

# Tautomerism of Anthraquinones: V\*. 1,5-Dihydroxy-9,10-anthraquinone and Its Substituted Derivatives

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**Abstract**—1,5-Dihydroxyanthraquinone and its substituted derivatives are capable of existence in the states structurally described as 9,10-, 1,10-, and 1,5-quinoid tautomerism, and as rotational isomerism involving a cleavage of intramolecular hydrogen bond. 1,5-Quinoid tautomers are characteristic only of substituted derivatives, and also appear in some metal complexes. The considerable color changes on introducing into the 1,5-dihydroxy-anthraquinone methyl, methoxy, and sulfo groups are caused by the shift in tautomeric and conformer equilibria.

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Anthraquinones form a class of organic compounds endowed with a wide range of practically significant applicability: natural and synthetic dyes, pigments, luminophors, biologically active substances and drugs, chemicals for storing and processing information, catalysts and inhibitors of important industrial chemical processes, sensitizers of photochemical reactions, analytical reagents, indicators, and a great deal more [2].

The anthraquinones chemistry [3] is based mainly on conception of their exclusively 9,10-anthraquinoid structures. However a growing amount of facts indicates a considerably greater role of tautomeric anthraquinones in chemical [4] and photochemical [5] processes than it has been imagined for a long time. The number of known anthraquinone derivatives reaches tens of thousand. Since the majority of the practical applications of anthraquinones concern their color, the spectrophotometry holds a special position among the physicochemical methods used in their investigation. The information on electron absorption spectra [6] is very important for establishing connections between the structure and properties. Therefore much attention is drawn to the studies of the influence on the character of absorption spectra of anthraquinones structure and of the nature of environment [7].

Quantum-chemical studies showed that anthraquinones as a rule were characterized by a single  $\pi_r\pi^*$ -transition [7]. However for many groups of anthra-

quinones a more complex, often multiband  $\pi_r\pi^*$ -absorption was characteristic, and this discrepancy did not find a plausible explanation for a long time. The certain cases of considerable difference in the character of spectra of similar in structure and even identical compounds registered by different researchers also remained unclear [6]. We established [1, 8–11] that these facts were due to the existence of tautomeric and conformer equilibria. For instance,  $\alpha$ -hydroxy-anthraquinones exist in a set of states whose structural distinctions are due to tautomerism and rotational isomerism involving rupture of intramolecular hydrogen bonds. Each among these states existing in a dynamic equilibrium is characterized by a single  $\pi_r\pi^*$ -absorption band, and the color of the compound is governed by the states corresponding to the given conditions [11].

The procedure we developed based on investigating linear correlations between the experimental  $\lambda_{\max}$  of  $\pi_r\pi^*$ -bands and those resulting from quantum-chemical calculations of tautomers [8, 9] proved to be an efficient instrument for the study of tautomerism in  $\alpha$ -hydroxy-anthraquinones. The correlation analysis of the mixture of tautomers and conformers with the use of  $\sigma^A$ -constants of free (OH) and bound (OH\*) hydroxy groups and oxido groups (O<sup>-</sup>) whose values were calculated for tautomeric anthraquinones [11] revealed a number of non-obvious, even unexpected structural features of these compounds. Therefore the study of tautomerism and rotational

\* For communication IV, see [1].

