

Tautomerism in Athraquinones: II. α -Hydroxy-substituted Anthraquinones

V.Ya. Fain, B.E. Zaitsev, and M.A. Ryabov

Russian University of Peoples' Friendship, Moscow 127349 Russia
e-mail: vfain@mail.ru

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Abstract—The fine structure of experimental π, π^* -absorption bands of the α hydroxyanthraquinones originates from the prototropic anthraquinoid tautomerism. The tautomeric transformations occur both in the ground and excited states of the molecules; therewith the excited states are more sensitive to the tautomerization than the ground ones. The wavelength and intensity of the π, π^* -bands, the values of all quantum-chemical characteristics studied for the tautomers of α hydroxyanthraquinones are linearly related to the number of hydroxy groups. The effect of the isomerism of di- and trihydroxyanthraquinones on this relationship was considered.

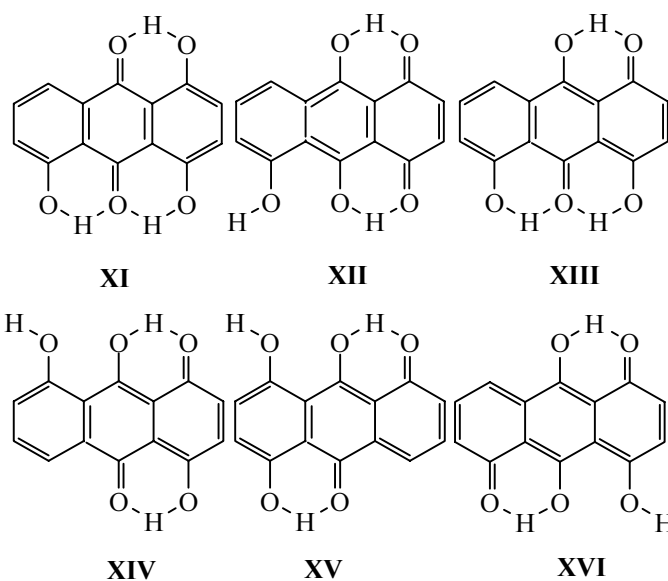
The prototropic tautomerism of α -hydroxyanthraquinones attract a close attention of researchers [2] mainly because of a wide application of these compounds as biologically active substances and drugs, natural dyes and intermediates for preparation of synthetic colorants, chemicals for conserving and processing information, analytic reagents, indicators etc. [3].

Numerous data indicate that the states with tautomer anthraquinoid structures take part in formation of the electronic spectra of 9,10 anthraquinones [2]. The comparison of experimental data on positions of the π, π^* -absorption bands with those calculated by quantum-chemical procedures for various tautomers and application of the correlation analysis method [4] made it possible to understand the complex character of the spectra belonging to 1,4-dihydroxy- and 1,2,4-trihydroxy-9,10-anthraquinones and their anions [5, 6], of 1,2-dihydroxy-9,10-anthraquinone anions [7], of metal complexes with dihydroxyanthraquinones [8], and to remove the discrepancies in the reports of different authors on the dihydroxyanthraquinones ionization [6]. These data serve a base for classification of the π, π^* -absorption bands of the anthraquinone derivatives [9, 10] for they permit an understanding of the fine structure origin in the π, π^* -absorption bands and of the number of the corresponding components. They show that the tautomer anthraquinoid structures play a more important part in the anthraquinone chemistry than it has been generally recognized up till now.

The goal of the present study was investigation of the effect of hydroxy groups accumulation on the tauto-

merism of α -hydroxyanthraquinones I–XX (Table 1). Some data on the tautomerism of α mono- and dihydroxy-9,10-anthraquinones were reported in [5, 6, 11]. The tautomerism of 1,4,5-tri- and 1,4,5,8-tetrahydroxy-9,10-anthraquinones was still unstudied; six prototropic tautomers were possible for the former compound: one each of 9,10-**XI**, 1,4- **XII**, and 1,5-anthraquinone **XVI**, and three 1,10-anthraquinones **XIII**–**XV**; for the second compound 4 tautomers were presumable **XVII**–**XX** (Table 1).

