Tautomerism of Anthraquinones:
I. Purpurin and Anions Derived Therefrom

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

Russian University of Peoples' Friendship, P.O. Box 453, Moscow, 127349 Russia
*e-mail: vfain@mail.ru*

Abstract—A procedure was proposed for quantitative analysis of tautomeric equilibria of organic compounds. Purpurin was found to exist mainly as 9,10-, 1,4-, and 1,10-anthraquinoid tautomers, its monoanion, as 1,10-anthraquinoid tautomer, the dianion, as 1,10- and 2,9-anthraquinoid tautomers, and the trianion, as 1,10-, 1,4-, and 2,9-anthraquinoid tautomers. Tautomeric transformations occur both in the ground and in the excited states, and the corresponding changes of quantum-chemical parameters in these states are essentially different. The excited states are more sensitive to tautomeric transformations than the ground states.

Anthraquinone derivatives constitute an important class of organic compounds which give rise to a very broad spectrum of practical applications. A number of natural and synthetic dyes, pigments, luminophores, biologicaly active substances and drugs, reagents for data recording and processing systems, catalysts and inhibitors of chemical processes, sensitizers for photochemical reactions, analytical reagents, and indicators are based on anthraquinone derivatives [1]. For many years, anthraquinones were referred to exclusively as 9,10-anthraquinones [2, 3], while isomeric anthraquinones with a different arrangement of the carbonyl groups were poorly studied. The chemistry of the latter [3] could be figuratively represented as a small separate branch on the huge branched anthraquinone chemistry tree. Rearrangements of 9,10-anthraquinones into isomeric compounds have long been known [3]; in the recent years they have attracted considerable interest and acquired specific importance as a result of studies on photochemical processes which are accompanied by tautomeric transformations of anthraquinoid structures [4].

The use of correlation methods in studying the effect of the structure of anthraquinones on their electron absorption spectra and quantum-chemical parameters [5] revealed a considerably more important role of tautomeric structures in the chemistry of anthraquinones than it was generally accepted previously [6, 7]. It was found [8, 9] that electron absorption spectra of dihydroxy-anthraquinones contain bands corresponding to states which are characterized by different contributions of various tautomeric anthraquinoid structures. Analysis of these states made it possible to interpret complicated electron absorption spectra of quinizarin and its anions [8, 9], alizarin anions [10], and dihydroxyanthraquinone metal complexes [11]. Therefore, we thought it reasonable to study the tautomerism of anthraquinones in more detail.

Prototropic tautomerism of hydroxyanthraquinones has already been the subject of extensive studies some of which have been reviewed in [6, 7]. However, these studies did not involve correlation analysis. It is convenient to examine tautomeric properties of hydroxyanthraquinones following shifts of the π_1,π^* bands in the electron absorption spectra. According to quantum-chemical calculations, each tautomer gives rise to a single π_1,π^* band, and the presence of several π_1,π^* bands in experimental spectrum indicates the presence of several tautomers in the equilibrium mixture. The PPP procedure fairly accurately simulates tautomeric equilibria of hydroxyanthraquinones [7–9]; therefore, for studying tautomeric equilibria it is reasonable to use quantum-chemical parameters which do not depend on the conditions of measurements and are free from experimental errors. Correlation analysis of quantum-chemical parameters [5] takes into consideration all formally possible tautomers rather than only those really formed, and quantitative relations between these

I   II   III

IV   V   VI
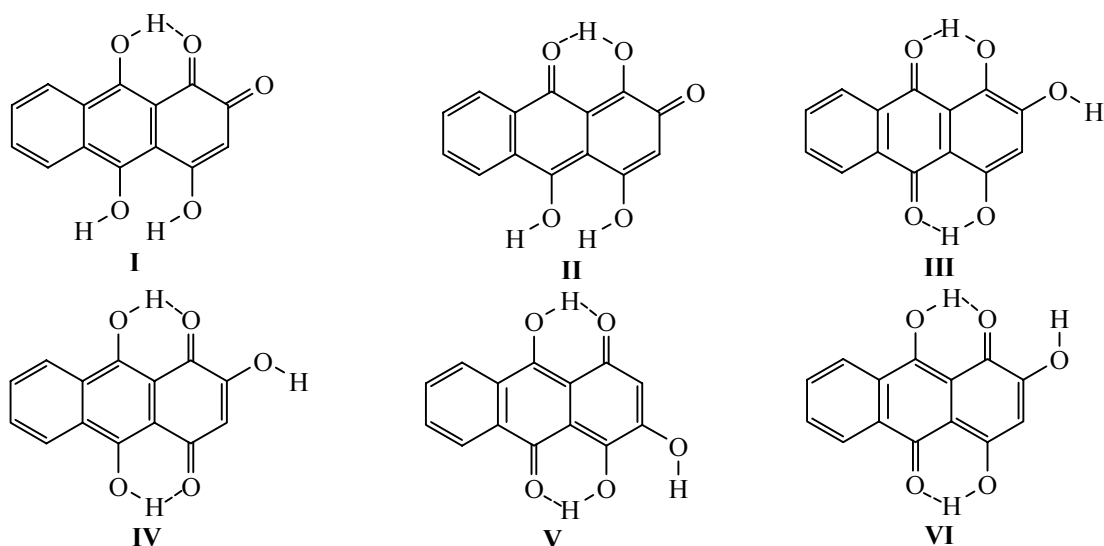
parameters and tautomer structure may thus be found. Correlation analysis requires that several compounds belonging to a single isostructural series be available. Consecutive ionization of polyhydroxyanthraquinones can be regarded as a convenient reaction producing such series. Quantitative relations holding in the ionization of hydroxyanthraquinones are characterized by very high correlation coefficients, which suggest the existence of linear functional dependences [9, 10]. Therefore, the number of hydroxy groups in the molecules under study can be minimized. 1,2,4-Trihydroxy-9,10-anthraquinone (purpurin) turned out to be a convenient model for studying tautomerism of anthraquinones on a quantitative level. Tautomeric transformations of purpurin and anions derived therefrom were not studied previously.

