ISSN 1070-4280, Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 10, pp. 1445–1451. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.Ya. Fain, B.E. Zaitsev, M.A. Ryabov, 2009, published in Zhurnal Organicheskoi Khimii, 2009, Vol. 45, No. 10, pp. 1462–1468.

Tautomerism of Anthraquinones: IX.* Protonated 1,5- and 1,8-Dihydroxyanthraquinones

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

Russian University of Peoples' Friendship, ul. Miklukho-Maklaya 6, Moscow, 117198 Russia
e-mail: vfain@mail.ru

Received October 10, 2008

Abstract—Fine structure of π_l,π^* absorption of mono- and dications derived from 1,5- and 1,8-dihydroxyanthraquinones originates from their existence as dynamic equilibrium mixtures of isomers differing by position of the positive charge, double bond distribution, and number of intramolecular hydrogen bonds. Protonation is accompanied by displacement of isomeric equilibria. Isomeric transformations of protonated dihydroxyanthraquinones involve mainly excited states of their molecules.

DOI: 10.1134/S1070428009100042

Anthraquinone derivatives constitute one of the most important classes of organic compounds, and their reactions in sulfuric acid are very important large-scale processes [2]. Many fast natural and synthetic dyes, pigments, luminophores, drugs, physiologically active compounds, materials for data storage and processing, analytical reagents, indicators, catalysts, inhibitors of large-scale chemical processes, sensitizers for photochemical reactions, etc., are derivatives of anthraquinones [3].

Hydroxyanthraquinones as synthetic dyes were produced on a large-scale in developed countries since XIXth century, and the first monograph including description of these compounds was published in 1900 [4]. Spectrophotometry arose in 1870 while studying electronic absorption spectra of solutions of dihydroxyanthraquinones in sulfuric acid [5]. However, about 100 years elapsed before chemists understood how important is to know the structure of products formed in reactions of dihydroxyanthraquinones with sulfuric acid.

1,5-Dihydroxyanthraquinone (anthrarufin) gives rise to dynamic equilibria between structurally different 9,10- and 1,10-quinoid tautomers and rotational isomers arising from rupture (formation) of intramolecular hydrogen bonds. 1,5-Quinoid tautomers were detected only for some substituted derivatives, e.g., 1,5-dihydroxy-3-methyl-anthraquinone (3-methylanthrarufin), and some complexes with metals [6].

α-Hydroxyanthraquinones in sulfuric acid undergo protonation first at the carbonyl group conjugated with hydroxy group and then at the second carbonyl group with consecutive formation of mono- and dications [7, 8]. The electronic absorption spectra of hydroxyanthraquinones in sulfuric acid, measured by different authors, differ considerably. For example, the elctronic absorption spectrum of anthrarufin was reported to contain one [9], two [10], three [7, 11], four [12], and five π_l,π^* bands [13], and the long-wave maximum responsible for the color of this compound was localized at λ 460 [9] to 570.7 nm [13]. Likewise, protonated 1,8-dihydroxyanthraquinone (chrysazine) displayed two [10, 14], three [7, 11], or four π_l,π^* bands [13] in the electronic absorption spectrum. The existing views on the structure of protonated anthraquinones cannot rationalize the above contradictory data. We performed quantum-chemical calculations of the electronic structure of mono- and dications derived from anthrarufin (Table 1) and chrysazine (Table 2), which showed that these species are characterized by only one π_l,π^* band determining their color. The observed discrepancy between the calculated and experimental data cannot be interpreted in terms of the generally accepted views.

However, this may be done assuming that the compounds under study exist as a mixture of several tautomers and conformers, each being capable of taking up protons in sulfuric acid to form the corresponding mono- and dications. Electronic absorption spectra contain very important information on tautomeric and conformational structure of compounds [15]. The pres-

* For communication VIII, see [1].

Table 1. Quantum-chemical calculations of 1,5-dihydroxyanthraquinone and its protonated forms