We carried out quantum-chemical calculations for all tautomers of α -hydroxyanthraquinones within a framework of the π electron PPP method applying Dewar version [12] with the use of approximation of variable β [13]. In Table 1 the wavelengths of the maxima (λ_{\max})



* For communication I see [1]

Table 1. Results of quantum-chemical calculations for α -hydroxyanthraquinones I–XX

Compd. no.	Compound name	λ , nm	f	ΔH , eV	M	E_{HOMO} , eV	E_{LUMO} , eV	E_{σ} , eV	E_{π} , eV
I	1-Hydroxy-9,10-anthraquinone	404	0.263	133.820	2.400	-9.129	-3.081	71.223	27.095
II	9-Hydroxy-1,10-anthraquinone	471	0.555	133.239	3.098	-8.671	-3.461	71.224	26.513
III	1,5-Dihydroxy-9,10-anthraquinone	411	0.446	139.393	3.017	-8.932	-2.952	75.262	28.628
IV	5,9-Dihydroxy-1,10-anthraquinone	476	0.632	138.847	3.757	-8.520	-3.355	75.264	28.081
V	9,10-Dihydroxy-1,5-anthraquinone	533	0.872	138.357	4.663	-8.403	-3.797	75.291	27.563
VI	1,8-Dihydroxy-9,10-anthraquinone	422	0.413	139.359	3.000	-8.903	-2.956	75.261	28.595
VII	8,9-Dihydroxy-1,10-anthraquinone	491	0.25	138.598	3.533	-8.76	-3.341	75.259	27.836
VIII	1,4-Dihydroxy-9,10-anthraquinone	479	0.382	139.308	2.958	-8.280	-2.920	75.267	28.538
IX	9,10-Dihydroxy-1,4-anthraquinone	502	0.460	138.924	3.296	-8.149	-3.009	75.216	28.205
X	4,9-Dihydroxy-1,10-anthraquinone	517	0.621	138.901	3.786	-8.067	-3.146	75.256	28.142
XI	1,4,5-Trihydroxy-9,10-anthraquinone	483	0.462	144.840	3.536	-8.149	-2.800	79.305	30.031
XII	5,9,10-Trihydroxy-1,4-anthraquinone	513	0.513	144.279	3.747	-7.951	-2.929	79.248	29.526
XIII	4,5,9-Trihydroxy-1,10-anthraquinone	513	0.686	144.462	4.403	-7.925	-3.049	79.295	29.663
XIV	4,8,9-Trihydroxy-1,10-anthraquinone	523	0.698	144.209	4.166	-7.883	-3.055	79.289	29.416
XV	5,8,9-Trihydroxy-1,10-anthraquinone	523	0.721	144.113	4.085	-8.146	-3.217	79.303	29.305
XVI	4,9,10-Trihydroxy-1,5-anthraquinone	568	0.908	143.753	5.029	-7.896	-3.519	79.318	28.930
XVII	1,4,5,8-Tetrahydroxy-9,10-anthraquinone	514	0.615	150.293	4.008	-7.819	-2.663	83.348	31.439
XVIII	5,8,9,10-Tetrahydroxy-1,4-anthraquinone	543	0.589	149.531	4.035	-7.612	-2.849	83.284	30.741
XIX	4,5,8,9-Tetrahydroxy-1,10-anthraquinone	549	0.783	149.709	4.659	-7.612	-2.931	83.334	30.869
XX	4,8,9,10-Tetrahydroxy-1,5-anthraquinone	604	0.999	149.074	5.305	-7.398	-3.266	83.349	30.218

Table 2. Wavelengths of π, π^* -absorption bands of α -hydroxyanthraquinones

Hydroxy group position	Solvent	Wavelengths of component of π, π^* -absorption and their assignment to the tautomers, λ_{max} , nm											Reference
		1	2	3	4	5	6	7	8	9	10	11	
					9,10	9,10	9,10	1,4		1,10	1,10	1,5	
1	Hexane					406					423		[9]
1	Ethanol					406					423		[14]
1,5	Heptane					418.5					434		[9]
1,5	Ethanol					418					437		[9]
1,8	Hexane					411	421		431.5	445.5	458.5		[9]
1,8	Ethanol					430					455		[15]
1,4	Cyclohexane				463	476	487			508	521		[16]
1,4	Ethanol					480		498 s		512			[17]
1,4,5	Cyclohexane		466	472	483	495		516		529			[18]
1,4,5	Cyclohexane	462 s	468		483	496	505 s	517		530		562	[19]
1,4,5	Methanol	457 s				490		510 s		525 s			[9]
1,4,5,8	Heptane			477.5	487.5	509.5	521	533	535 s	546	559.5	592.5	[20]
1,4,5,8	Cyclohexane				490	513	524			548	563		[21]
1,4,5,8	Ethanol				486.5	508	519			544	558	604	[9]

and oscillator force (f) of the π, π^* - absorption band, atomization energy (ΔH), solvation factor (M), the energy of the highest occupied (E_{HOMO}) and the lowest unoccupied (E_{LUMO}) molecular orbitals, and energy of σ - and π -bonds (E_{σ} and E_{π}) are compiled.

