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# Quantum-Chemical and Correlation Study of the Tautomerism and Ionization of 1,2,3-Trihydroxy-9,10-anthraquinone

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**Abstract**—1,2,3-Trihydroxy-9,10-anthraquinone (anthragallol) exists as an equilibrium mixture of the 9,10-, 2,9-, 1,2-, and 2,3-quinoid tautomers. Its anion was detected in the 9,10-, 1,10-, 2,9-, and 2,3-quinoid forms, and its metal complexes, the 9,10- and 2,9-quinoid forms. Ionization and complexation of anthragallol can shift the tautomeric equilibrium.

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As has been shown in our preceding publications [1–5], all hydroxy-substituted anthraquinones characteristically undergo tautomerism. In this connection the chemistry of these compounds cannot be further developed in the framework of traditional 9,10-anthraquinoid structures exclusively. An excellent tool for investigation of tautomerism is a combination of spectrophotometric, quantum-chemical, and correlation methods. These methods allow one to establish the structure of hydroxyquinones and related anions and complexes, and their results have a predictive power. On the other hand, the great variety of and many contradictions in the results of absorption spectra measurements for these compounds could first be explained in terms of their tautomeric transformations.

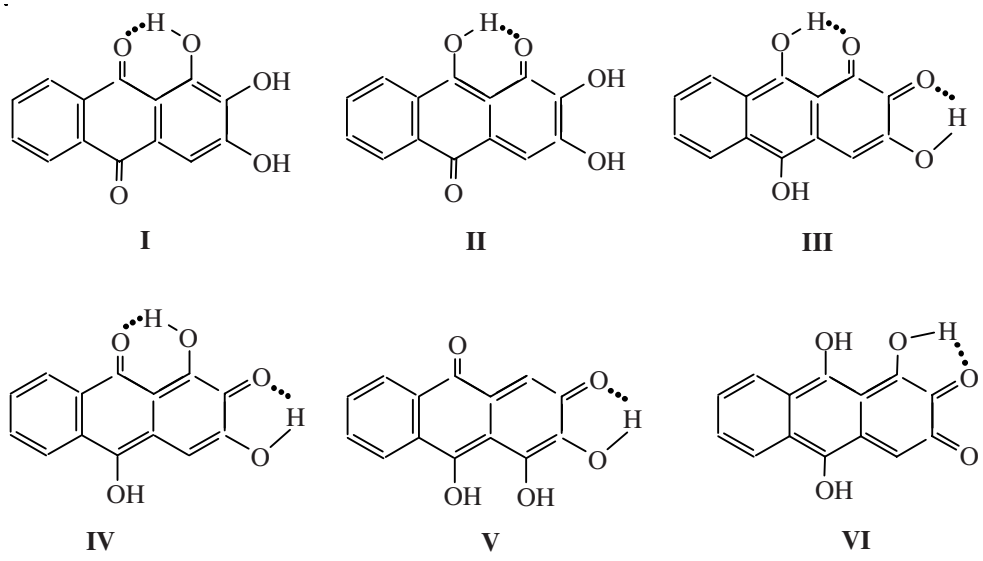
Study of tautomeric transformations becomes a priority challenge in the chemistry of quinones. This is even more important due to wide and diverse of anthraquinones. They include natural and synthetic dyes, pigments, luminophores, medicines and physiologically active preparations, chemicals for producing means for storage and treatment of information, analytical reagents, indicators, catalysts and inhibitors of important processes of chemical industry, sensitizers of photochemical reactions, etc. [6].

This work is a first published investigation of the tautomersm of 1,2,3-trihyroxy-9,10-anthraquinone (anthragallol), a natural anthraquinone that found practical application as a mordant dye, C.I. Mordant Brown 42, a reagent for quantitative and qualitative determination of metals, and as antioxidant for various technical oils [6]. Anthragallol contains three neighboring hydroxy groups and is an interesting object for studying the effect of the structure of hydroxyquinones on their tautomeric transformations and ionization.

Like with other hydroxyquinones, the contradictory published data on the electronic absorption spectra of anthragallol and its anions cannot be explained exclusively from the traditional viewpoint of their 9,10-antraquinoid structure. It is not clear, e.g. why, according to data of different researchers, the spectrum of anthragallol in ethanol contains different numbers of $\pi_l,\pi^*$ bands responsible for the color of this compound: one [7] or two [8]. Why the reported positions of its long-wave absorption bands in the same solvent vary so significantly: from 410 [9] to 450 nm [10]? Why the known test on β-hydroxy groups does not work with this compound: Adding sodium acetate to an ethanol solution of anthragallol does not induce a bathochtomic shift of the $\pi_l,\pi^*$ band (450 nm) due to ionization of the β-hydroxy group [10]? The above-mentioned contradictions can all be explained in terms of tautomeric equilibria of these compounds.

