H(\mathbf{A}) - \Delta H(\mathbf{B})$ characterizes the stability of the *p*-quinoid forms relative to *ana*-quinoid forms in the gas phase, and the difference between the solvation coefficients $\Delta M = M(\mathbf{A}) - M(\mathbf{B})$ characterizes their relative stability in solution.

Table 1 shows that, in all the cases, the atomization energies ΔH of the *p*-quinoid forms are higher than the energies of the corresponding *ana*-quinoid tautomers ($\Delta\Delta H > 0$). For form **A** of **I**, $\Delta\Delta H$ is 56 kJ mol^{-1}, in agreement with data of [8]. Thus, in the gas phase, the *p*-quinoid forms are more stable than the *ana*-quinoid forms.

For all the compounds studied, the quantities $\Delta H(\mathbf{A})$ and $\Delta H(\mathbf{B})$ are linearly correlated [Eq. (1)]:

$$\Delta H(\mathbf{B}) = (1.001 \pm 0.01)\Delta H(\mathbf{A}), \text{ eV mol}^{-1} \quad (1)$$

(number of compounds n 29, correlation coefficient r 0.998, standard deviation s 0.02 eV mol^{-1}).

At the same time, the solvation coefficients appeared to be higher for *ana*-quinoid forms ($\Delta M < 0$). This suggests stabilization of *ana*-quinoid forms relative to *p*-quinoid forms in solutions, especially in polar solvents.

The parameters $M(\mathbf{A})$ and $M(\mathbf{B})$ are linearly correlated within each separate series of compounds with the same position of substituent R in the anthraquinone core [Eq. (2)]:

$$M(\mathbf{B}) = KM(\mathbf{A}) + C, \text{ eV mol}^{-1}. \quad (2)$$

The parameters of Eq. (2) are listed in Table 2. The factor K characterizes the sensitivity of the tautomerism of **I** (form **A**) in solutions to introduction of substituents R into various positions of the anthraquinone core. For positions 3, 5, 6, and 7, this sensitivity is independent of the nature of the substituent; for positions 2 and 4, the sensitivity to electron-donor substituents is higher; and for position 8, electron-acceptor substituents exert a stronger effect. The values of K suggest that the prototropic tautomerism in solutions is favored to the greatest extent by electron-donor substituents in position 2, whereas the same substituents in position 8 exert the weakest effect.

As a rule, the absolute values of ΔM are somewhat higher than those of $\Delta\Delta H$. Therefore, the values of ΔH and M do not allow unambiguous conclusion about what tautomer is more stable in solution.

The effects of substituents in the gas phase and in solutions are qualitatively similar. The parameters $\Delta\Delta H$ and ΔM are linearly correlated within each series of x-R-substituted derivatives; e.g., for $x = 2$,

$$\Delta M = (0.849 \pm 0.084)\Delta\Delta H - (1.168 \pm 0.042), \text{ eV mol}^{-1}; \quad (3)$$

$$n\ 6,\ r\ 0.981,\ s\ 0.017.$$

According to [3], introduction of electron-acceptor substituents into positions 2 and 4 of the anthraquinone core, enhancing the acidity of the OH group, facilitates the proton transfer with the formation of the *ana*-quinoid tautomers. Introduction of electron-donor substituents into positions 3, 6, and 8 should lead to the same result, as they enhance the proton-acceptor activity of the carbonyl group in position 9.

The $\Delta\Delta H$, ΔM, and K values obtained by us do not confirm this trend, which is rather unexpected. The quantities $\Delta\Delta H$ and ΔM show that the *ana*-quinoid form is stabilized by introduction of electron-donor amino, hydroxy, and methyl groups into positions 4 and especially 2, of electron-acceptor nitro and carboxy groups into position 8, and of carboxy group into position 2. The *p*-quinoid form is stabilized by the nitro group in position 2. Introduction of the examined substituents into the other positions of the anthraquinone core has no appreciable effect on the relative stability of the tautomers. This is apparently consistent with data of [5], according to which the true nature of the prototropic tautomerism of α-hydroxyanthraquinones consists in redistribution of bonds as a result of deformation of the aromatic core, rather than in the proton transfer in space.