The assignment of the experimental bands to the tautomer forms is performed by comparison with those calculated by the quantum-chemical method. The fidelity criterion of the assignment is not the closest coincidence of these values but their linear correlation [4]. At the

Table 3. Correlation parameters of equations (3)

Hydroxy groups positions	Solvent	<i>N</i>	<i>r</i>	σ , nm	<i>k</i>	λ_0 , nm
1,4	Cyclohexane	5	0.996	2.3	0.817 ± 0.040	62 ± 21
1,8	Hexane	5	0.996	1.8	0.955 ± 0.046	-76 ± 25
1,4,5	Cyclohexane	6	0.998	2.3	0.782 ± 0.025	100 ± 13
1,4,5,8	Ethanol	6	0.996	4.4	1.163 ± 0.054	-82 ± 29

same time the number of absorption bands in the visible region of the experimental spectra of some compounds exceeded the number of probable tautomers, for instance, in the case of 1,4,5,8-tetrahydroxy-9,10-anthraquinone 6 bands were observed in ethanol and 9 bands in heptane (Table 2).

As seen from Fig. 1, the points corresponding to tautomeric anthraquinones are located on two straight lines: From the common line 1 separated line 2 for 1,10-anthraquinones. These straight lines are described by equations (1) and (2) respectively (Table 3).

$$\lambda_{\max}(\text{ethanol}) = (0.954 \pm 0.025)\lambda_{\text{calc}} + (24 \pm 11), \text{ nm} \quad (1)$$

Number of points *N* 9, correlation factor *r* 0.998, standard deviation *s* 4.5.

$$\lambda_{\max}(\text{ethanol}) = (1.779 \pm 0.093)\lambda_{\text{calc}} - (413 \pm 47), \text{ nm} \quad (2)$$

N 6, *r* 0.995, *s* 6.3.

In hydrocarbon solvents the analogous relations are valid with *r* 0.989 and 0.996 respectively.

Angular coefficient of equation (2) is 1.779 : 0.954 \approx 1.9 times greater than that of equation (1). The value indicates that the PPP method simulated the position of the π_j, π^* -bands of the 1,10-tautomers nearly twice less accurately than for the other tautomers.

The accuracy of the assignments presented in Table 2 is additionally proved by several mutually independent correlations. For instance, a proportional response of the experimental λ_{\max} values of various α -hydroxyanthraquinones to the tautomerism was observed fitting, e.g., to equation (3) (Table 3).

$$\lambda_{\max}(\text{exp}) = k \lambda_{\max}(1,4,5,8) + \lambda_0, \text{ nm} \quad (3)$$

Here $\lambda_{\max}(\text{exp})$ correspond to the spectra of 1,4-, 1,8-dihydroxy-, 1,4,5-trihydroxy-, and 1,4,5,8-tetra-

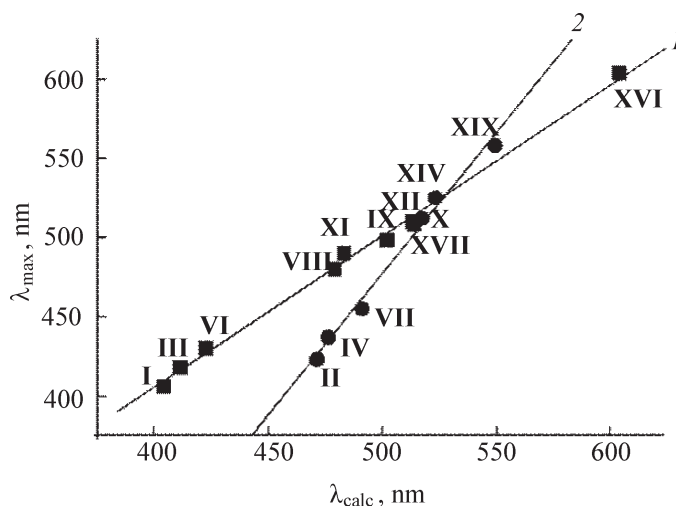


Fig. 1. Correlation of λ_{\max} on the spectra of α -hydroxy-anthraquinones in ethanol with λ_{calc} calculated by PPP method: (1) 9,10-, 1,4-, and 1,5-anthraquinones; (2) 1,10-anthraquinones. Here and on the other figures the compounds are numerated as in Table 1.

hydroxyanthraquinones measured in different solvents, $\lambda_{\max}(1,4,5,8)$ are wavelengths of π_j, π^* -bands of tautomers 1,4,5,8-tetrahydroxyanthraquinone in heptane, *k* is the angular coefficient, $\lambda_0 = \lambda_{\max}(\text{exp})$ at $\lambda_{\max}(1,4,5,8) = 0$.

Linearly related to each other are $\lambda_{\max}(\text{exp})$ belonging to bands 5 and 7 (Table 2) (*N* 4, *r* 1.00000), 9 and 10 (*N* 5, *r* 0.99990) with the assumption that the maximum at 544 nm in the spectrum of 1,4,5,8-tetrahydroxyanthraquinone taken in ethanol belongs to the band 9 and not to the band 7. Therewith the validity of this band assignment to 1,10- and not to 1,4-tautomer is confirmed. Correlations with the calculated values permitted assignment of band 6 to 9,10- but not to 1,4-tautomer. The existence of all these correlations and also poor correlations with the wavelengths of π_j, π^* -bands that we calculated using the INDO/S [22] method confirm the π_j, π^* -character of the bands under consideration [2].