Theoretically, purpurin can exist as six tautomers: 1,2-, 2,9-, 9,10-, and 1,4-anthraquinones **I–IV** and two 1,10-anthraquinone derivatives **V** and **VI**. Taking into account the presence of three hydroxy groups, each tautomer could give rise to three successively ionized forms: 3 monoanions (**a–c**), 3 dianions (**d–f**), and one trianion (**g**). The structures are numbered in the order corresponding to increase in the calculated λ_{max}. Total of 18 monoanions, 18 dianions, and 6 trianions are formally possible. Insofar as hydroxy groups which are not involved in intramolecular hydrogen bonding undergo ionization first, no anions containing such groups can exist. Therefore, only 8 monoanions and 14 dianions can be formed really.

We performed quantum-chemical calculations of all purpurin tautomers and anions derived therefrom in terms of the Dewar version of the π electron PPP procedure [12] using variable beta approximation [13]. Table 1

contains the positions of absorption maxima (λ_{max}) and oscillator strengths (*f*) of π_1,π^* transitions, energies of the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) molecular orbitals, and energies of the σ- and π-bonds (E_σ and E_π). The data for hypothetic anions (which cannot be formed really) are italicized; these data are necessary for quantitative correlations between the substrate structure and its quantum-chemical parameters.

Absorption bands in the experimental electronic spectra were assigned to particular tautomers on the basis of the results of quantum-chemical calculations; here, the main factor was not the similarity between the calculated and experimental values but the existence of linear correlation between these values [5]. The assignment of
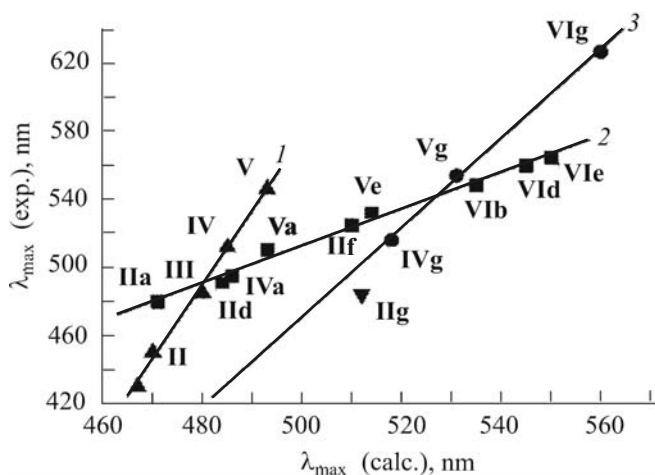

Fig. 1. Correlations between the calculated absorption maxima of purpurin and its anions with the experimental values: (*1*) purpurin in methanol [14], (*2*) mono- and dianions [15, 16], and (*3*) trianions in 1-pentanol [15].