Table 2. Parameters of the linear correlation between $M(\mathbf{A})$ and $M(\mathbf{B})$ for x-R-hydroxyanthraquinones [Eq. (2)][a]

x	n	r	s, eV mol^{-1}	K	C, eV mol^{-1}
2	6	0.992	0.19	0.902 ± 0.057	1.13 ± 0.22
2[b]	4	0.9995	0.017	1.527 ± 0.034	–0.550 ± 0.092
3	6	0.9996	0.039	1.040 ± 0.015	0.564 ± 0.054
4	6	0.997	0.10	0.981 ± 0.037	0.830 ± 0.136
4[b]	4	0.99995	0.007	1.233 ± 0.009	0.138 ± 0.025
5	6	0.9994	0.044	0.964 ± 0.016	0.833 ± 0.062
6	6	0.9995	0.043	0.959 ± 0.015	0.856 ± 0.057
7	6	0.9986	0.072	0.993 ± 0.026	0.745 ± 0.096
8	6	0.982	0.291	1.18 ± 0.11	(0.15 ± 0.42)
8[b]	4	0.9994	0.013	0.736 ± 0.018	1.336 ± 0.052

[a] (x) Position of substituent R, (n) number of compounds, (r) correlation coefficient, (s) standard deviation, and (K, C) parameters of Eq. (2). [b] For electron-donor substituents.

The PPP calculations of the absorption spectra of some 1-hydroxy-x-R-9,10-anthraquinones have been reported [12], and our results are well consistent with these data. All the quantum-chemical calculations of the absorption spectra of these compounds indicate that there is a single allowed π_l,π^* transition. Hence, the presence in the experimental spectrum of two π_l,π^* bands could suggest the coexistence of both tautomers in solution. Therefore, it is important to correctly interpret the fine structrue of the long-wave absorption in the spectra of α-hydroxyanthraquinones.

The experimental values of $\lambda_{\max}$ of 2-R- and 4-R-substituted derivatives of **I** linearly correlate [13] with the spectroscopic σ^A constants of substituents R, suggested for anthraquinones. They allow calculation of $\lambda_{\max}$ of compounds of these series containing any substituents R for which σ^A is known. Such a correlation is also observed for the calculated absorption maxima of 2-, 3-, 4-, and 8-R-substituted anthraquinones **I** [Eq. (4), Table 3].

Table 3. Parameters of linear correlations of λ_{max} of 1-hydroxy-*x*-R-9,10-anthraquinones and 9-hydroxy-*x*-R-1,10-anthraquinones with σ^A constants of substituents R [Eq. (4)] and with each other [Eq. (5)]

x	*n*	*r*	*s*, nm	*K*	*C*, nm
1-Hydroxy-*x*-R-9,10-anthraquinones [Eq. (4)]					
2	5	0.988	3.8	–58.1 ± 5.2	403 ± 2
3	5	0.993	2.2	–45.9 ± 3.1	404 ± 1
4	5	0.958	15.5	–101 ± 17	419 ± 9
8	5	0.944	10.2	–57.6 ± 11.6	401 ± 6
9-Hydroxy-*x*-R-1,10-anthraquinones [Eq. (4)]					
2	4	0.995	4.2	–82.0 ± 6.0	473.9 ± 2.8
3	5	0.915	7.1	–38.4 ± 9.7	472.1 ± 4.1
4	4	0.998	2.0	–59.7 ± 2.4	471.8 ± 1.4
5	4	0.93	3.7	–16.3 ± 4.5	470.2 ± 2.6
6	4	0.993	2.0	–34.8 ± 2.9	472.9 ± 1.4
8	4	0.952	7.2	–38.6 ± 8.8	473.9 ± 8.8
Eq. (5)					
2	6	0.978	6.6	1.39 ± 0.15	–88.4 ± 61.8
3	6	0.955	4.7	0.86 ± 0.13	124.4 ± 55.4
4	6	0.967	7.1	0.54 ± 0.07	246.3 ± 32.4
5	4	0.990	1.5	0.31 ± 0.03	348.3 ± 13.2
8	6	0.978	3.9	0.65 ± 0.07	212.5 ± 29.1