Compound	λ_{calc}, nm (*f*)	ΔH, eV	*M*, eV	E_σ, eV	E_π, eV	E_{HOMO}, eV	E_{LUMO}, eV
1,5-Dihydroxy-9,10-anthraquinone	411 (0.449)	139.370	3.015	75.262	28.606	–8.927	–2.955
1,5,9-Trihydroxy-10-oxo-10*H*-anthracen-9-ium (**I**)	428 (0.473)	143.365	2.893	75.267	28.156	–8.934	–3.127
1,5,9,10-Tetrahydroxyanthracene-9,10-diium (**V**)	444 (0.499)	147.372	2.775	75.273	27.718	–8.946	–3.283
5,9-Dihydroxy-1,10-anthraquinone	476 (0.639)	138.831	3.757	75.265	28.063	–8.514	–3.360
1,5,9-Trihydroxy-1-oxo-1*H*-anthracen-10-ium (**III**)	492 (0.635)	142.843	3.616	75.274	27.627	–8.526	–3.493
5,9,10-Trihydroxy-10-oxo-10*H*-anthracen-1-ium (**II**)	478 (0.636)	142.948	3.778	75.277	27.730	–8.567	–3.455
1,5,9,10-Tetrahydroxyanthracene-1,10-diium (**VI**)	492 (0.642)	146.960	3.634	75.285	27.293	–8.580	–3.581
9,10-Dihydroxy-1,5-anthraquinone	534 (0.896)	138.299	4.633	75.292	27.504	–8.386	–3.812
1,9,10-Trihydroxy-5-oxo-4*H*-anthracen-1-ium (**IV**)	539 (0.866)	142.425	4.658	75.303	27.179	–8.440	–3.884
1,4,9,10-Tetrahydroxyanthracene-1,5-diium (**VII**)	543 (0.846)	146.554	4.683	75.314	26.859	–8.495	–3.952

ence of several π_l,π^* bands in the electronic absorption spectra of protonated hydroxyanthraquinones indicates that they exist as different isomers characterized by different positions of the positive charge, double bond distribution patterns, and numbers of intramolecular hydrogen bonds.

Formalistically, four isomeric structures **I**–**IV** may be proposed for monoprotonated 1,5-dihydroxyanthraquinone, and the corresponding dication may exist as three isomers **V**–**VII**. Chrysazine could give rise to three mono- (**VIII**–**X**) and two dications (**XI**, **XII**). The formation of C^+–O–H···O–H rather than O–H···O–C^+ intramolecular hydrogen bond was substantiated in [7, 8]. Each tautomer **I**–**VII** and **VIII**–**XII** may be represented by different conformers arising from rotation about single C–O bonds, which is accompanied by rupture of intramolecular hydrogen bonds. An example is shown below for anthrarufin 9,10-dication which is denoted as $\mathbf{V}_c$-9,10. Here, the subscript "c" denotes a conformer, and the indices "9"

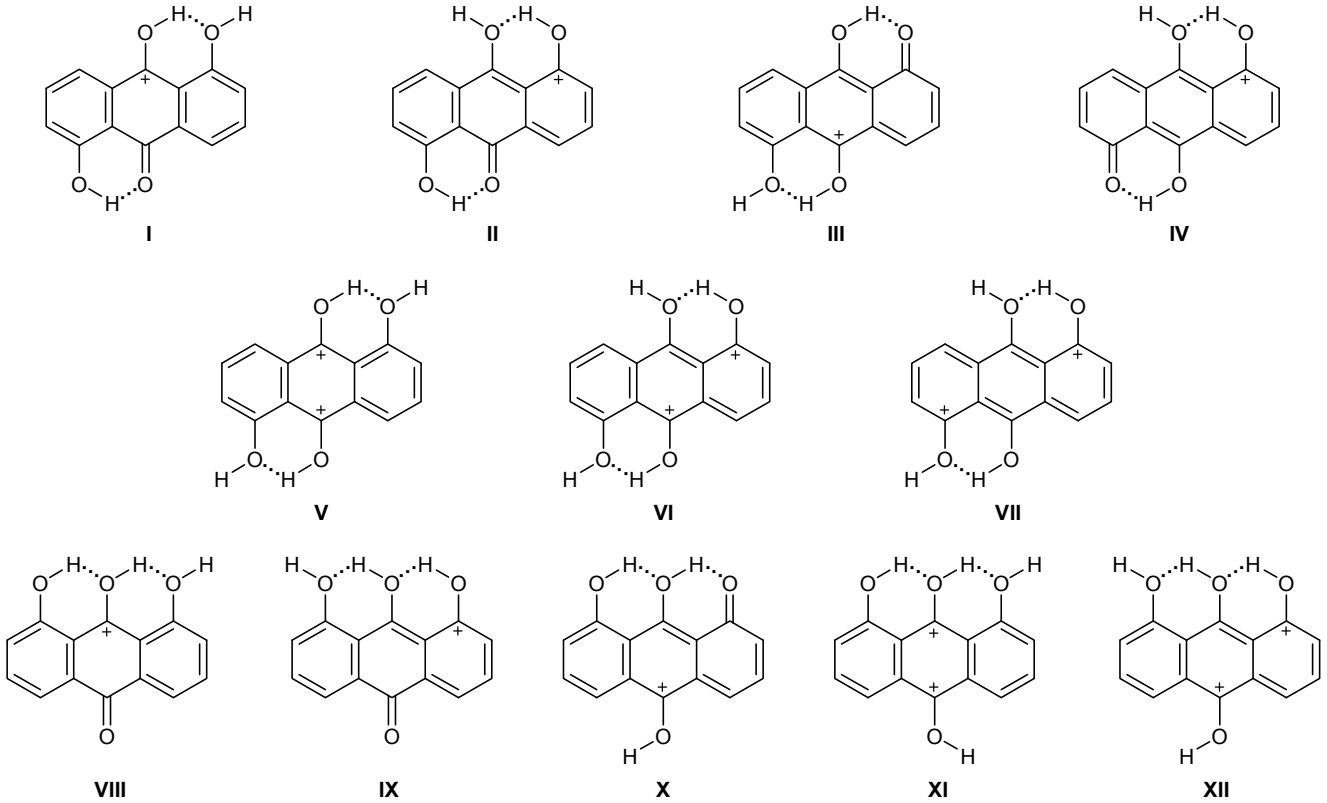
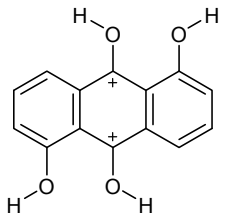