**Table 1.**  $\pi, \pi^*$ -Absorption bands in the electronic spectra of 1,5-dihydroxyanthraquinones

Substituents in 1,5-dihydroxyanthraquinone	Solvent	$\pi, \pi^*$ -Bands of quinoid tautomers, nm			References	
		9,10-	1,10-	1,5-		
H	Ethanol	400in <sup>a</sup>	416	431	[12]	
2-CH <sub>3</sub>	Ethanol	396in <sup>a</sup>	420	442	[13]	
	Ethanol			436	[14]	
2-CH <sub>2</sub> OH	Ethanol		420	430	[13]	
2-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Chloroform	404	426	436	[15]	
3-CH <sub>3</sub>	Ethanol			433	[16]	
	Ethanol	400		430	470	[17]
3-CH <sub>2</sub> OH	Methanol		418	428	[18]	
2,6-(CH <sub>2</sub> OH) <sub>2</sub>	Methanol		411	436	[19]	
2,6-(SO <sub>3</sub> H) <sub>2</sub>	Water, pH 3–6		425		[20]	
2,7-(SO <sub>3</sub> H) <sub>2</sub>	Water, pH 4.0			480	[6]	
3,7-(CH <sub>3</sub> ) <sub>2</sub>	Ethanol		417	437	[21]	
7-CH <sub>3</sub> -3-OCH <sub>3</sub>	Ethanol	400		435	475	[17]
	Methanol		418			[22]
4-OAc	Methanol		420	436	[23]	
4-OCH <sub>3</sub>	Ethanol			474	[24]	
6-CH <sub>3</sub> -2,3-(OCH <sub>3</sub> ) <sub>2</sub>	Ethanol		427.5		[6]	
7-CH <sub>3</sub> -2,3-(OCH <sub>3</sub> ) <sub>2</sub>	Ethanol		420		[25]	

<sup>a</sup> “in” means inflection in the absorption spectrum.

isomerism becomes one of urgent goals of the anthraquinone chemistry. This publication is dedicated to the study of 1,5-dihydroxyanthraquinone and its substituted derivatives.

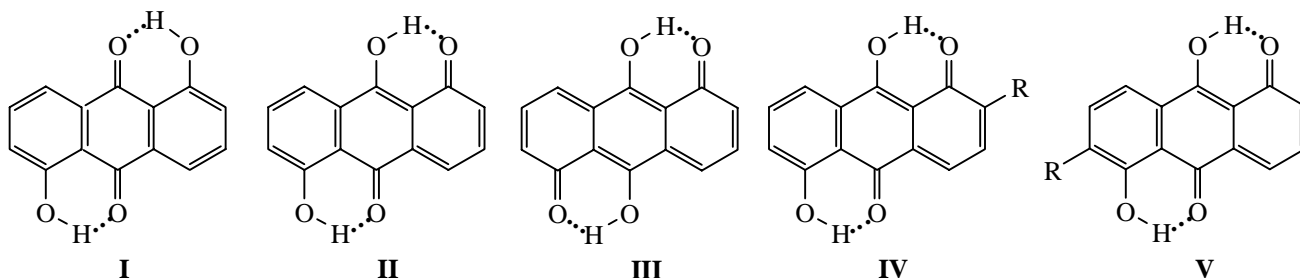
Some published data on  $\pi, \pi^*$ -bands of these compounds are compiled in Table 1.

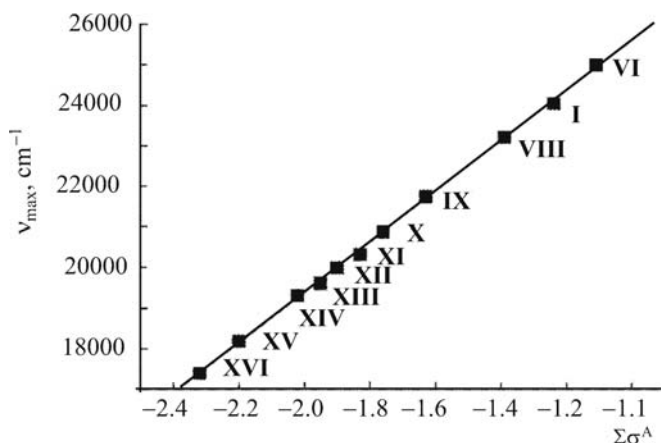
These contradictory data cannot be understood basing on the traditional concept of the exclusively 9,10-anthraquinoid structure. For instance, it is not clear why the longwave band of 1,5-dihydroxy-9,10-anthraquinone-2,6-disulfonic acid appears at 425 nm, and the corresponding band of 2,7-disulfonic acid, at 480 nm; why the spectrum of 1,5-dihydroxy-7-methyl-3-methoxy-9,10-anthraquinone in methanol contains a single  $\pi, \pi^*$ -band at 418 nm, and

in ethanol, three bands with a longwave absorption at 475 nm; why the data of different authors on the absorption spectrum of 1,5-dihydroxy-3-methyl-9,10-anthraquinone in ethanol are unlike.