Table 1. Calculated parameters of purpurin and anionic species derived therefrom

Comp. no.	Compound name	λ_{max}, nm	f	E_{HOMO}, eV	E_{LUMO}, eV	E_σ, eV	E_π, eV
I	4,9,10-Trihydroxy-1,2-anthraquinone	467	0.579	−8.026	−2.700	79.252	29.261
II	1,4,10-Trihydroxy-2,9-anthraquinone	470	0.801	−7.976	−3.046	79.280	29.254
III	1,2,4-Trihydroxy-9,10-anthraquinone	480	0.403	−7.950	−2.665	79.292	29.806
IV	2,9,10-Trihydroxy-1,4-anthraquinone	485	0.464	−7.989	−2.745	79.275	29.709
V	3,4,9-Trihydroxy-1,10-anthraquinone	493	0.596	−7.932	−2.925	79.284	29.424
VI	2,4,9-Trihydroxy-1,10-anthraquinone	522	0.624	−7.699	−2.857	79.310	29.656
Ia	9,10-Dihydroxy-4-oxido-1,2-anthraquinone	466	0.575	−7.967	−2.641	79.255	29.240
Ib	4,9-Dihydroxy-10-oxido-1,2-anthraquinone	478	0.587	−7.886	−2.651	79.255	29.236
Ic	4,10-Dihydroxy-9-oxido-1,2-anthraquinone	479	0.548	−7.857	−2.630	79.255	29.245
IIa	1,10-Dihydroxy-4-oxido-2,9-anthraquinone	471	0.696	−7.923	−2.988	79.282	29.233
IIb	1,4-Dihydroxy-10-oxido-2,9-anthraquinone	483	0.830	−7.830	−2.980	79.284	29.245
IIc	4,10-Dihydroxy-1-oxido-2,9-anthraquinone	500	0.654	−7.765	−2.933	79.284	29.277
IIIa	1,4-Dihydroxy-2-oxido-9,10-anthraquinone	484	0.422	−7.853	−2.620	79.293	29.772
IIIb	1,2-Dihydroxy-4-oxido-9,10-anthraquinone	497	0.390	−7.784	−2.603	79.293	29.769
IIIc	2,4-Dihydroxy-1-oxido-9,10-anthraquinone	497	0.410	−7.769	−2.605	79.294	29.771
IVa	9,10-Dihydroxy-2-oxido-1,4-anthraquinone	486	0.470	−7.927	−2.679	79.280	29.689
IVb	2,10-Dihydroxy-9-oxido-1,4-anthraquinone	500	0.461	−7.808	−2.667	79.277	29.691
IVc	2,9-Dihydroxy-10-oxido-1,4-anthraquinone	504	0.456	−7.788	−2.677	79.278	29.685
Va	4,9-Dihydroxy-3-oxido-1,10-anthraquinone	493	0.596	−7.884	−2.876	79.286	29.396
Vb	3,9-Dihydroxy-4-oxido-1,10-anthraquinone	512	0.597	−7.760	−2.839	79.285	29.417
Vc	3,4-Dihydroxy-9-oxido-1,10-anthraquinone	515	0.575	−7.732	−2.833	79.287	29.427
VIa	2,4-Dihydroxy-9-oxido-1,10-anthraquinone	533	0.621	−7.532	−2.757	79.310	29.660
VIb	4,9-Dihydroxy-2-oxido-1,10-anthraquinone	535	0.626	−7.582	−2.790	79.314	29.636
VIc	2,9-Dihydroxy-4-oxido-1,10-anthraquinone	540	0.594	−7.552	−2.774	79.309	29.640
Id	9-Hydroxy-4,10-dioxido-1,2-anthraquinone	477	0.580	−7.826	−2.591	79.258	29.221
Ie	10-Hydroxy-4,9-dioxido-1,2-anthraquinone	478	0.543	−7.805	−2.571	79.258	29.225
If	4-Hydroxy-9,10-dioxido-1,2-anthraquinone	487	0.555	−7.727	−2.562	79.255	29.265
IId	1-Hydroxy-4,10-dioxido-2,9-anthraquinone	484	0.787	−7.775	−2.921	79.286	29.230
IIe	10-Hydroxy-1,4-dioxido-2,9-anthraquinone	503	0.571	−7.714	−2.873	79.286	29.260
IIf	4-Hydroxy-1,10-dioxido-2,9-anthraquinone	510	0.720	−7.629	−2.869	79.288	29.267
IIId	1-Hydroxy-2,4-dioxido-9,10-anthraquinone	500	0.407	−7.700	−2.558	79.294	29.737
IIIe	4-Hydroxy-1,2-dioxido-9,10-anthraquinone	502	0.432	−7.671	−2.557	79.295	29.743

Table 2. (Contd.)

Comp. no.	Compound name	λ_{max}, nm	f	E_{HOMO}, eV	E_{LUMO}, eV	E_σ, eV	E_π, eV
IVd	10-Hydroxy-2,9-dioxido-1,4-anthraquinone	500	0.467	−7.748	−2.602	79.282	29.673
IVe	9-Hydroxy-2,10-dioxido-1,4-anthraquinone	505	0.460	−7.726	−2.613	79.283	29.665
IVf	2-Hydroxy-9,10-dioxido-1,4-anthraquinone	518	0.459	−7.619	−2.601	79.280	29.668
Vd	9-Hydroxy-3,4-dioxido-1,10-anthraquinone	511	0.601	−7.709	−2.787	79.287	29.397
Ve	4-Hydroxy-3,9-dioxido-1,10-anthraquinone	514	0.580	−7.685	−2.786	79.289	29.398
Vf	3-Hydroxy-4,9-dioxido-1,10-anthraquinone	532	0.585	−7.571	−2.751	79.288	29.418
VId	4-Hydroxy-2,9-dioxido-1,10-anthraquinone	545	0.630	−7.420	−2.691	79.315	29.641
VIe	9-Hydroxy-2,4-dioxido-1,10-anthraquinone	550	0.599	−7.448	−2.708	79.313	29.622
VIf	2-Hydroxy-4,9-dioxido-1,10-anthraquinone	551	0.597	−7.391	−2.677	79.309	29.642
Ig	4,9,10-Trioxido-1,2-anthraquinone	488	0.555	−7.669	−2.522	79.261	29.207
IIg	1,4,10-Trioxido-2,9-anthraquinone	512	0.656	−7.575	−2.809	79.290	29.256
IIIg	1,2,4-Trioxido-9,10-anthraquinone	517	0.420	−7.528	−2.496	79.296	29.710
IVg	2,9,10-Trioxido-1,4-anthraquinone	518	0.463	−7.559	−2.537	79.285	29.651
Vg	3,4,9-Trioxido-1,10-anthraquinone	531	0.592	−7.520	−2.701	79.290	29.397
VIg	2,4,9-Trioxido-1,10-anthraquinone	560	0.605	−7.291	−2.613	79.314	29.625

absorption bands is illustrated by Fig. 1. The linear correlations shown in Fig. 1 are described by Eq. (1) whose parameters are given in Table 2:

$$\lambda_{max}(exp.) = k\,\lambda_{max}(calc.) - \lambda_0, \text{ nm.} \qquad (1)$$

Here, k is the slope which characterizes the sensitivity of a compound to tautomeric transformations, and λ_0 is equal to $\lambda_{max}(exp.)$ at $\lambda_{max}(calcd.) = 0$.