$$\lambda_{max} = K\sigma^A + C,\ \text{nm}. \qquad (4)$$

The angular coefficient *K* in Eq. (4) characterizes the sensitivity of long-wave absorption bands of hydroxyanthraquinones to the effect of substituents R. The parameters *K* (Table 3) show that form **A** is the most sensitive to introduction of substituents into position 4; for positions 2 and 8, the sensitivity is lower by a factor of 1.7, and for position 3, by a factor of 2.2. Substituents in positions 5, 6, and 7 exert a still weaker effect on the position of the long-wave absorption band of form **A**, and the correlation for these positions is poor.

The effect of substituents on the absorption spectra of substituted 1,10-anthraquinones was not studied previously. Figure 1 illustrates a linear correlation between λ_{max} and the spectroscopic σ^A constants of substituents R by the example of 4-R-substituted derivatives.

The dependences found are also quantitatively described by Eqs. (4); their parameters are listed in Table 3.

The coefficients *K* (Table 3) show that form **A** is more sensitive to substituents than form **B**. The only exception is that substituents in position 2 affect tautomer **B** more strongly than tautomer **A**. Form **A** is the most sensitive to introduction of substituents into position 4.

The positions of substituents can be ranked in the following order with respect to the effect on the absorption spectra of tautomer **IB**: 2 > 4 > 3, 6, 8 > 5 > 7. The effect of substituents in position 7 is so weak that Eq. (4) does not describe it.

The quantities λ_{max}(**A**) and λ_{max}(**B**) calculated, respectively, for *p*- and *ana*-quinoid forms linearly correlate with each other for each series of *x*-R-substituted derivatives except *x* = 6 and 7. In the two latter series the shifts of the π_l,π^* bands are very small. Figure 2 illustrates such a relationship for 2-R-hydroxyanthraquinones.

This relationship is quantitatively described by

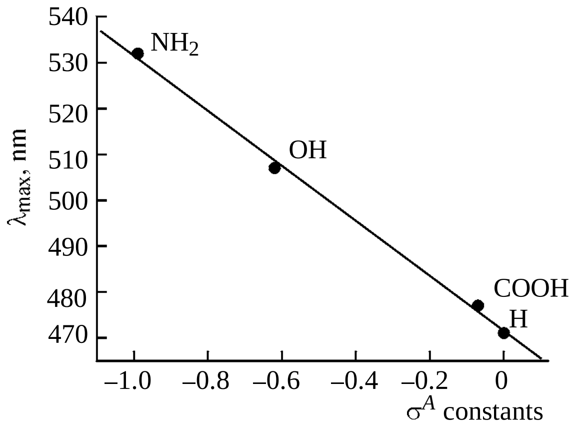


Fig. 1. Correlation of λ_{max} of 9-hydroxy-4-R-1,10-anthraquinones (PPP calculations) with spectroscopic σ^A constants of substituents R (*r* 0.9987).

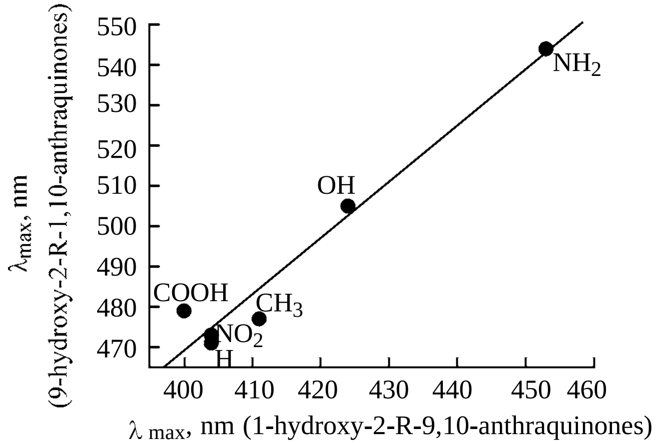


Fig. 2. Mutual correlation of λ_{max} values calculated for *p*- and *ana*-quinoid forms of 2-R-hydroxyanthraquinones (*r* 0.98).