These and a number of other similar facts become understandable by considering the prototropic tautomerism and rotational isomerisms in compounds under investigation.

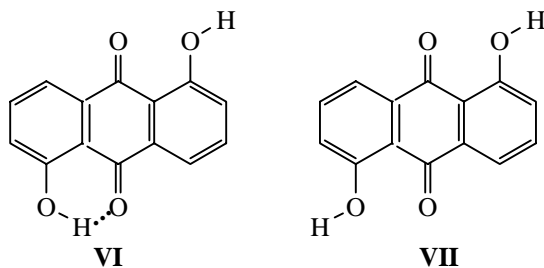
For 1,5-dihydroxy-9,10-anthraquinone and its symmetrically substituted derivatives three tautomers, 9,10- (**I**), 1,10- (**II**), and 1,5-anthraquinones (**III**) are presumable. In the case of unsymmetrical derivatives 1,10-anthraquinone may exist in the form of two tautomers, for instance, **IV** and **V**.





**Fig. 1.** Correlation of  $v_{\max}$  of 1,5-dihydroxyanthraquinone and its anions in ethanol with sum of  $\sigma^A$ -constants of hydroxy and oxido groups. Conformer ( $\lambda_{\max}$ , nm): 1,5-(OH)<sub>2</sub>-9,10- (I), (416); 1-OH-5-OH\*-9,10- (VI), (400); 5-OH-9-OH\*-1,10- (VIII), (431); 5-OH-1-O<sup>-</sup>-9,10- (IX), (460); 5-OH-9-O<sup>-</sup>-1,10- (X), (480); 9-OH-5-O<sup>-</sup>-1,10- (XI), (492); 5-OH\*-9-O<sup>-</sup>-1,10- (XII), (500); 9-OH\*-5-O<sup>-</sup>-1,10- (XIII), (510); 1,5-(O<sup>-</sup>)<sub>2</sub>-9,10- (XIV), (518); 9-OH\*-10-O<sup>-</sup>-1,5- (XV), (550); 5,9-(O<sup>-</sup>)<sub>2</sub>-1,10-anthraquinones (XVI), (580).

Each tautomer may possess conformers where one or both hydroxy groups are located in *trans*-position with respect to the carbonyl group, e.g., VI and VII.



The comparison of experimental and calculated absorption spectra of 1,5-dihydroxyanthraquinone and its anions  $\text{av}\delta\text{pa-X}\theta\text{vOva}$  we established [9] that these compounds existed as 9,10- and 1,10-quinoid tautomers. Bands corresponding to 1,5-anthraquinones were observed only in the spectra of some complexes of 1,5-dihydroxyanthraquinone with metals. The correlation of experimental  $v_{\max}$  values with the sum of  $\sigma^A$ -constants of hydroxy and oxido groups [Fig. 1, equation (1)] made it possible to refine some assignments in [9] and to establish certain structural features of 1,5-dihydroxyanthraquinone and its anions.

$$v_{\max} = (6243 \pm 54)\Sigma\sigma^A + (31859 \pm 97), \text{cm}^{-1} \quad (1)$$

Number of states  $N$  11, correlation factor  $r$  0.9997, standard deviation  $s$  62  $\text{cm}^{-1}$ .

