ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 10, pp. 1469–1472. © Pleiades Publishing, Inc., 2006.
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Tautomerism of Anthraquinones: IV.* 1-Hydroxy-9,10-anthraquinone and Its Substituted Derivatives

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

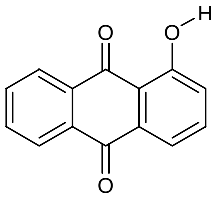
Received June 30, 2005

Abstract—1-Hydroxyanthraquinone and its substituted derivatives exist as equilibrium mixtures of four tautomers and rotational isomers. Their anions have 9,10- and 1,10-quinoid structures. Each tautomer or conformer is characterized by a single π_l,π^* band in the electronic absorption spectrum.

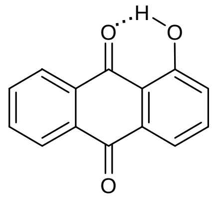
DOI: 10.1134/S1070428006100113

Over the past 150 years, anthraquinone derivatives attract persistent interest due to their wide application as natural and synthetic dyes, biologically active substances, medical agents, analytical reagents, indicators, catalysts for industrially important processes, materials for data storage and processing devices, etc. [2]. In the recent time, the interest in this class of compounds has considerably grown due to their ability to undergo tautomeric transformations. Using quantum-chemical and correlation methods, it was found that the complex character and diversity of electronic absorption spectra of anthraquinones originate from their tautomeric equilibria [3–5]. A procedure has been proposed [6] for studying tautomeric equilibria on a quantitative level on the basis of linear correlations between the experimental π_l,π^*-absorption maxima (λ_{max}) and those calculated by quantum-chemical methods for different tautomers. However, this approach turned out to be inapplicable to such simple substances as 1-hydroxy-9,10-anthraquinone and its substituted derivatives since the above correlations are valid only to a particular quinoid tautomer taken separately [7]; therefore, four points corresponding to hydroxy- and oxido-substituted tautomeric 9,10- and 1,10-anthraquinones gave rise to two isostructural series.

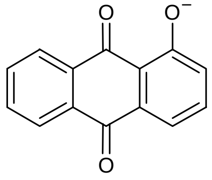
On the other hand, the number of π_l,π^* bands in the experimental absorption spectra of 1,4-di- [8], 1,4,5-tri-, and 1,4,5,8-tetrahydroxyanthraquinones [9] exceeds the number of possible tautomers; the reason is that, apart from tautomeric species, there exist rotational isomers in which the hydroxy groups are not involved in intramolecular hydrogen bonds [1]. We proposed to perform correlation analysis of α-hydroxyanthraquinone tautomers and conformers with the use of constants σ^A for free hydroxy groups (OH), H-bonded hydroxy groups (OH*), and oxido groups (O^-), which were calculated for different tautomeric anthraquinones [1]. The results revealed some unobvious and even unexpected structural features of these compounds, which stimulated a more detailed study of various groups of hydroxyanthraquinones.



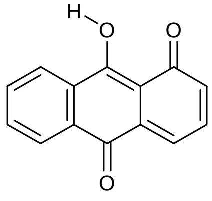
I, $\sigma^A = -0.49$



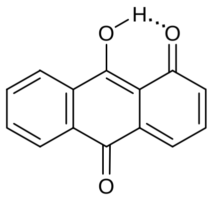
II, $\sigma^A = -0.62$



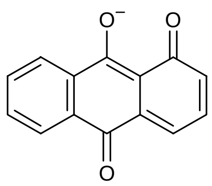
III, $\sigma^A = -1.01$



IV, $\sigma^A = -0.60$



V, $\sigma^A = -0.72$



VI, $\sigma^A = -1.09$

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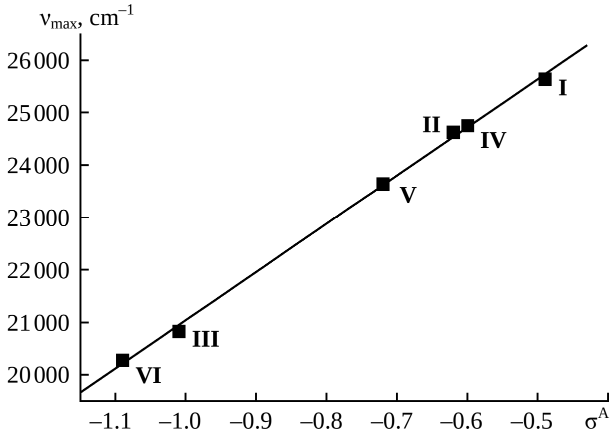
* For communication III, see [1].

Table 1. Tautomers and conformers of some substituted 1-hydroxyanthraquinones

Substituent	Solvent	λ_{max}, nm						Reference
		I	**IV**	**II**	**V**	**III**	**VI**	
H	Ethanol	390 sh		406	423			[10]
H	Ethanol		404		425			[11]
H	Ethanol					484		[12]
H	Ethanol						500	[13]
2-Me	Ethanol		404					[14]
2-Me	Ethanol	396 sh		413	430 sh		510	[15]
2-Pr-*i*	Ethanol	395	413		435			[16]
2-COOH	Ethanol			400				[17]
2-COOH	Methanol				425			[18]
2-COOH	Ethanol + NaOH					490	510	[19]
3-Me	Ethanol	389 sh		404	422			[20]
3-CH_2OH	Methanol	387 sh		402				[21]
4-Me	Ethanol		406		420	478		[14]
5-SO_3H	Water	395				483		[22]
5-SO_3H	Water, pH 9.55						503	[23]

1-Hydroxyanthraquinone and anions derived therefrom could give rise to six forms characterized by six π_l,π^* bands and six constants σ^A.