The above data support the assignment of bands 4, 5, and 6 to 9,10- and bands 9 and 10 to 1,10-anthraquinones. Due to insufficient data the bands 1–3 may only tentatively be regarded as the components of the vibronic structure of the π_j, π^* -bands of 9,10-anthraquinones, and band 8 as those of 1,10-anthraquinones.

Hence the presence in the visible region of the experimental spectra of α -hydroxyanthraquinones of more bands than predicted by the quantum-chemical calculations is due to the appearance of vibronic structure on the π_j, π^* -bands of 9,10- and 1,10-tautomers, especially developed in the spectra measured in nonpolar hydro-

Table 4. Correlation parameters of equations (4)

Characteristics	Tautomer	<i>N</i>	Point not fitting to the line ^a	<i>r</i>	<i>s</i>	<i>k</i>	<i>Y</i> ₀
λ , nm	9,10-	4	III, VI, VIII	0.997	4.4	37.57 ± 1.95	366 ± 5
	1,10- (<i>I</i>)	3	X	0.9996	0.8	21.00 ± 0.58	449.7 ± 1.2
	1,10- (<i>2</i>)	4		1.00000	0.0	26.00 ± 0.00	445.0 ± 0.0
	1,10- (<i>3</i>)	3	X	0.99997	0.4	36.50 ± 0.58	403.2 ± 0.9
	1,4-	3		0.966	7.7	20.5 ± 5.5	458 ± 17
<i>f</i>	1,5-	3		0.99997	0.4	35.50 ± 0.29	461.8 ± 0.9
	9,10-	4	III, VI	0.993	0.021	0.1147 ± 0.0093	0.143 ± 0.025
	1,10- (<i>I</i>)	4		0.998	0.008	0.0760 ± 0.0027	0.4835 ± 0.0037
	1,10- (<i>2</i>)	4		0.996	0.006	0.0669 ± 0.0037	0.4897 ± 0.0085
	1,4-	3		0.995	0.009	0.0645 ± 0.0066	0.327 ± 0.021
ΔH , eV	1,5-	3		0.9988	0.007	0.0995 ± 0.0049	0.604 ± 0.015
	9,10-	4	VI, VIII	0.998	0.57	5.59 ± 0.25	127.85 ± 0.70
	1,10-	8		0.9997	0.140	5.489 ± 0.057	127.79 ± 0.15
	1,4-	3		0.99998	0.044	5.306 ± 0.031	128.32 ± 0.10
<i>M</i> , eV	1,5-	3		1.00000	0.031	5.358 ± 0.022	127.652 ± 0.067
	9,10-	6		0.998	0.040	0.533 ± 0.017	1.909 ± 0.043
	1,10- (<i>I</i>)	5		0.997	0.052	0.528 ± 0.023	2.535 ± 0.064
	1,10- (<i>2</i>)	3		0.9996	0.014	0.636 ± 0.017	2.495 ± 0.041
E_{π} , eV	1,4-	3		0.992	0.068	0.371 ± 0.048	2.58 ± 0.070
	1,5-	3		0.997	0.037	0.321 ± 0.026	4.04 ± 0.08
	9,10-	6		0.9997	0.040	1.445 ± 0.018	25.683 ± 0.044
	1,10- (<i>I</i>)	5		0.9992	0.076	1.458 ± 0.033	24.996 ± 0.093
	1,10- (<i>2</i>)	4		0.99976	0.035	1.575 ± 0.025	24.950 ± 0.052
E_{σ} , eV	1,4-	3		0.9997	0.043	1.268 ± 0.031	25.687 ± 0.095
	1,5-	3		0.99985	0.032	1.327 ± 0.023	24.921 ± 0.071
	9,10-	6		1.00000	0.0024	4.0417 ± 0.0010	67.180 ± 0.003
	1,10-	8		1.00000	0.0047	4.0365 ± 0.0019	67.187 ± 0.005
	1,4-	3		1.00000	0.0016	4.034 ± 0.001	67.147 ± 0.004
E_{HOMO} , eV	1,5-	3		1.00000	0.0016	4.029 ± 0.001	67.232 ± 0.004
	9,10-	4	III, VI, VIII	0.996	0.066	0.449 ± 0.029	-9.572 ± 0.080
	1,10- (<i>I</i>)	3		0.9991	0.032	0.356 ± 0.015	-9.02 ± 0.04
	1,10- (<i>2</i>)	3		0.994	0.036	0.227 ± 0.025	-8.54 ± 0.08
	1,10- (<i>3</i>)	3	IV	0.9992	0.033	0.574 ± 0.023	-9.895 ± 0.072
E_{LUMO} , eV	1,4-	3		0.985	0.058	0.265 ± 0.041	-8.720 ± 0.127
	1,5-	3		1.00000	0.0037	0.502 ± 0.003	-9.406 ± 0.008
	9,10-	5	VIII	0.9991	0.008	0.1415 ± 0.0035	-3.230 ± 0.009
	1,10- (<i>I</i>)	4		0.997	0.009	0.1220 ± 0.0067	-3.587 ± 0.014
	1,10- (<i>2</i>)	4		0.996	0.010	0.1075 ± 0.0071	-3.368 ± 0.022
	1,4-	3		1.00000	0.000	0.080 ± 0.000	-3.169 ± 0.000
	1,5-	3		0.9996	0.010	0.265 ± 0.007	-4.324 ± 0.022