Table 2. Quantum-chemical calculations of 1,8-dihydroxyanthraquinone and its protonated forms

Compound	λ_{calc}, nm (*f*)	ΔH, eV	*M*, eV	E_σ, eV	E_π, eV	E_{HOMO}, eV	E_{LUMO}, eV
1,8-Dihydroxy-9,10-anthraquinone	422 (0.412)	139.386	3.000	75.261	28.622	–8.909	–2.953
1,8,9-Trihydroxy-10-oxo-10*H*-anthracen-9-ium (**VIII**)	442 (0.393)	143.351	2.816	75.269	28.141	–8.917	–3.150
1,8,9,10-Tetrahydroxyanthracene-9,10-diium (**XI**)	463 (0.431)	147.387	2.746	75.272	27.734	–8.911	–3.288
8,9-Dihydroxy-1,10-anthraquinone	491 (0.629)	138.619	3.537	75.260	27.856	–8.472	–3.343
1,8,9-Trihydroxy-1-oxo-1*H*-anthracen-10-ium (**IX**)	509 (0.596)	142.607	3.348	75.272	27.393	–8.495	–3.488
8,9,10-Trihydroxy-10-oxo-10*H*-anthracen-1-ium (**X**)	493 (0.626)	142.740	3.568	75.271	27.527	–8.521	–3.436
1,4,9,10-Tetrahydroxyanthracene-1,8-diium (**XII**)	509 (0.601)	146.727	3.377	75.283	27.064	–8.545	–3.575

and "10" indicate the positions of hydroxy groups that are turned apart.



V$_c$9,10

The experimental values of λ_{max} are assigned to tautomeric structures by comparing them with those calculated by quantum-chemical methods for the corresponding tautomers. Here, the validity of the assignment is judged by not similarity between the calculated and experimental values but by the existence of a linear correlation between them [16]. The Dewar version of the Pariser–Parr–Pople (PPP) π-electron method [17] with the use of variable β approximation [18] remains so far the only semiempirical quantum-chemical method which was shown to reliably simulate structural variations in numerous anthraquinone derivatives [6, 15, 19, 20].

The energy of atomization ΔH characterizes the stability of a compound in the gas phase, and solvation coefficient *M*, in solution. Isomeric mono- and dications of anthrarufin rank as follows with respect to their stability in the gas phase: 9,10 > 1,10 > 1,5. The reverse series is observed for solution: 1,5 > 1,10 > 9,10. This means that solvation favors isomer transformations accompanying protonation. Analogous relations are typical of protonated chrysazine species.

Successive protonation of anthrarufin and chrysazine in the gas phase increases the stability of each isomer. In going to solution, different isomers behave differently: successive protonation enhances the stability of the 1,5-isomers, the 9,10-isomers become less stable, while no definite relation is observed for the 1,10-isomers (Tables 1, 2).

The calculated absorption maxima (λ_{calc}) and oscillator strengths *f* for anthrarufin mono- and dications show a proportional response to variation of their isomeric structure [Eqs (1) and (2)]:

$$\lambda_{calc}(\text{dication}) = (0.8899\pm0.0353)\lambda_{calc}(\text{monocation}) + (64 \pm 17), \text{ nm}; \quad (1)$$

number of isomers $N = 3$, correlation coefficient $r = 0.9992$, standard deviation $s = 2.8$ nm;

$$f(\text{dication}) = (0.8832\pm0.0027)f(\text{monocation}) + (0.0809\pm0.0018); \quad (2)$$

$$N = 3,\ r = 1.00000,\ s = 0.0007.$$

The slopes of correlations (1) and (2) indicate that the parameters λ_{calc} and *f* for the dication are less sensitive (by 11–12%) to isomeric composition than λ_{calc} and *f* for the monocation.