The π_l,π^* absorption of 1-hydroxyanthraquinone is a broad band centered at λ ~405 nm with two shoulders at λ ~390 and 425 nm. The experimental π_l,π^* bands (Table 1) were assigned to the corresponding structures using correlation (1) (see figure, Table 2). Similarity in the σ^A values suggests that structures **II** and **IV** are difficult to distinguish by spectrophotometry.



Correlation between ν_{max} for 1-hydroxyanthraquinone and its anions in ethanol and constants σ^A for hydroxy and oxido groups. For compound numbering, see text.

$$\nu_{max}\ (\mathrm{cm}^{-1}) = k\sigma^A + \nu_o. \tag{1}$$

Here, k characterizes the sensitivity of a compound to ionization and isomerization, and $\nu_o = \nu_{max}$ at $k = 0$.

These data confirm the assignment of the long-wave absorption bands of 1-hydroxyanthraquinone and its anion to 1,10-quinoid structures.

The values of ν_{max} for 9,10-anthraquinones with oxygen-containing substituents in ethanol are linearly related [1] to σ^A (σ^A_α and σ^A_β for α- and β-substituted derivatives, respectively [3]); this relation is described by Eq. (2):

$$\nu_{max}\ (\mathrm{cm}^{-1}) = (10\,093 \pm 129)\sigma^A + (30\,903 \pm 67); \tag{2}$$
$$N = 12,\ r = 0.9992,\ s = 123.$$

Using Eq. (2) we calculated ν_{max} for the π_l,π^* band of 1-hydroxy-9,10-anthraquinone with free hydroxy group, ν_{max} = 25 960 cm^{-1} (λ_{max} = 385 nm). Therefore, the band with its maximum at about λ 390 nm should be assigned to structure **I**, i.e., conformers having a free hydroxy group also exist for 1-hydroxyanthraquinone that is the simplest representative of α-hydroxyanthraquinones.

Contradictory published data on the substituent effect on the color of substituted anthraquinone derivatives [5] cannot be rationalized on the basis of conventional views implying exclusively 9,10-quinoid structure of these compounds. For example, it remains unclear why the long-wave absorption band of 1-hydroxy-2-methylanthraquinone in ethanol is located at λ_{max} 404 nm [14], while 1-hydroxy-2-(2-propyl)anthraquinone absorbs at λ_{max} 435 nm [16], and why introduction of a hydroxy group into the side chain of 1-hydroxy-3-methylanthraquinone induces a blue shift of the π_l,π^* band (from 422 [20] to 402 nm [21]). Different positions of the long-wave absorption maxima were reported for 1-hydroxyanthraquinone-5-sulfonic acid in alkaline medium: λ_{max} 483 [22] and 503 nm [23]. These and many other analogous findings may be rationalized by considering prototropic tautomerism and rotational isomerism of hydroxyanthraquinones. The color of each substituted 1-hydroxyanthraquinone is determined primarily by its tautomeric or conformational structure. Considerable changes in λ_{max} in the above examples are induced by displacement of tautomeric and conformational equilibria (Table 1). Table 2 shows the results of correlation analysis of ν_{max} for substituted 1-hydroxyanthraquinones.

Substituent-induced shifts of the π_l,π^* bands corresponding to similar isomers are predictable, and they depend on the substituent constants σ^A. Examples are correlations between the red shifts of π_l,π^* bands and substituent constants σ_α^A in the series of 4-substituted 1-hydroxy-9,10- [3] and 9-hydroxy-1,10-anthraquinones [24]. Correlation analysis makes it possible to not only assign π_l,π^*-absorption maxima of substituted 1-hydroxyanthraquinones to a particular tautomer and conformer but also estimate on a quantitative level the effect of the substituent nature and its position on the sensitivity of anthraquinone derivatives to ionization and isomerization. As follows from the values of coefficients *k* given in Table 2, the sensitivity depends on the position of methyl group in the anthraquinone nucleus: it decreases in the series *3 > 2 > 4*. The sensitivity of the 3-methyl-substituted anthraquinone is higher by a factor of 11157 : 9464 = 1.18 than that of the 4-methyl analog.

Analysis of published data indicates that each hydroxyanthraquinone may exist as different combinations of tautomers and conformers, but it is impossible to determine factors responsible for state of tautomeric and conformational equilibria. Systematic studies in this line should be important from the practical viewpoint, specifically for the chemistry of natural anthraquinones, where the position of π_l,π^* bands is used to determine the structure of compounds isolated from natural sources.

Table 2. Parameters of correlation (1) for substituted 1-hydroxyanthraquinones in ethanol

Substituent	*N*[a]	*r*[b]	*s*[c]	*k*	ν_o
H	6	0.9994	97	9199 ± 179	30242 ± 141
2-Me	4	0.9992	119	9518 ± 267	30030 ± 204
3-Me	3	0.9993	52	11157 ± 405	31712 ± 255
4-Me	4	0.9994	86	9464 ± 225	30519 ± 166
2-Pr-*i*	3	1.00000	8	10119 ± 50	30278 ± 30
2-COOH	4	0.9996	88	10956 ± 218	31503 ± 191
5-SO_3H[d]	4	0.9991	144	10852 ± 325	31686 ± 279

[a] Number of points.
[b] Correlation coefficient.
[c] Standard deviation, cm^{-1}.
[d] In water.

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