1,5-Dihydroxy-9,10-anthraquinone in ethanol exists as two conformers, and its 1,10-quinoid tautomer, as one conformer. Equation (1) permits calculation of position of the  $\pi, \pi^*$ -band of the other theoretically presumable conformers: 1,5-(OH)<sub>2</sub>-9,10- (VII) 381 nm, 5,9-(OH)<sub>2</sub>-1,10- (XVII) 418 nm, 5-OH\*-9-OH-1,10- (XVIII) 434 nm, 5,9-(OH\*)<sub>2</sub>-1,10- (XIX) 448 nm, 9,10-(OH)<sub>2</sub>-1,5- (XX) 449 nm, 9-OH\*-10-OH-1,5- (XXI) 466 nm, and 9,10-(OH\*)<sub>2</sub>-1,5-anthraquinones (XXII) 485 nm. Among the numerous experimental spectra of 1,5-dihydroxyanthraquinone [6, 26] we have not found a single one containing the  $\pi, \pi^*$ -bands calculated for conformers VII, XXI, and XXII. Conformers I and XVII, VIII and XVIII are virtually spectrophotometrically indistinguishable. Only in two spectra a band was observed similar to those calculated for spectrophotometrically indistinguishable compounds XIX and XX, a shoulder at ~450 nm in ethanol and a maximum at 444 nm in chloroform. In the absolute majority of the spectra this band is absent. Consequently, for 5,9-dihydroxy-1,10-anthraquinone the structure with two intramolecular hydrogen bonds is less characteristic than the structure with one free OH group.

$\pi$  Electron PPP method in Dewar version [27] using approximation of variable  $\beta$  [28] remains yet the only semiempirical quantum-chemical procedure that by numerous examples was shown to be able to adequately simulate the results of structural changes in hydroxyanthraquinones. The calculations performed by this method for 1,5-dihydroxy-2-methyl-9,10-anthraquinone and its tautomers made it possible to determine the position of the methyl group in 1,10-quinoid tautomer. Of two possible states IV and V the formation of the more stable isomer is preferred. The stability of a compound in vapor is characterized by the value of atomization energy  $\Delta H$ , and in solution, by the solvation factor  $M$ . For 5,9-dihydroxy-2-methyl-1,10-anthraquinone both these values (149.461 and 3.906 eV respectively) proved to be greater than those for 5,9-dihydroxy-6-methyl-1,10-anthraquinone (149.266 and 3.863 eV). Consequently, the former structure is more stable than the latter.

Yet the calculated by PPP method  $\lambda_{\text{calc}}$  values of 1,5-dihydroxy-2- and 3-methylanthraquinones, their tautomers and anions are not in good correlation with the experimental values. The reason of this discrepancy was revealed by the correlation analysis of the experimental findings with the help of the sum of  $\sigma^A$  constants of hydroxy and oxido groups which provided a possibility to

refine the structures of tautomers. It turned out that two of the three tautomers of each of these compounds had the conformer structure containing hydroxy groups not involved into an intramolecular hydrogen bond with a carbonyl group [Fig. 2, equations (2 and 3)]. The use in the correlations of  $\lambda_{\max}$  and  $\nu_{\max}$  values gives identical results [11].

$$\lambda_{\max}(\text{2-methyl}) = (231.3 \pm 6.6) - (150.61 \pm 4.62)\Sigma\sigma^A, \text{ nm}; \quad (2)$$

$N 4, r 0.9991, s 2.5 \text{ nm}.$

$$\lambda_{\max}(\text{3-methyl}) = (315.7 \pm 4.0) - (85.37 \pm 2.82)\Sigma\sigma^A, \text{ nm}; \quad (3)$$

$N 3, r 0.9995, s 1.6 \text{ nm}.$

The given assignment of absorption bands was confirmed by a proportional response  $\lambda_{\max}$  values of 1,5-dihydroxy- and 1,5-dihydroxy-2-methyl-anthraquinones measured in ethanol [equation (4)].

$$\lambda_{\max}(\text{2-methyl}) = (1.4840 \pm 0.0096)\lambda_{\max}(\text{1,5-}) - (197.5 \pm 4.0), \text{ nm}; \quad (4)$$

$N 3, r 0.99998, s 0.2 \text{ nm}.$

An assumption of assignment of the 1,10-anthraquinoid tautomers to conformers containing the bound OH\* groups results in distortion of the correlation. The calculations by PPP procedure do not take into account these structural features and as a consequence the calculated values do not correlate with the experimental ones.