^aNumbers of compounds are given not consistent with this relationship.

carbons. These facts are consistent with findings previously obtained [5] for 1,4-dihydroxyanthraquinone.

It was remarked in [11] that the position of the short-wave π, π^* -band at 403.5 nm of compound **I** was in

agreement with that calculated by PPP method (404 nm) whereas the λ_{max} of the long-wave band at 423 nm was considerably different from the value calculated for compound **II** (471 nm). On these grounds it was concluded

that in the spectrum a band corresponding to the absorption of 1,10-anthraquinoid tautomer was lacking, and the band at 423 nm was regarded as n,π^* -band. However the point II corresponding to the band at 423 nm is located on the straight line 2 (Fig. 1) proving that it belongs to the π,π^* -absorption of the 1,10-tautomer. This is a clear example of rectifying the error in band assignment with the help of correlation analysis.

Experimental values of λ_{\max} and especially those of the molar extinction coefficients ϵ_{\max} significantly depend on the purity of compounds. Therefore the investigation of the tautomerism effect on the wavelength and intensity of the π,π^* -band is more convenient to perform on the calculated values of λ_{calc} and f free of the solvent influence and of the experimental errors. We reported in [1] on the specific features of the proportional response of these values to the tautomerism of 1,2,4-trihydroxy-9,10-anthraquinone. A similar relation is observed also for the other hydroxy-anthraquinones. For instance, with the 1,4,5-trihydroxyanthraquinone it was revealed in the form of two intersecting lines (Fig. 2).

The values of quantum-chemical characteristics Y of α -hydroxy-anthraquinones are linearly related to the number of the hydroxy groups n [equation (4), Table 4].

$$Y = kn + Y_0 \quad (4)$$

This dependence appears separately for each series of tautomeric anthraquinones. Due to the existence of isomeric di- and trihydroxyanthraquinones the relationship is rather peculiar. The values M , E_σ , and E_π of dihydroxy-9,10-anthraquinones differ insignificantly, and equation (4) is valid for all six 9,10-anthraquinones. To the lines (4) fit E_{LUMO} values of two dihydroxyanthraquinones, f and ΔH of one, and the λ_{calc} and E_{HOMO} of all the three dihydroxy-9,10-anthraquinones deviate from these lines, but their arithmetic means fit to the lines (Table 4).

In the case of 1,10-anthraquinones only parameters ΔH and E_σ of all 8 compounds are in agreement with a unique equation (4). For λ_{calc} and E_{HOMO} this relation appears in the form of three straight lines, and a point corresponding to one of the dihydroxyanthraquinone is outside of all the three (Fig. 3, Table 4). The remaining characteristics are described by two straight lines (e.g., Fig. 4, Table 4). For 1,4- and 1,5-anthraquinones all possible compounds are in agreement with this relationship.

The values of factors k of equations (4) (Table 4) show that as a rule the characteristics of 9,10-anthraquinones are the most sensitive to the accumulation of

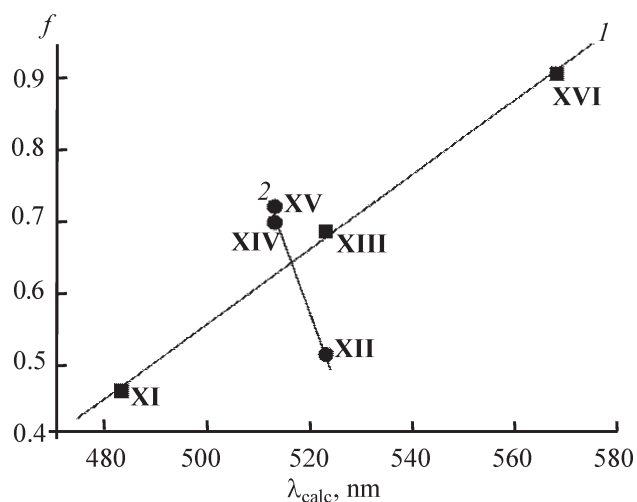


Fig. 2. Proportional response of λ_{calc} and f of 1,4,5-trihydroxy-9,10-anthraquinone to tautomerism.