The calculated λ_{max} values fit the relations obtained by various versions of the proportional response procedure [5], according to which similar structural variations lead to proportional change of the physicochemical parameters. As an example, Eq. (2) illustrates proportional response of λ_{max} to replacement of hydroxy group by oxido (Fig. 2).

$$\lambda_{max}(O^-) = k\,\lambda_{max}(OH) + \lambda_0, \text{ nm.} \qquad (2)$$

Here, the slope k characterizes the sensitivity of $\lambda_{max}(O^-)$ to variation of $\lambda_{max}(OH)$, and $\lambda_0 = \lambda_{max}(O^-)$ at $\lambda_{max}(OH) = 0$. Analogous relations were found for each position in all purpurin tautomers. The corresponding correlation coefficients are very high, and the standard deviations do not exceed 1 nm (Table 3). The lesser r value for 1-X-2,9-anthraquinones where the variable

substituent is located between two carbonyl groups indicates a more complex relation which should be elucidated by studying tautomeric transformations of polyhydroxyanthraquinones.

The data in Table 3 show that replacement of the hydroxy group by oxido in position *2* of 1,4 anthraquinones, in position *3* of 1,10-anthraquinones, and in position *4* of 1,2- and 2,9-anthraquinones almost does not affect λ_{max}; i.e., the position of these bands does not depend on the electron-donor power of the substituent. The largest red shift ($\Delta\lambda = 20$–22 nm) is observed when such replacement occurs in position *9* of 3-substituted 1,10-anthraquinones. These data, together with those given in [17],

Table 2. Parameters of correlation equation (1)

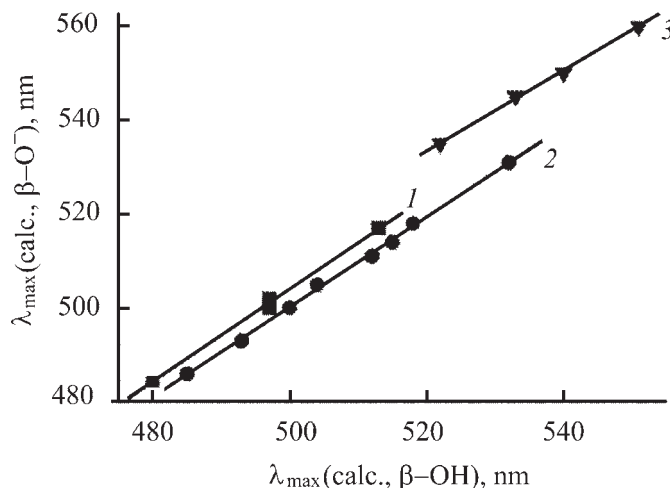| Compound	Number of tautomers N	Correlation coefficient r	Standard deviation s, nm	k	λ_0, nm
Purpurin	5	0.9975	3.8	4.347± 0.179	1598± 86
Mono- and dianions	9	0.993	3.8	1.079± 0.047	−27±24
Trianions	3	0.9993	2.9	2.622± 0.096	840±51

Fig. 2. Proportional response of λ_{max} to replacement of the β-hydroxy group by oxido: (*1*) 2-X-9,10-anthraquinones, (*2*) 2- and 3-X-1,10-anthraquinones, and (*3*) 2-X-1,4-anthraquinones (X is a variable substituent).

constitute the first information on the effect of the donor power of substituents on the position of π_1,π^*-bands in the electron absorption spectra of poorly studied isomeric anthraquinones.

Scanty experimental data on the intensity of absorption bands in the electron spectra of purpurin in alcohols are often contradictory. The results of quantum-chemical calculations allowed us to reveal quantitative relations governing variations in the π_1,π^*-band intensity for different tautomers. The oscillator strength grows in the series **III** < **IV** < **I** < **V** < **VI** < **II** which is common for neutral purpurin and all anionic species derived therefrom. It follows that the *f* values of tautomeric purpurin anions are linearly related to the *f* values of neutral purpurin tautomers [Eq. (3)]. Only a few points for tautomers **II** deviate from the straight line. The reason for the observed deviation is to be clarified; most probably, it originates from the specific structure of 2,9-anthraquinones which differentiates them from the other anthraquinone isomers.

$$f(\text{anion}) = k f(\text{purpurin}) + f_0. \quad (3)$$

Here, the coefficient k characterizes the sensitivity of $f(\text{anion})$ to variation of $f(\text{purpurin})$, and $f_0 = f(\text{anion})$ at $f(\text{purpurin}) = 0$. Table 4 gives the correlation parameters for Eq. (3).