Eq. (5); its correlation parameters are given in Table 3.

$$\lambda_{\max}(\mathbf{B}) = K\lambda_{\max}(\mathbf{A}) + C, \text{ nm.} \quad (5)$$

The shift of the π_l,π^* transition band due to tautomerism is sensitive to substituents in various positions to a different extent; the sensitivity characterized by the coefficient K decreases in the order $2 > 3 > 8 > 4 > 5$.

The correlation of $\lambda_{\max}$ with the σ^A constants of substituents allowed us to correct the values given by our quantum-chemical calculations for some nitro, carboxy, and methyl derivatives (marked with an asterisk in Table 1). The corrected values fit the correlations in Table 3.

According to [12], there is a linear correlation between the experimental (in dichloromethane) and calculated (PPP) $\lambda_{\max}$ values, common for all the anthraquinones. Our data (for ethanolic solutions) show that this correlation is actually more complex: The straight line for compounds 4-R-**IA** lies apart from that for other compounds *x*-R-**IA** (Fig. 3).

The "splitting" of the correlation is apparent when considering the points for 4-carboxy, 4-nitro, 4-methyl, 2-amino, and 3-amino derivatives for which no data are given in [12]. Nevertheless, the correlations opens additional prospects for prediction of unknown $\lambda_{\max}$ values for compounds *x*-R-**IA**.

The majority of the experimental absorption spectra of tautomer **IA** measured in various solvents [14] contain a single π_l,π^* band at ~400 nm; its position is only weakly dependent on the solvent. In nonpolar and weakly polar solvents, this band has a fine structure. Analysis of the second derivative of the absorption spectrum of **IA** in CCl_4 revealed five components of the fine structure of the π_l,π^* band (370, 388, 406.5, 427, and 450 mn) and showed that these bands are vibronic with the difference of ~1200 cm^{-1}, corresponding to COH stretching vibrations [6]. In polar solvents, especially alcohols, the vibronic structure of the π_l,π^* bands is untypical of monosubstituted anthraquinones [15]. However, a second long-wave absorption band at ~430 nm is detected in the spectra of some substituted derivatives of **IA** in alcohols [14]. This band is located in the same region as the longest-wave component of the n,π^* band of unsubstituted 9,10-anthraquinone (424 nm [16]). In the absorption spectra of α-RO-anthraquinones in which the hydroxyl hydrogen is substituted and hence the prototropic isomerism is impossible, the fine structure of the π_l,π^* band is absent [14, 17]. The absorption spectra of substituted anthraquinones **I** in form **A** usually differ insignificantly from the spectrum of unsubstituted tautomer **A** [17].

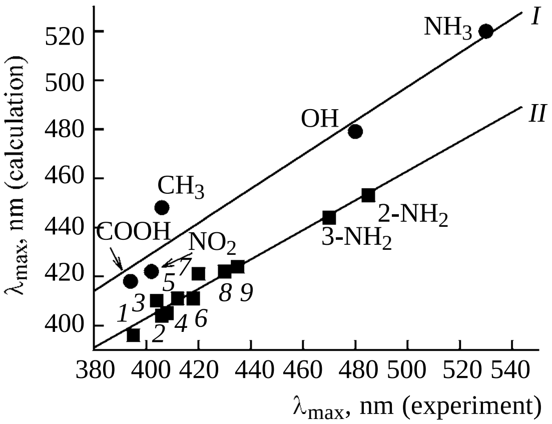


Fig. 3. Correlation between the experimental and calculated $\lambda_{\max}$ values for 1-hydroxy-*x*-R-anthraquinones. *x*-R: (*1*) 7-HO, (*2*) H, (*3*) 3-CH_3, (*4*) 6-HO, (*5*) 2-CH_3, (*6*) 5-HO, (*7*) 3-HO, (*8*) 8-HO, and (*9*) 2-HO. (*I*) 1-Hydroxy-4-R-9,10-anthraquinone (*r* 0.975) and (*II*) other 1-hydroxy-*x*-R-9,10-anthraquinones (*r* 0.983).