Gorelik et al. [7] were the only authors to correlate the spectra of protonated anthrarufin and chrysazine with the degree of their protonation. Anthrarufin monocation was reported to display two π_l,π^* bands, λ_{max} (log ε): 400 (3.60) and 508 nm (4.85), and three π_l,π^* bands were found for the dication: 495 (3.70), 527 (4.25), and 567 nm (4.40) [7]. Protonated chrysazine was characterized by three π_l,π^* bands for both monocation [440 sh (3.78), 500 sh (4.08), 530 nm (4.09)] and dication [500 (3.80), 550 (4.05), 592 nm (4.10)].

By correlating λ_{max} of anthrarufin dication with λ_{calc} we assigned three π_l,π^* bands to isomers **V**–**VII** (Fig. 1, straight line *1*):

$$\lambda_{max} = (0.728\pm0.034)\lambda_{calc} + (171\pm17), \text{ nm}; \quad (3)$$

$$N = 3,\ r = 0.9989,\ s = 2.4 \text{ nm}.$$

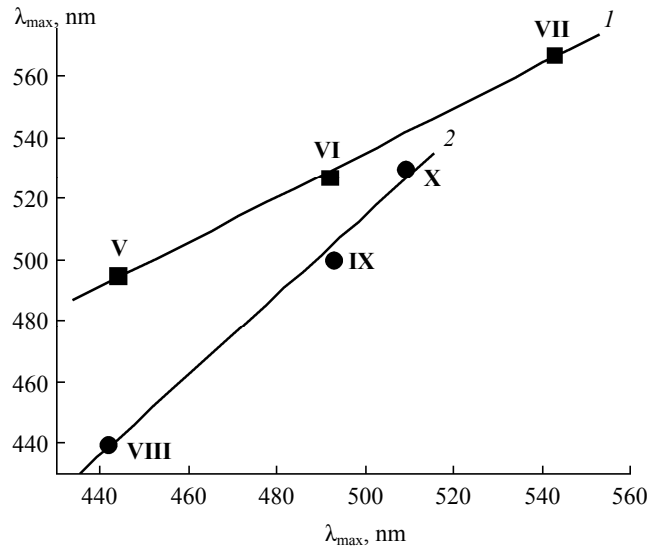


Fig. 1. Correlations between the experimental (λ_{max}) and calculated (λ_{calc}) absorption maxima of (*1*) anthrarufin dication and (*2*) chrysazine monocation.

This assignment is confirmed by independent correlation of λ_{max} for the dication with λ_{max} of 3-methylanthrarufin in ethanol [20]:

$$\lambda_{max}(\text{dication}) = (1.0270\pm0.0187)\lambda_{max}(\text{3-Me}) + (85\pm8), \text{ nm}; \quad (4)$$
$$N = 3,\ r = 0.9998,\ s = 0.9 \text{ nm}.$$

Analogous correlation analysis of λ_{max} for anthrarufin monocation cannot be performed because of insufficient number of points. However, we can presume with high probability that the value λ_{max} = 400 nm corresponds to 9,10-monocation **I**, and λ_{max} = 508 nm, to 1,10-monocation **II** or **III**. Insofar as the coefficient of solvation of isomer **II** is larger than that of **III** (Table 1), the latter absorption maximum (λ 508 nm) should be assigned preferably to 1,10-monocation **II**.

Table 3. Correlation analysis of the electronic absorption spectra of anthrarufin dication in sulfuric acid

λ_{max}, nm						Reference
$\mathbf{V_c}$-1,5	**V**	$\mathbf{VI_c}$-9	**VI**	$\mathbf{VII_c}$-9	**VII**	
	495		527		567	[7]
	482 sh		525 sh		564	[11]
465.5	494.5		527.4		573	[12]
	487.1	517.7	528.5	557.7	570.7	[13]
	490 sh		530		569	[14]
	491[a]		527[a]		569[a]	[21]
460						[9]
			525		568	[10]
0.98	1.24	1.41	1.53	1.67	1.80	$-\sum\sigma^A$

[a] Boron acetate complex.