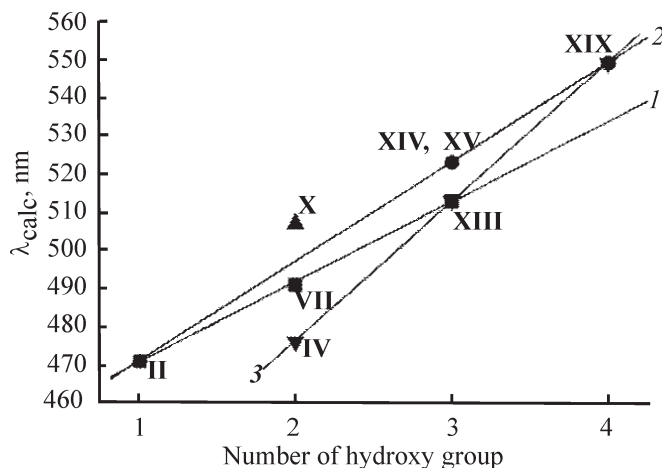


Fig. 3. Wavelengths of π,π^* -bands of hydroxy-1,10-anthraquinones as a function of the hydroxy groups number. 1, 2: 9-hydroxyanthraquinones; 3: 5-hydroxyanthraquinones.

the hydroxy groups, and those of 1,4 anthraquinones are the least sensitive.

The atomization energy ΔH characterizes the compound stability in the vapor state, and solvation factors M correspond to the stability in solution. It follows from the ΔH values (Table 1) that the anthraquinoid tautomer in keeping with their stability in pairs form a series: 9,10 > 1,10 > 1,4 > 1,5. The M values show that the stability in solution is described by a nearly opposite sequence: 1,5 > 1,10 > 1,4 > 9,10. The k values of equations (4) demonstrate an essentially different influence of the tautomerism on the sensitivity of these characteristics to the hydroxy groups accumulation: Whereas for ΔH this effect is insignificant (the alteration does not exceed 5%), they are twice larger for M . These

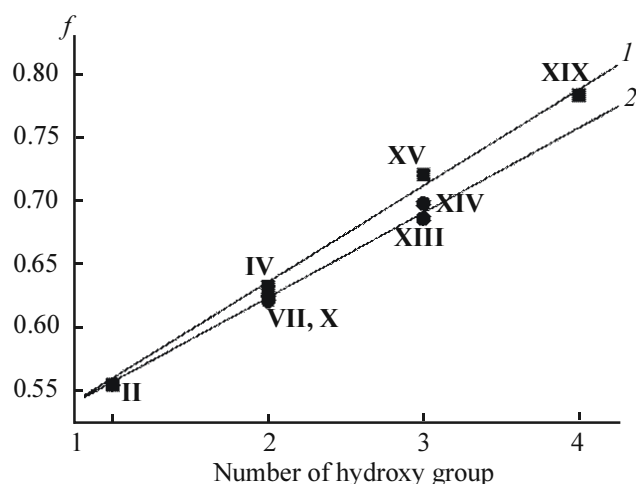


Fig. 4. Dependence of f for 1,10-anthraquinones on the hydroxy groups number.

data suggest that the solvation of α -hydroxyanthraquinone molecules significantly facilitates the tautomeric transformations.

The tautomerism affects the energy of π -bonds to a notably greater extent than the energy of σ -bonds (up to 4% against 0.9%) (Table 1). These changes are qualitatively dissimilar: the E_π and E_σ values for the same tautomers do not correlate with each other. For every tautomeric anthraquinone the E_π and E_σ values grow linearly with the growing number of the hydroxy groups, and the E_σ values are thrice as sensitive to the hydroxy

Table 5. Correlation parameters of equations (5)

Hydroxy groups positions	N	r	s , nm	k	λ_0 , nm
1,4	3	0.9990	1.0	0.735 ± 0.033	124 ± 17
1,5	3	0.997	6.2	1.43 ± 0.10	-278 ± 54
1,4,5,8	4	0.998	2.8	0.941 ± 0.044	$-(0.7 \pm 24.1)$

Table 6. Correlation parameters of equations (6)

Y	r	s	k	Y_0
f	0.99998	0.002	1.0378 ± 0.0058	0.057 ± 0.004
ΔH	0.9997	0.011	0.890 ± 0.021	21.2 ± 3.1
M	0.9997	0.021	0.990 ± 0.023	0.32 ± 0.10
E_{HOMO}	0.994	0.018	0.970 ± 0.103	$-(0.087 \pm 0.829)$
E_{LUMO}	0.99998	0.002	0.7085 ± 0.0049	-0.773 ± 0.016
E_σ	0.99985	0.0008	0.923 ± 0.016	10.11 ± 1.26
E_π	0.99995	0.005	0.885 ± 0.009	4.62 ± 0.26

groups accumulation as the E_π values (Table 4). These findings show that the tautomerism occurs due to changes in the energy of both π - and σ bonds, but the contribution of the former prevails.