Table 3. Parameters of correlation equation (2)

Compound series	$\Delta\lambda$, nm	N	r	s, nm	k	λ_0, nm
2-X-9,10-Anthraquinones	3–5	4	0.998	1.0	1.000 ± 0.043	4.0 ± 21.3
1-X-9,10-Anthraquinones	16–17	4	0.997	0.8	0.954 ± 0.050	39.4 ± 24.4
4-X-9,10-Anthraquinones	15–17	4	0.9991	0.5	0.933 ± 0.029	49.0 ± 13.8
2-X-1,4- and 3-X-1,10-Anthraquinones	−1–0	8	0.9992	0.6	0.960 ± 0.016	20.0 ± 8.1
2-OH(O⁻)-9-X-1,10-Anthraquinones	10–11	4	0.9991	0.6	0.972 ± 0.029	25.7 ± 15.6
3-OH(O⁻)-9-X-1,10-Anthraquinones	20–22	4	0.9991	0.5	0.919 ± 0.027	61.4 ± 13.8
2- and 3-OH(O⁻)-4-X-1,10-Anthraquinones	15–18	8	0.9985	1.0	0.943 ± 0.021	46.8 ± 10.8
2-X-1,10-Anthraquinones	9–13	4	0.9992	0.5	0.854 ± 0.024	89.4 ± 12.8
9-X-1,4-Anthraquinones	13–15	4	0.9986	0.7	0.945 ± 0.035	41.3 ± 17.4
10-X-1,4-Anthraquinones	18–19	4	1.00000	0.03	0.931 ± 0.002	52.4 ± 1.2
4-X-1,2-Anthraquinones	−1	3	1.00000	0.00	1.000 ± 0.000	$−1.0 \pm 0.0$
9-X-1,2-Anthraquinones	11–12	4	0.99996	0.06	0.910 ± 0.006	54.1 ± 2.7
10-X-1,2-Anthraquinones	10–11	4	0.99997	0.06	0.917 ± 0.005	49.6 ± 2.3
4-X-2,9-Anthraquinones	1–3	4	0.9994	0.8	1.040 ± 0.026	17.8 ± 12.6
10-X-2,9-Anthraquinones	9–13	4	0.99985	0.3	0.886 ± 0.011	16.6 ± 5.2
1-X-2,9-Anthraquinones	27–31	4	0.982	1.3	0.743 ± 0.099	152 ± 47

The relation between λ_{max} and f of tautomers is specific for purpurin and each series of its anions. Figure 3 shows the relation between λ_{max} and f for neutral purpurin. Tautomers **I** and **III–VI** give rise to two crossing straight lines; the π_l,π^*-band in their electron absorption spectra originates from intramolecular charge transfer (ICT) between positions *1,9* and *4,10*. No such ICT occurs in tautomer **II**, and the corresponding point deviates from the straight lines.

One of the main problems concerning tautomerism of hydroxyanthraquinones is whether the tautomeric equilibrium involves the ground or excited state? The positions of the π_l,π^*-absorption maxima which characterize the electron transition from the ground to excited state can provide necessary information. The values of λ_{max} for purpurin and anions derived therefrom correlate with the frontier molecular orbital energies E_{HOMO} and E_{LUMO} which correspond to the ground and excited states, respectively, through Eq. (4) (Fig. 4, Table 5).

$$\lambda_{max} = k\,E + \lambda_0, \text{ nm.} \qquad (4)$$

Here, E stands for E_{HOMO} or E_{LUMO}, k is the sensitivity of λ_{max} to variation of the frontier molecular orbital energy on successive ionization of purpurin, and $\lambda_0 = \lambda_{max}$ at $E = 0$. It is seen that λ_{max} of purpurin and its anions is sensitive to both E_{HOMO} and E_{LUMO} and that the dependence is specific for each tautomer. For example, the k_{LUMO}/k_{HOMO} ratio equal to 217.2 : 108.5 ≈ 2.0 shows that the sensitivity of λ_{max} to E of 1,10-anthraquinoid

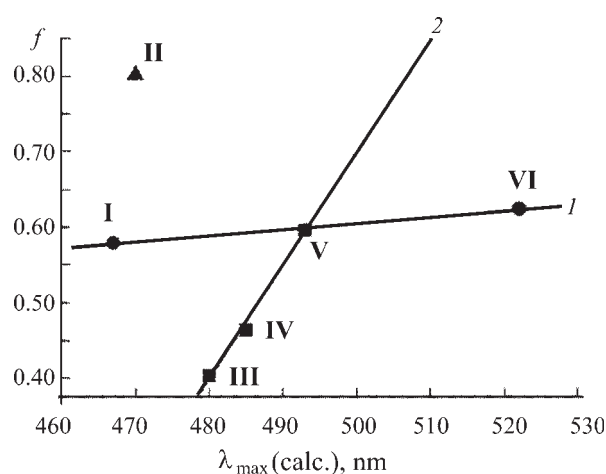**Table 4.** Parameters of correlation equation (3)

Anions	N	r	s	k	f_0
Monoanions (**a**)	5	0.998	0.006	0.911 ± 0.034	0.027 ± 0.018
Monoanions (**b**)	5	0.9994	0.004	0.968 ± 0.020	0.017 ± 0.011
Monoanions (**c**)	5	0.9990	0.005	0.937 ± 0.024	0.041 ± 0.013
Dianions (**d**)	5	0.995	0.009	0.875 ± 0.050	0.049 ± 0.027
Dianions (**e**)	5	0.998	0.006	0.901 ± 0.031	0.044 ± 0.016
Dianions (**f**)	6	0.9984	0.008	0.915 ± 0.026	0.054 ± 0.015
Trianions (**g**)	5	0.994	0.010	0.855 ± 0.052	0.071 ± 0.028