Comparison of the λ_{max} values reported in [8–12] with those given in [7] allowed us to assigned them to isomeric dications. The presence of four or five π_l,π^* bands [12, 13] suggests the existence of several conformers in solution. Taking into account that the PPP approximation cannot be applied to calculation of rotational isomers, we used correlations of ν_{max} with the sum of constants σ^A for free and H-bonded hydroxy groups. The constants σ^A were proposed for substituents in the anthraquinone series [16], while protonated hydroxyanthraquinones cannot be regarded as substituted anthraquinones. On the other hand, the existence of proportional response of the position of the π_l,π^* bands of substituted anthraquinones and their protonated forms to variation of their isomeric composition [see, e.g., Eq. (4)] suggests that the σ^A approach can also be applied to the protonated species. Each isomeric cation may be characterized by the sum of constants σ^A for all hydroxy groups [15]:

$$\nu_{max} = k\sum\sigma^A + \nu_o, \text{ cm}^{-1}. \quad (5)$$

Using Eq. (5) for correlation analysis of the electronic absorption spectra of protonated anthrarufin, reported by different authors, we succeeded in confirming the assignment of π_l,π^* bands made on the basis of quantum-chemical calculations of tautomers and determining the conformer structures (Tables 3, 4).

The electron absorption spectra of boron complexes of α-hydroxyanthraquinones almost coincide with the spectra of α-hydroxyanthraquinones in sulfuric acid [7, 20, 21] (Table 3), indicating similarity of their structures. Analysis of the NMR spectra of the boron complexes of anthrarufin and chrysazine in terms of traditional views implying 9,10-quinoid structure of anthraquinones led the authors to presume bond redistribution pattern intrinsic to the 1,10- and 1,5-quinoid structures [7, 8]. In fact, these data support our assumption that these compounds exist as isomer mixtures.

By comparing the experimental values of λ_{max} for chrysazine with the calculated ones (λ_{calc}) we assigned three π_l,π^* bands to three isomers **VIII**–**X** (Fig. 1, straight line *2*):

$$\lambda_{max} = (1.303\pm0.134)\lambda_{calc} + (137\pm65), \text{ nm}; \quad (6)$$
$$N = 3,\ r = 0.995,\ s = 6.5 \text{ nm}.$$

Relatively large value of s may be due to appearance of two of the three π_l,π^* bands as shoulders, for determination of the corresponding absorption maxima involves an appreciable error. The above assignment is confirmed by the correlation of the experimental $\log\varepsilon_{max}$ values with the calculated oscillator strengths f:

$$\log\varepsilon_{max} = (1.384\pm0.125)f + (3.238\pm0.069); \quad (7)$$
$$N = 3,\ r = 0.996,\ s = 0.022.$$

This approach cannot be applied to assignment of π_l,π^* bands belonging to chrysazine dication. The number of experimental π_l,π^* bands is larger than that predicted by quantum-chemical calculations, indicating that isomeric equilibria involve different conformers. Using $\sum\sigma^A$ values [Fig. 2; Eqs. (8), (9)] we assigned the middle absorption band to the monocation (**IX**$_c$-1) and π_l,π^* bands to the dication (**XI**, **XII**$_c$-1, and **XII**). Analogous correlation analysis performed for the four π_l,π^* bands of chrysazine in sulfuric acid (λ_{max} 467, 496, 534, 573.5 nm) according to the data of [12] showed that they belong to dication isomers **XI** and **XII** and conformers **XI**$_c$-8,9 and **XII**$_c$-1 [Fig. 2, Eq. (10)].

$$\nu_{max} = (10576\pm495)\sum\sigma^A + (40415\pm934),\ cm^{-1}; \quad (8)$$
$$N = 3,\ r = 0.9989,\ s = 131\ cm^{-1};$$
$$\nu_{max} = (4365\pm103)\sum\sigma^A + (29227\pm258),\ cm^{-1}; \quad (9)$$
$$N = 3,\ r = 0.9997,\ s = 52\ cm^{-1};$$
$$\nu_{max} = (4006\pm216)\sum\sigma^A + (28778\pm511),\ cm^{-1}, \quad (10)$$
$$N = 4,\ r = 0.997,\ s = 161\ cm^{-1}.$$

Thus we succeeded in assigning each known experimental π_l,π^* band of protonated anthrarufin and chrysazine to appropriate isomer. Anthrarufin and its mono- and dications can give rise to different numbers of π_l,π^* bands, which supports the relation observed by us previously [22, 23]: chemical reactions are often accompanied by shifts of tautomeric and conformational equilibria.

The methodology developed by us for correlation analysis of electronic absorption spectra was justified by the results obtained for various compounds. Very large number of examples, high correlation coefficients r, and low values of s leave no doubt in reliability of the revealed relations despite minimal number of points involved in the correlations.