The slopes of equations (2) and (3) indicate that the transfer of the methyl group from 2 into position 3 of the anthraquinone framework results in the decrease in the sensitivity of  $\lambda_{\max}$  to tautomeric and conformer transitions  $150.61 : 85.37 = 1.8$  times.

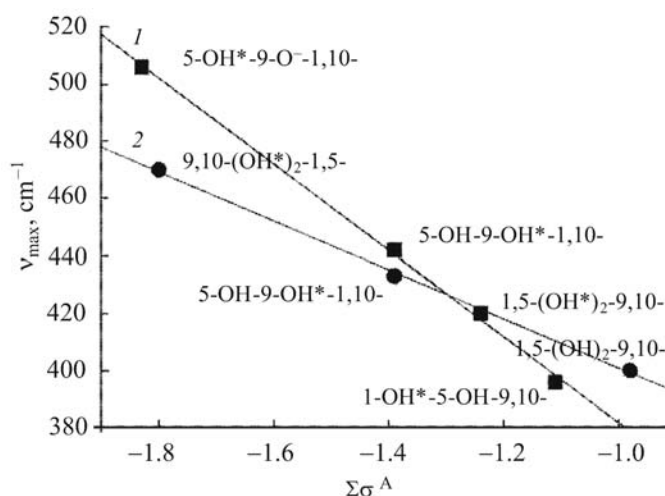
Analogously the three  $\pi, \pi^*$ -bands of 1,5-dihydroxy-2-propyl-anthraquinone were assigned to 1-OH\*-5-OH-2-propyl-9,10-, 9-OH\*-5-OH-2-propyl-1,10-, and 5,9-(OH\*)<sub>2</sub>-2-propyl-1,10-anthraquinones [equation (5)].

$$\lambda_{\max} = (319.2 \pm 2.4) - (78.53 \pm 1.77)\Sigma\sigma^A, \text{ nm}; \quad (5)$$

$N 3, r 0.9997, s 0.5 \text{ nm}.$

The slopes of equations (2) and (5) evidence that the replacement of 2-methyl group by propyl one led to the decrease in the sensitivity of  $\lambda_{\max}$  to tautomeric and conformer transitions by a factor of  $150.61 : 78.53 = 1.9$ .

Correlation analysis of the known  $\lambda_{\max}$  values of 1,5-dihydroxy-7-methyl-3-methoxyanthraquinone in ethanol using sums of  $\sigma^A$  constants of hydroxy and oxido



**Fig. 2.** Correlation of  $\lambda_{\max}$  of 1,5-dihydroxy-2- (1) and 3-methylanthraquinones (2) in ethanol with sum of  $\sigma^A$ -constants of hydroxy and oxido groups.

groups [equation (6)] allowed their assignment to 1-OH\*-5-OH-9,10-, 1,5-(OH\*)<sub>2</sub>-9,10-, 5-OH-9-OH\*-1,10-, and 9-OH-10-OH\*-1,5-anthraquinones.

$$\lambda_{\max} = (252.1 \pm 5.5) - (133.01 \pm 3.99)\Sigma\sigma^A, \text{ nm}; \quad (6)$$

$N 4, r 0.9991, SD 1.7 \text{ nm}.$

The regular character of these relationships, very high  $r$  and low  $s$  values confirm their reliability even when the number of experimental points is small.

The examples mentioned permit a conclusion that for 1,5-dihydroxyanthraquinones and their substituted derivatives an existence of conformers with free hydroxy groups is characteristic. The shift of the  $\pi, \pi^*$  absorption band on introducing into the 1,5-dihydroxyanthraquinone molecule such substituents as methyl, methoxy, and sulfo groups is caused mainly by the displacement of the existing tautomeric and conformer equilibria. It was therefore possible to make a classification of  $\pi, \pi^*$ -bands of various substituted derivatives in keeping with the structural features of these compounds (Tables 1 and 2). Unlike 1,5-dihydroxyanthraquinone some of its substituted derivatives are capable of existence in the form of 1,5-anthraquinones (Table 1).