structures in the excited state is higher than in the ground state by a factor of 2. The values of k from Eq. (4) can be used for quantitative estimation of the sensitivity of ground and excited states of molecules to tautomeric transformations. From the ratios $k_{HOMO}(1,10)/k_{HOMO}(9,10) = 108.5 : 101.3 = 1.07$ and $k_{LUMO}(9,10)/k_{HOMO}(1,10) = 266.3 : 217.2 = 1.23$ it follows that the excited state is more sensitive than the ground state to the transformation of 9,10-anthraquinoid tautomer into 1,10-tautomer by a factor of 1.23 : 1.07 = 1.15; the sensitivity of λ_{max} to variation of the molecular orbital energy is higher in the ground state than in the excited state.
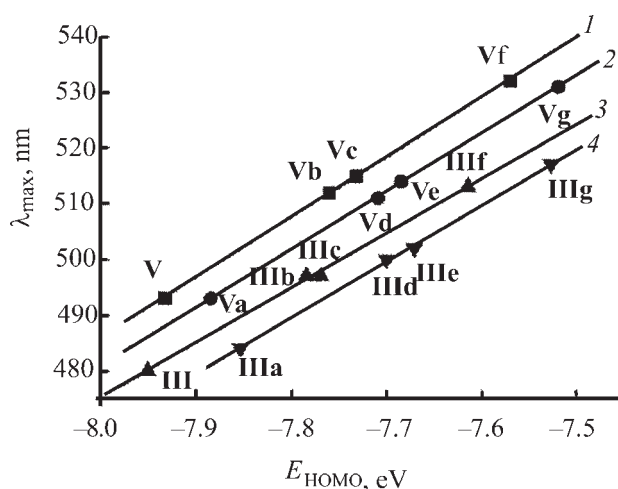

Fig. 3. Correlations between oscillator strengths f and absorption maxima λ_{max} of purpurin tautomers for which the π_l,π^*-band originates from intramolecular charge transfer (*1*) from position *1* to *9* or vice versa ($r = 0.997$) and (*2*) from position *4* to *10* or vice versa ($r = 0.994$).

Fig. 4. Correlations between the absorption maxima λ_{max} of purpurin and its anions and E_{HOMO}: (*1, 2*) 1,10-anthraquinoid tautomers, (*3, 4*) 9,10-anthraquinoid tautomers; (*1, 3*) compounds with an invariable hydroxy group in position *3* (or *2*); (*2, 4*) anions with an invariable oxido group in position *3* (or *2*).

Table 5. Parameters of correlation equation (4)

Tauto-mer	Invariable substituent	r	s, nm	k	λ_0, nm
		E_{HOMO}			
1,10	3-OH	0.99989	0.3	108.1 ± 1.1	1350 ± 9
1,10	3-O⁻	0.99992	0.2	108.5 ± 1.0	1317 ± 7
9,10	2-OH	0.9990	0.7	98.3 ± 3.1	1261 ± 24
9,10	2-O⁻	0.9996	0.5	101.3 ± 2.0	1279 ± 16
		E_{LUMO}			
1,10	3-OH	0.9989	0.9	224.5 ± 7.4	1150 ± 21
1,10	3-O⁻	0.997	1.4	217.2 ± 11.2	1118 ± 31
9,10	2-OH	0.9996	0.4	270.4 ± 5.2	1201 ± 13
9,10	2-O⁻	0.9985	0.9	266.3 ± 10.3	1182 ± 26

The effects of tautomeric transformations of purpurin and its anions on the ground and excited states are qualitatively different. Figure 5 illustrates this difference for purpurin. The relation between λ_{max} for tautomeric pupurrin trianions and the HOMO energies is represented by two straight lines including structures **I**, **II**, **IV**, **V** ($r = 0.997$) and **II**, **III**, **VI** ($r = 0.998$), but no correlation is observed with the LUMO energies.

Other correlations also indicate qualitatively different characters of variation of the quantum-chemical parameters versus molecular orbital energies, depending on tautomeric transformations. For example, the solvation
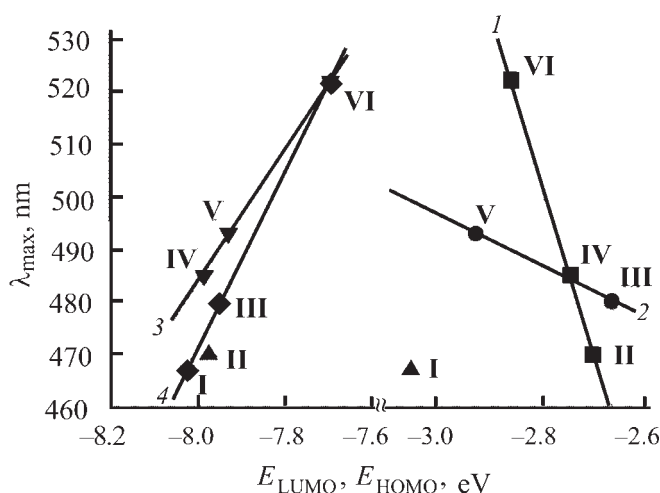
coefficients M and π-bond energies E_π correlate with the LUMO energies E_{LUMO}, giving rise to straight lines for tautomers **II**, **IV**, and **VI** ($r = 0.9990$) and **II**, **III**, **IV**, and **V** ($r = 0.9993$), respectively; however, correlation with E_{HOMO} is absent. The very high correlation coefficients r and very small standard deviations unambiguously indicate that these correlations are regular despite the minimal number of points. The absence of a correlation means only that purpurin is a too simple model to reveal all tautomeric interrelations intrinsic to polyhydroxyanthraquinones. The reason for the observed differences is to be elucidated.