According to [7, 8], the positive charge in protonated hydroxyanthraquinones is delocalized over π-electron system of the anthraquinone core, and their structure should be represented by canonical formulas with charge delocalization. Our results suggest essential charge localization on particular carbon atoms and existence of distinct cationic centers in molecules of protonated hydroxyanthraquinones. It was also noted [7, 8] that intramolecular hydrogen bonds OH···O–C$^+$ in chrysazine cations are weakened or even broken. In keeping with the ν_{max}—$\sum\sigma^A$ correlations, intramolecular hydrogen bonds do exist: the given correlation parameters were obtained using the constant σ^A for H-bonded hydroxy group. Otherwise (i.e., using the constant σ^A for free hydroxy group), no correlation was found.

Table 4. Parameters of correlation equation (5)

No.	Reference	r	s, cm^{-1}	k	ν_o, cm^{-1}
1	[7]	0.9990	83	4576±209	25909±325
2	[10]	0.9986	112	5393±282	27391±434
3	[12]	0.9988	105	4853±171	26263±243
4	[13]	0.992	172	5355±393	27032±606
5	[14]	0.9996	60	5062±150	25345±193
6	[21]	0.99975	44	4983±111	26564±171

Correlation of the experimental absorption maxima (λ_{max}) of isomeric anthrarufin dications with the calculated energies of the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) [Fig. 3; Eqs. (11), (12)] showed that differences between iso-

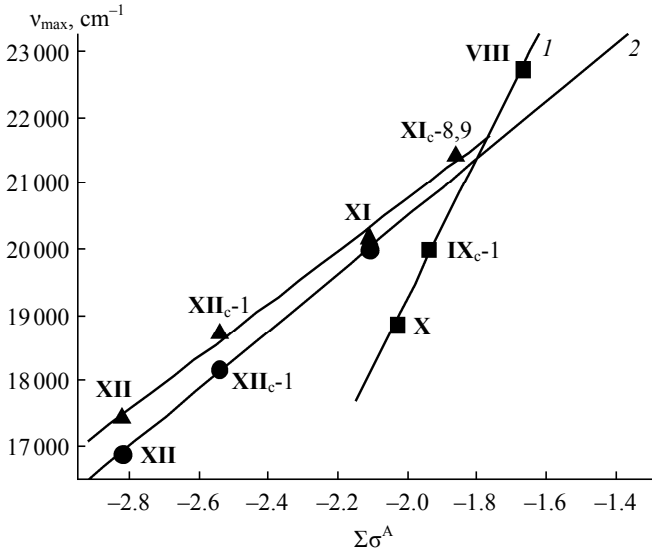


Fig. 2. Correlation of the experimental absorption maxima ν_{max} and the sum of constants σ^A for free and H-bonded hydroxy groups for (*1*) chrysazine monocation and (*2*, *3*) its dication according to the data of (*1*, *2*) [7] and (*3*) [12].

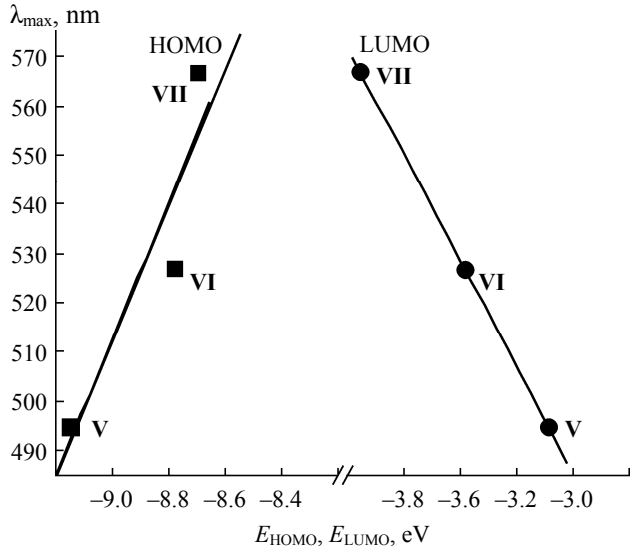


Fig. 3. Correlation of the experimental absorption maxima λ_{max} of isomeric anthrarufin dications with the energies of their highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals.

meric structures are related mainly to the excited states characterized by the E_{LUMO} values and that the role of the ground states is insignificant.

$$\lambda_{max} = (138\pm60)E_{HOMO} + (1727\pm520),\ \text{nm}; \quad (11)$$
$$N = 3,\ r = 0.92,\ s = 20\ \text{nm};$$
$$\lambda_{max} = (141.6\pm0.5) - (107.63\pm0.12)E_{LUMO},\ \text{nm}; \quad (12)$$
$$N = 3,\ r = 1.00000,\ s = 0.006\ \text{nm}.$$