The calculated position of the π_l,π^* band for tautomer **IA** (404 nm) coincides with the value observed experimentally in hexane [14]. At the same time, the wavelength calculated for form **IB** (471 nm) significantly differs from the experimental value for the second band (426 nm in hexane [14]). This fact shows that the second band cannot be assigned to the π_l,π^* transition in *ana*-quinoid tautomer **IB**.

The appearance of the second, bathochromically shifted band in the experimental electronic absorption spectra may be associated with the vibronic structure of the π_l,π^* band or with the manifestation of n–π^* transitions which cannot be calculated by the PPP method. To elucidate the origin of this band, we calculated the absorption spectra of the *p*- and *ana*-quinoid tautomers of **I** and 2-amino derivative of **I** by the INDO/S method [18] (Table 4).

Table 4 shows that the electronic spectrum of each compound contains one strong π_l,π^* band and two weak n,π^* bands corresponding to transition of the lone electron pairs of the oxygen atoms of two nonequivalent carbonyl groups to the π system of the molecule. Comparison of these bands with the n,π^* bands in the spectrum of unsubstituted 9,10-anthraquinone [16] allows the short-wave $n,\pi^*(1)$ band to be assigned to interaction of the 10-carbonyl group with the unsubstituted benzene ring of the anthraquinone system, and the long-wave $n,\pi^*(2)$ band, to interaction of the 9-carbonyl group with the substituted benzene ring. Introduction of the amino group

Table 4. Wavelengths λ (nm) and oscillator strengths *f* for 1-hydroxy- and 2-amino-1-hydroxyanthraquinones in the *p*-quinoid (**A**) and *o*-quinoid (**B**) forms, according to INDO/S calculations

Compound	A		B	
	λ	*f*	λ	*f*
1-Hydroxyanthraquinone	463	$<10^{-4}$	496	0.0002
	430	$<10^{-4}$	432	$<10^{-4}$
	347	0.43	418	0.67
	296	0.06	317	0.02
2-Amino-1-hydroxyanthraquinone	457	$<10^{-4}$	483	0.0001
	420	$<10^{-4}$	444	0.63
	371	0.33	425	$<10^{-4}$
	320	0.002	359	0.07

causes a bathochromic shift of the strong band from 347 to 371 nm and a weak hypsochromic shift of weak *n*,π*-transition bands: from 430 to 420 and from 463 to 457 nm. Similar to the PPP calculations, in going from the *p*-quinoid to *ana*-quinoid tautomer, the absorption bands shift bathochromically. For example, the strong absorption band in the spectrum of **IA** shifts from 347 to 418 nm, i.e., by 71 nm (by 67 nm according to PPP calculations), and in the spectrum of 2-amino-1-hydroxyanthraquinone, from 371 to 444 nm, i.e., by 73 nm (by 82 nm according to PPP calculations). The shifts of the *n*,π* bands are considerably smaller: 2 and 5 nm for the *n*,π*(1) band, and 33 and 26 nm for the *n*,π*(2) band in **IA** and 2-aminoanthraquinone, respectively.

Thus, the second band in the experimental spectra of tautomers **A** of **I** and its derivatives should be assigned to the *n*,π transition.

It should be noted that the positions of the absorption bands calculated by the INDO/S method are worse consistent with the experiment than the results of the PPP calculations. This is due to specific features of the calculation procedure: The molecular geometry is not optimized, and formation of intramolecular hydrogen bonds is not taken into account. At the same time, the relative changes in the spectra upon introduction of substituents and in going from one tautomer to another are similar in both calculation procedures.

Thus, in the electronic absorption spectra of 1-hydroxy-*x*-R-anthraquinones we found no bands assignable to the *ana*-quinoid forms.

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