A proportional response of λ_{calc} values to tautomerization is characteristic of various α -hydroxyanthraquinone [equation (5), Table 5].

$$\lambda_{\text{calc}} = k\lambda(1,4,5) + \lambda_0, \text{ nm} \quad (5)$$

Here λ_{calc} corresponds to 1,4- and 1,5-di- and 1,4,5,8-tetrahydroxyanthraquinones, and $\lambda(1,4,5) = \lambda_{\text{calc}}$ of 1,4,5-trihydroxyanthraquinone.

The k factors of equation (5) evidence that with the accumulation of hydroxy groups (1,4 – 1,4,5 – 1,4,5,8) the sensitivity of λ_{calc} to the tautomerism decreases. A similar relation was observed in the other characteristics, for instance, for the 1,4,5-trihydroxy- and 1,4,5,8-tetra-hydroxyanthraquinones [equation (6), Table 6]. This relation is usually valid only for the anthraquinones containing a carbonyl group in position 1, whereas the points belonging to the 9,10-tautomers as a rule deviate from the straight lines. The exception forms only the line for E_{HOMO} where the deviating point belongs to 1,5-anthraquinones.

$$Y(1,4,5,8) = kY(1,4,5) + Y_0 \quad (6)$$

The k factors of equation (6) evidence that the introduction of the fourth hydroxy group into the molecule ambiguously affects the sensitivity of the quantum-chemical characteristics toward the tautomerism: the most of them decrease to various extent, but f slightly increases. Thus the change in a single parameter is not sufficient for any conclusions on the effect of structural alterations on the sensitivity of a given compound to the tautomeric transformations..

Table 7. Correlation parameters of equations (7)

Tautomer	N	r	s	k	Y_0
9,10- (1)	3	0.997	0.025	0.312 ± 0.026	-0.241 ± 0.217
9,10- (2)	3	0.990	0.004	0.0530 ± 0.0075	-2.481 ± 0.066
1,10-	7	0.9945	0.021	0.499 ± 0.024	0.880 ± 0.191
1,4-	3	0.989	0.017	0.291 ± 0.044	-0.627 ± 0.349
1,5-	3	0.9998	0.0083	0.528 ± 0.012	0.647 ± 0.092

The E_{HOMO} characterizes the ground state of the molecules, and E_{LUMO} corresponds to the excited state. In every tautomeric anthraquinone the accumulation of hydroxy groups results in the mutually proportional changes in these characteristics along equation (7) (Table 7).

$$E_{\text{LUMO}} = kE_{\text{HOMO}} + E_0, \text{ eV} \quad (7)$$

The peculiar feature of this relation consists in the following: In event of 9,10-anthraquinone the points belonging to the isomeric dihydroxyanthraquinones do not fit to the line 1 but form a separate straight line 2, and from the unique line for 1,10-anthraquinones deviates the point corresponding to compound VII. The values of k factors of equation (7) show that the relative sensitivity of the main and excited states of the tautomeric anthraquinones to the hydroxy groups accumulation grows in the series $1,4 < 9,10 < 1,10 < 1,5$.

The comparison of various characteristics with E_{HOMO} and E_{LUMO} values made in [1] revealed that the tautomerisation of purpurin and its anions occurred both in the ground and in the excited states of molecules; the accompanying changes in the quantum-chemical characteristics were qualitatively different for both states, and therewith the excited states were more sensitive to the tautomeric transformations than the ground states. The same trends were observed in the case of α -hydroxyanthraquinones. Let us consider as an example the changes in the λ_{calc} values. Correlations described by equation (8) are characteristic of different tautomers, but each series of 9,10- and 1,10-anthraquinones separates in two parts (Fig. 5, Table 8).

Here $E = E_{\text{HOMO}}$ or E_{LUMO} .

$$\lambda_{\text{calc}} = kE + \lambda_0, \text{ nm} \quad (8)$$

The k factors of equation (8) evidence that the λ_{calc} values are very sensitive to the changes both in E_{HOMO} and E_{LUMO} and the relationship is qualitatively different for unlike tautomers. The mentioned sensitivity is higher in the excited than in the ground state: for 9,10-tautomers $1791:12.44 \approx 19$ times, for 1,4-tautomers $256.25:77.66 \approx 3$ times, for 1,10- and 1,5-tautomers $145.7:63.82 \approx 153.58:70.64 \approx 2$ times.