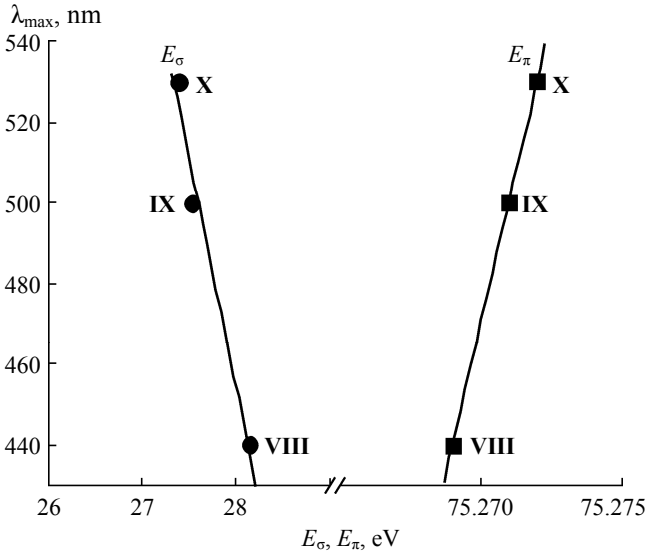


Fig. 4. Correlation of the experimental absorption maxima λ_{max} of chrysazine monocation with the energies of σ- and π-bonds.

Analogous result was obtained by correlating the experimental values of λ_{max} for 3-methylanthrarufin [20] with E_{HOMO} and E_{LUMO}:

$$\lambda_{max} = (115.5\pm45.8)E_{HOMO} + (1427\pm394),\ \text{nm}; \quad (13)$$
$$N = 3,\ r = 0.93,\ s = 18\ \text{nm};$$
$$\lambda_{max} = (157\pm14) - (81.8\pm4.1)E_{LUMO},\ \text{nm}; \quad (14)$$
$$N = 3,\ r = 0.9987,\ s = 2.5\ \text{nm}.$$

Therefore, isomeric transformations promoted by protonation of anthrarufin involve mainly excited states of the protonated species. As we found previously, the excited states of α- [24] and α,β-hydroxy-substituted anthraquinones [25] are more sensitive to tautomeric transformations than their ground states.

Shifts of λ_{max} for 3-methylanthrarufin and anthrarufin dication, accompanying their isomer transformations, are related to the energy of both σ- and π-bonds:

$$\lambda_{max}(\text{3-Me}) = (1996\pm17)E_{\sigma} - (149837\pm54920),\ \text{nm}; \quad (15)$$
$$N = 3,\ r = 0.94,\ s = 17\ \text{nm};$$
$$\lambda_{max}(\text{3-Me}) = (2217\pm132) - (63.56\pm4.71)E_{\pi},\ \text{nm}; \quad (16)$$
$$N = 3,\ r = 0.997,\ s = 3.7\ \text{nm};$$
$$\lambda_{max}(\text{1,5-H}_2^+) = (1686\pm291)E_{\sigma} - (126442\pm21914),\ \text{nm}; \quad (17)$$
$$N = 3,\ r = 0.985,\ s = 8.7\ \text{nm};$$
$$\lambda_{max}(\text{1,5-H}_2^+) = (2818\pm133) - (83.85\pm4.87)E_{\pi},\ \text{nm}; \quad (18)$$
$$N = 3,\ r = 0.998,\ s = 3.0\ \text{nm}.$$

The correlations with E_{π} are more distinct (the corresponding correlation coefficients are considerably higher), but λ_{max} is more sensitive to variation of the σ-bond energy, as compared to the π-bond energy (by a factor of 1686 : 83.85 ≈ 20 for anthrarufin dication).

Differences between the chrysazine monocation isomers show a stronger relation with the σ-bond energy (Fig. 4), and the sensitivity to variation of the σ-bond energy is higher by a factor of 30000 : 113.3 = 265 [Eqs. (19), (20)].

$$\lambda_{max} = (2.258\pm0)E_{\sigma} - (30000\pm0),\ \text{nm}; \quad (19)$$
$$N = 3,\ r = 1.00000,\ s = 0.0\ \text{nm};$$
$$\lambda_{max} = (3628\pm522) - (113.3\pm18.8)E_{\pi},\ \text{nm}; \quad (20)$$
$$N = 3,\ r = 0.986,\ s = 10.6\ \text{nm}.$$

Thus using 1,5- and 1,8-dihydroxyanthraquinones as examples we showed that isomerism is also typical of protonated anthraquinones. We were the first to reveal that absorption maxima of π_l,π^* bands in the electronic absorption spectra of these compounds

characterize their isomeric structures. The results of the present study demonstrated once more that tautomerism and rotational isomerism in organic chemistry play a more important role than it was believed so far and proved the efficiency of our methodology for studying such transformations on new compounds.