Linear relations between E_{HOMO} and E_{LUMO}, which are described by Eq. (5), are specific for each series of tautomers of purpurin and its anions.

$$E_{HOMO} = k\, E_{LUMO} + E_0,\ eV \qquad (5)$$

Here, $E_0 = E_{HOMO}$ at $E_{LUMO} = 0$. The relations are different for different tautomers. 9,10-Anthraquinones are characterized by two closely located straight lines for derivatives with 2-hydroxy and 2-oxido groups, while 1,10-anthraquinones give rise to a single straight line for both neutral species and all anionic forms (Fig. 6). The coefficient k in Eq. (5) is greater than unity, indicating that the HOMO is more sensitive than LUMO to successive ionization. The formation of tautomeric structures leads to decrease of k; for example, in the
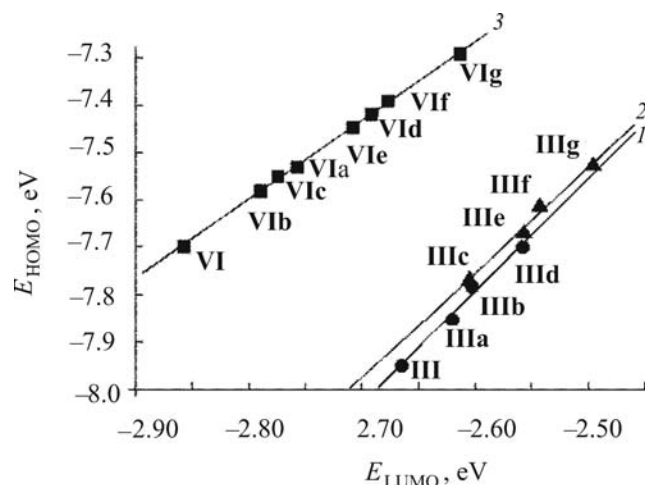

Fig. 5. Correlations between the absorption maxima λ_{max} of purpurin tautomers and (*1, 2*) LUMO and (*3, 4*) HOMO energies: (*1*) $r = 0.9998$, $s = 0.56$ nm, $k = 126.7 ± 2.6$; (*2*) $r = 1.00000$, $s = 0.17$ nm, $k = 168.0 ± 0.7$; (*3*) $r = 1.00000$, $s = 0.08$ nm, $k = -(331.0 ± 0.7)$; (*4*) $r = 0.996$, $s = 0.8$ nm, $k = -(49.1 ± 4.2)$.

Fig. 6. Correlations between the HOMO and LUMO energies of (*1*) 9,10-anthraquinones with an invariable hydroxy group in the 2-position [$r = 0.993$, $s = 0.015$ eV; $k = 2.379 ± 0.198$; $E_0 = -(1.609 ± 0.517)$ eV], (*2*) 9,10-anthraquinones with an invariable oxido group in the 2-position [$r = 0.995$, $s = 0.013$ eV; $k = 2.249 ± 0.165$, $E_0 = -(1.932 ± 0.420)$ eV], and (*3*) 1,10-anthraquinones [$r = 0.9997$, $s = 0.004$ eV; $k = 1.670 ± 0.18$, $E_0 = -(2.93 ± 0.05)$ eV].

transformation of 9,10-anthraquinoid structures into 1,10-anthraquinoid k decreases by a factor of $2.379 : 1.670 \approx 1.4$.

Analysis of the E_{HOMO} and E_{LUMO} values for different tautomers shows how tautomeric transformations affect the energy of the ground and excited states. The series of 9,10- and 1,10-anthraquinoid tautomers with a 2-oxido group fit Eqs. (6) and (7):

$$E_{LUMO}(1,10) = (1.151 \pm 0.064) E_{NSMO}(9,10)$$
$$+ 0.255 \pm 0.164), eV;$$
$$N = 4, r = 0.997, s = 0.057 \ eV; \tag{6}$$

$$E_{HOMO}(1,10) = (1.079 \pm 0.019) E_{HOMO}(9,10)$$
$$+ (0.825 \pm 0.144), eV;$$
$$N = 4, r = 0.9997, s = 0.003 \ eV. \tag{7}$$

As follows from the slopes of Eqs. (6) and (7), the 9,10–1,10-anthraquinoid tautomeric transformation affects the energy of the excited state to a slightly stronger extent (by ~7%) than the energy of the ground state.