The k values from equation (8) may be used for quantitative estimation of the sensitivity of the ground and excited states of molecules to the displacements of the π, π^* -bands resulting from the tautomeric transformations. For instance, the ratios $k_{\text{HOMO}}(1,10)/$

Table 8. Correlation parameters of equations (8)

E	Tautomer	Compds. ^a	r	s , nm	k	λ_0 , nm
E_{HOMO}	9,10-(1)	I, VI, VIII	0.9996	1.5	89.01 ± 2.49	1216 ± 22
E_{HOMO}	9,10-(2)	III, XI, XVII	1.0000	0.4	92.44 ± 0.45	1237 ± 4
E_{LUMO}	9,10-(3)	I, XI, XVII	0.9987	4.0	265.8 ± 13.4	1224 ± 38
E_{LUMO}	9,10-(4)	III, VI, VIII	0.97	13	1791 ± 463	5708 ± 1362
E_{HOMO}	1,10-(1)	II, IV, X, XIII, XIV	0.991	3.5	63.82 ± 4.94	1022 ± 41
E_{HOMO}	1,10-(2)	VII, XV, XIX	0.9998	0.8	50.56 ± 0.98	934 ± 8
E_{LUMO}	1,10-(3)	II, VII, XIX	0.9995	1.8	145.7 ± 4.6	976 ± 15
E_{LUMO}	1,10-(4)	IV, X, XIV	0.9992	1.4	155.2 ± 6.4	996 ± 20
E_{HOMO}	1,4-	IX, XII, XVIII	0.994	3.3	77.66 ± 8.65	1133 ± 68
E_{LUMO}	1,4-	IX, XII, XVIII	0.966	7.8	256.25 ± 68.56	1170 ± 201
E_{HOMO}	1,5-	V, XVI, XX	0.99991	0.7	70.64 ± 0.94	1126 ± 7
E_{LUMO}	1,5-	V, XVI, XX	0.9994	1.8	153.58 ± 4.72	1040 ± 17

^a The compound numbers are reported that fit to the given relationship.

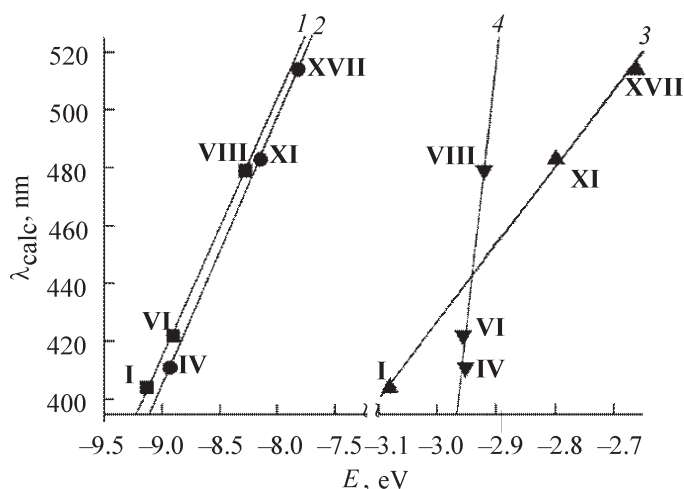


Fig. 5. Correlation between λ_{calc} of hydroxy-9,10-anthraquinones with E_{HOMO} (1, 2) and E_{LUMO} (3, 4).

$k_{\text{HOMO}}(9,10) = 63.82:12.44=5.1$ and $k_{\text{LUMO}}(9,10)/k_{\text{LUMO}}(1,10) = 1791:145.7=12.3$ indicate that the excited state is 12.3:5.1 = 2.4 times more sensitive to 9,10-1,10-anthraquinoid rearrangement than the ground state; therewith the sensitivity of λ_{calc} to the energy change of the molecular orbital is greater in the ground state and decreases in the excited state.

Hence the values of the quantum-chemical characteristics of α -hydroxyanthraquinones are governed by the known correlation dependences [4]: the proportional response of various parameters in one series of compounds or of a single parameter from two series of compounds to versatile structural alterations: introductions of substituent, changes in its position, and tautomerism. The most of these dependences occurs with very high, often with the limiting correlation factors presenting an unassailable proof of their certainty irrespective of the small and even minimum objectively possible number of points.

Therewith our data show that the relationship between the structure and characteristics are not always unambiguous and predictable. This is confirmed, for instance, by unlike participation of isomeric dihydroxyanthraquinones in the linear dependences of various parameters on the number of hydroxy groups (Table 4). This is also supported by the absence of the proportional response of E_{π} and E_{σ} to the tautomerism in 1,4,5-trihydroxy- and 1,4,5,8-tetrahydroxyanthraquinones in contrast to that shown by purpurin [1]. The relatively low (less than 0.990) r values of some correlations for the 1,4-anthraquinones (Tables 4 and 7) probably also indicate the more complicated character of these relations.

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