In alkaline media the 1,5-dihydroxyanthraquinone and its substituted derivatives exist mostly as 1,10-quinoid monoanions (Table 2).

In [9] where the ionization of 1,5-dihydroxyanthraquinone was studied for the first time a discrepancy was observed between some  $\lambda_{\text{calc}}$  and experimental  $\lambda_{\text{max}}$  values. The deviating  $\lambda_{\text{calc}}$  were subjected to correction

**Table 2.**  $\pi, \pi^*$  Absorption bands of ionized 1,5-dihydroxyanthraquinones

Substituents in 1,5-dihydroxyanthraquinone	Solvent	$\pi, \pi^*$ -Bands of anions, nm							Ref.	
		mono-					di-	mono-		di-
		9,10-	1,10-				9,10-	1,5-		1,10-
		OH*	5-OH	9-OH	5-OH*	9-OH*		9-OH*		
H	Water, pH 11.4	460							[29]	
H	Alkaline ethanol		480						[26]	
H	Alkaline ethanol			492					[26]	
H	Ethanol + EtONa				500				[26]	
H	Alkaline ethanol					510			[13]	
H, complex with Nd(III)	(Solid substance)				501		518	562	576	[30]
H, complex with Th(IV)	50% aqueous. ethanol + 0.01 M. solution of NaClO <sub>4</sub>							550		[26]
H, complex with UO <sub>2</sub> (2+)	50% aqueous. ethanol + 0.01 M. solution of NaClO <sub>4</sub>								580	[26]
2-CH <sub>3</sub>	Alkaline ethanol				506					[31]
2,6-(SO <sub>3</sub> H) <sub>2</sub>	Water, pH>12					515				[32]
2,6-(SO <sub>3</sub> H) <sub>2</sub> , complex with Sc(II)	Water + deficit of Sc(II)	455								[32]
	Water + excess Sc(II)				500					[32]
2,7-(SO <sub>3</sub> H) <sub>2</sub>	Water, pH 12.4				505					[33]
6-CH <sub>3</sub> -2-OCH <sub>3</sub>	Ethanol + EtONa						520			[34]
7-CH <sub>3</sub> -2,3-(OCH <sub>3</sub> ) <sub>2</sub>	Alkaline ethanol			494						[25]

by the procedure of proportional response. As showed later studies, the cause of these discrepancies lay in the leaving out in the calculations by the applied version of PPP method of the rotational isomerism of hydroxy groups. The correlations of experimental  $\lambda_{\max}$  values with the sums of  $\sigma^A$ -constants of hydroxy and oxido groups permitted refining of the assignment of the  $\pi, \pi^*$ -bands of anions (Table 2). By equation (1) the position of  $\pi, \pi^*$ -band was calculated for the other theoretically possible anions of 1,5-dihydroxyanthraquinone: 5 OH-1-O-9,10- (**XXIII**) 444 nm, 9-OH-10-O-1,5 (**XXIV**) 528 nm, and 9,10 (O<sup>-</sup>)<sub>2</sub>-1,5-anthraquinones (**XXVI**) 640 nm. They were not detected in alkaline media.

The absorption spectra of 1,5-dihydroxyanthraquinone and its substituted derivatives in complexes with metals correspond to the state of the ligand [35]. The correlations of experimental  $\lambda_{\max}$  values of complexes with the sums of  $\sigma^A$ -constants of hydroxy and oxido groups permitted refining the structure of ligands in the given complexes (Table 2). It was confirmed that the band 550 nm in the spectrum of Th(IV) complex belonged to 1,5-quinoid

monoanion **XV**. Yet the band 580 nm in the uranyl complex proved to correspond to 1,10 quinoid dianion **XVI**. We established the reason, why positions of the  $\pi, \pi^*$ -band of the complex of dihydroxyanthraquinone-2,6-disulfonic acid with scandium(II) at deficit and excess of metal salt were different: In the former case the ligand had the structure of 9,10-quinoid monoanion, in the latter, of 1,10-quinoid monoanion.

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