Purpurin is a too simple model to reveal all relations holding in the energies of the σ- and π-bonds in different tautomers. The existence of a linear relation between E_σ and E_π for tautomers having a carbonyl group in position 9 [**II**, **III**, and **V**; Eq. (8)] suggests that the given tautomeric transformation involves variation of the π-bond energies, the σ-bond energy remaining almost unchanged:

$$E_\sigma = (0.0216 \pm 0.0006) E_\pi + (78.648 \pm 0.018), eV;$$
$$N = 3, r = 0.9996, s = 0.0002 \ eV. \tag{8}$$

Thus correlation analysis of quantum-chemical parameters shows that tautomeric transformations occur both in the ground and excited states of purpurin and its anions and allows quantitative estimation of various aspects of these processes. Our results led us to draw a number of important conclusions which must be taken into account while studying tautomeric transformations:

(1) Tautomeric transformations differently affect different molecular parameters. The lack of variation of some parameter does not mean that tautomeric equilibrium does not exist;

(2) When a compound gives rise to several tautomeric equilibria, they can be accompanied by different variations of the same parameter;

(3) Variation of different parameters as a result of tautomeric transformations may differently depend on the

energy of the ground and excited states; therefore, change of only one parameter gives no grounds to conclude whether the tautomeric transformation occurs in the ground or excited state.

For example, the absence of bands assignable to 1,10-anthraquinoid tautomer [17] in the electron absorption spectra of 1-hydroxy-X-R-anthraquinones does not mean that these compounds are incapable of undergoing tautomeric transformations. Likewise, the occurrence of short- and long-wave fluorescence of 1,5- and 1,8-di-hydroxyanthraquinones and only short-wave fluorescence of the 1,4-isomer cannot be interpreted [18] as the absence of tautomeric transformations in the excited state of the latter.

To conclude, it should be noted that the approach proposed in the present work is applicable to tautomeric transformations of not only hydroxyanthraquinones but also other organic compounds.

REFERENCES

1. Fain, V.Ya., *9,10-Antrakhinony i ikh primenenie* (9,10-Anthraquinones and Their Application), Moscow: Tsentr Fotokhimii Ross. Akad. Nauk, 1999.
2. Fain, V.Ya., *Tablitsy elektronnykh spektrov poglo-shcheniya antrakhinona i ego proizvodnykh* (Tabulated Electron Absorption Spectra of Anthraquinone and Its Derivatives), Leningrad: Khimiya, 1970.
3. Gorelik, M.V., *Khimiya antrakhinonov i ikh proizvodnykh* (Chemistry of Anthraquinones and Their Derivatives), Moscow: Khimiya, 1983, p. 29.
4. Smith, T.P., Zaklika, K.A., Thakur, K., Walker, G.C., Tominaga, K., and Barbara, P.F., *J. Phys. Chem.*, 1991, vol. 95, p. 10 465; Marzocchi, M.P., Mantini, A.R., Cazu, M., and Smulevich, G. J., *Chem. Phys.*, 1998, vol. 108, p. 534; Klimenko, L.S., *Doctoral (Chem.) Dissertation*, Novosibirsk, 2003.
5. Fain, V.Ya., *Korrelyatsionnyi analiz elektronnykh spektrov pogloshcheniya* (Correlation Analysis of Electron Absorption Spectra), Moscow: Sputnik+, 2002, p. 8.
6. Fain, V.Ya., *Elektronnye spektry pogloshcheniya i stroenie 9,10-antrakhinonov. I. 9,10-Antrakhinon i ego mono-zameshchennye* (Electron Absorption Spectra and Struc-ture of 9,10-Anthraquinones. I. 9,10-Anthraquinone and Its Monosubstituted Derivatives), Moscow: Sputnik+, 2003.
7. Fain, V.Ya., *Elektronnye spektry pogloshcheniya i stroenie 9,10-antrakhinonov. I. 9,10-Antrakhinon i ego monoza-meshchennye* (Electron Absorption Spectra and Structure of 9,10-Anthraquinones. II. Disubstituted 9,10-Anthra-quinones), Moscow: Sputnik+, 2003.
8. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Russ. J. Gen. Chem.*, 2003, vol. 73, p. 1595.

9. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Russ. J. Gen. Chem.*, 2003, vol. 73, p. 1925.

10. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Russ. J. Gen. Chem.*, 2004, vol. 74, p. 1558.

11. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Koord. Khim.*, 2003, vol. 29, p. 395; *ibid.*, 2004, vol. 30, pp. 385, 390.

12. Dewar, M.J.S., *The Molecular Orbital Theory of Organic Chemistry*, New York: McGraw–Hill, 1969. Translated under the title *Metod molekulyarnykh orbitalei v organicheskoi khimii*, Moscow: Mir, 1971, p. 590.

13. Nishimoto, K. and Forster, L.S., *Theor. Chim. Acta*, 1966, vol. 4, p. 155.

14. Fain, V.Ya. and Kuvshinova, N.N., *Reakts. Sposobn. Org. Soedin*. 1973, vol. 10, p. 129.

15. Formanek, J., *Spektralanalytischer Nachweis kunstlicher organischer Farbstoffe*, Berlin: Springer, 1900, p. 774.

16. Hüttig, G.F., *Z. Phys. Chem.*, 1914, vol. 88, p. 172; Schultz, G. and Lehmann, L., *Farbstofftabellen*, Leipzig: Akademie, 1930, 7th ed., vol. 1, nos. 12/13–14/15; Muzychkina, R.A., *Prirodnye antrakhinony. Biologicheskie svoistva i fiziko-khimicheskie kharakteristiki* (Natural Anthraquinones. Biological Properties and Physico-chemical Parameters), Tolstikov, G.A., Ed., Moscow: Fazis, 1998, p. 864.

17. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Russ. J. Gen. Chem.*, 2003, vol. 73, p. 621.

18. Nagaoka, S. and Nagashima, U., *Chem. Phys.*, 1996, vol. 206, p. 353.