REFERENCES

1. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Russ. J. Org. Chem*., 2009, vol. 45, p. 374.
2. Gorelik, M.V., *Khimiya antrakhinonov i ikh proizvodnykh* (Chemistry of Anthraquinones and Their Derivatives), Moscow: Khimiya, 1983.
3. Fain, V.Ya., *9,10-Antrakhinony i ikh primenenie* (9,10-Anthraquinones and Their Applications), Moscow: Tsentr Fotokhimii Ross. Akad. Nauk, 1999.
4. Formánek, J., *Spektralanalytischer Nachweis künstlicher organischer Farbstoffe*, Berlin: Springer, 1900.
5. Perkin, W.H., *J. Chem. Soc*., 1870, vol. 23, p. 133.
6. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Russ. J. Org. Chem*., 2006, vol. 42, p. 1662.
7. Gorelik, M.V., Nesterova, N.I., Mikhailova, T.A., and Kukushkina, M.L., *Zh. Org. Khim*., 1989, vol. 25, p. 2046.
8. Kukushkina, M.L., Shapet'ko, N.N., Bogachev, Yu.S., and Gorelik, M.V., *Zh. Obshch. Khim*., 1990, vol. 60, p. 914.
9. Khakhalkina, I.G., Khlyupina, L.L., and Minin, A.A., *Teoriya i praktika kompleksoobrazovaniya v gomogennykh i geterogennykh sistemakh* (Theory and Practice of Complex Formation in Homogeneous and Heterogeneous Systems), Izhevsk, 1990, p. 67.
10. Gillet, H., *These Doct. Ing. Fac. Sci. Univ. Clermont-Ferrand*, 1970.
11. Marriott, G.J. and Robinson, R., *J. Chem. Soc*., 1934, p. 1631.
12. Krüss, G., *Z. Phys. Chem*., 1888, vol. 2, p. 312.
13. Schultz, G. and Lehmann, L., *Farbstofftabellen. Auflage 7. Bd. 1. Lieferungs 12/13-14/15*, Leipzig: Akademische Verlagsgesellschaft, 1930, p. 505.
14. Szadkowski, M. and Kups, W., *Biul. Inf. Barw. Srodki Pomocn*., 1986, vol. 30, p. 2.
15. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Russ. J. Org. Chem*., 2006, vol. 42, p. 1464.
16. Fain, V.Ya., *Korrelyatsionnyi analiz elektronnykh spektrov pogloshcheniya* (Correlation Analysis of Electronic Absorption Spectra), Moscow: Sputnik+, 2002.
17. Dewar, M.J.S., *The Molecular Orbital Theory of Organic Chemistry*, New York: McGraw–Hill, 1969.
18. Nishimoto, K. and Forster, L.S., *Theor. Chim. Acta*, 1966, p. 155.
19. Fain, V.Ya., *Elektronnye spektry pogloshcheniya i stroenie 9,10-antrakhinonov. I. 9,10-Antrakhinon i ego monozameshchennye* (Electronic Absorption Spectra and Structure of 9,10-Anthraquinones. I. 9,10-Anthraquinones and Its Monosubstituted Derivatives), Moscow: Sputnik+, 2003.
20. Fain, V.Ya., *Elektronnye spektry pogloshcheniya i stroenie 9,10-antrakhinonov. II. Dizameshchennye 9,10-antrakhinony* (Electronic Absorption Spectra and Structure of 9,10-Anthraquinones. II. Disubstituted 9,10-Anthraquinones), Moscow: Sputnik+, 2003.
21. Kazmi, M., Malik, A., Hameed, S., Akhtar, N., and Ali, S.N., *Phytochemistry*, 1994, vol. 36, p. 761.
22. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Russ. J. Org. Chem*., 2007, vol. 43, p. 1460.
23. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Russ. J. Gen. Chem*., 2005, vol. 75, p. 1264; *ibid*., 2006, vol. 76, p. 1431; *ibid*., 2007, vol. 77, p. 1769.
24. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Russ. J. Org. Chem*., 2005, vol. 41, p. 707.
25. Fain, V.Ya., Zaitsev, B.E., and Ryabov, M.A., *Russ. J. Org. Chem*., 2005, vol. 41, p. 38.