Formally, anthragallol can exist as 6 tautomers: 9,10- (**I**), 1,10- (**II**), 1,2- (**III**), two 2,9- (**IV, V**), and 2,3-anthraquinones (**VI**).

The following positions of the $\pi_l,\pi^*$-absorption bands of anthragallol have been reported, nm: in ethanol, 407.5, 413.5 [8], 410 [9], 414 [7, 11, 12], 420



**I** **II** **III**

**IV** **V** **VI**

[13], 421 [14], and 450 nm [10] and in methanol, depending on the concentration, 412 or 424 nm [15]. The data of Thompson [8] are confirmed by our measurements. Experimental $\lambda_{max}$ of anthragallol are assigned to tautomeric structures **I–VI** are assigned from a comparison with those calculated for respective tautomers by quantum-chemical methods. A criterion of correct assignment is not the best fit of calculated to experimental values but their linear correlation [16]. The Pariser–Parr–Pople (PPP) π-electron method in the Dewar version [17] in the approximation of varied β [18] still remains a unique semiempirical quantum-chemical procedure capable, as extensively exemplified, of modeling structural variations of hydroxyanthraquinones. The results obtained by such calculations are listed in the table. **VI**

Anthragallol differs from hydroxyanthraquinones we studied previously: Its theoretical absorption spectra contain 2–3 $\pi_l,\pi^*$ bands rather than one. Tautomers **I, III**, and **VI** give two bands and tautomers **II, IV**, and **V**, three bands. The $\pi_l,\pi^*$ bands of tautomer **IV** are separated by a weak $\pi,\pi^*$ band, and the absorption spectrum of tautomer **VI** features two additional weak long-wave $\pi,\pi^*$ bands.

Stability of a compound in the vapor phase is commonly characterized by the atomization energy $\Delta H$ and in solution, by the solvation coefficient $M$. For anthragallol, the $\Delta H$ values decrease in the order: **I** > **IV** > **IV** > **II** > **V** > **VI**, whereas the $M$ values decrease in quite a different order: **II** > **IV** > **V** > **IV** > **VI** > **I**. While in vapor the most stable is the 9,10-quinoid structure, in solutions it is the least stable. Hence, solvation promotes tautomeric transformations of 1,2,3-trihydroxy-9,10-anthraquinone (**I**).

Correlation between the experimental $\lambda_{max}$ and calculated $\lambda_{calc}$ values is illustrated by plot *1* in the figure and is described by Eq. (1).

$$\lambda_{max} = (0.1063\pm0.0040)\lambda_{calc} + (363\pm2), \text{ nm}. \quad (1)$$

Results of quantum-chemical calculations of anthragallol tautomers

| Comp. no. | Tautomer | $\lambda_{calc}$, nm (oscillator strength $f$) | $\Delta H$, eV | $M$, eV |
|---|---|---|---|---|
| **I** | 1,2,3-Trihydroxy-9,10-anthraquinone | 438 (0.209), 414 (0.118) | 144.307 | 2.973 |
| **II** | 2,3,9-Trihydroxy-1,10-anthraquinone | 607 (0.297), 437 (0.307), 362 (0.117) | 143.958 | 3.772 |
| **III** | 3,9,10-Trihydroxy-1,2-anthraquinone | 569 (0.489), 435 (0.005), 395 (0.233) | 144.040 | 3.088 |
| **IV** | 1,3,10-Trihydroxy-2,9-anthraquinone | 565 (0.564), 464 (0.235), 374 (0.221) | 143.971 | 3.759 |
| **V** | 3,4,10-Trihydroxy-2,9-anthraquinone | 810 (0.133), 442 (0.175), 366 (0.599) | 143.279 | 3.153 |
| **VI** | 1,9,10-Trihydroxy-2,3-anthraquinone | 1602 (0.073), 513 (0.002), 463 (0.270), 401 (0.328) | 142.646 | 3.003 |

Here the number of points $N$ = 6, correlation coefficient $r$ = 0.997, and standard deviation $s$ = 1.3 nm.

All the known experimental $\lambda_{max}$ values could be assigned to certain tautomeric structures. They turned to belong to five of the six possible anthragallol tautomers. The most unexpected fact was that the only tautomer not found in known experiments proved to be 1,10-tautomer **II** which is the most stable in solutions. Surely, further measurements in methanol may detect $\lambda_{max}$ 427.5 nm, that is predicted by Eq. (1) for tautomer **II**. However, it is obvious that the $M$ values not always unequivocally relate to the direction of tautomeric transformations, because they do not account for the effect of intramolecular hydrogen bonding and for the possible differences in the structures of complexes formed by anthragallol tautomers with ethanol.

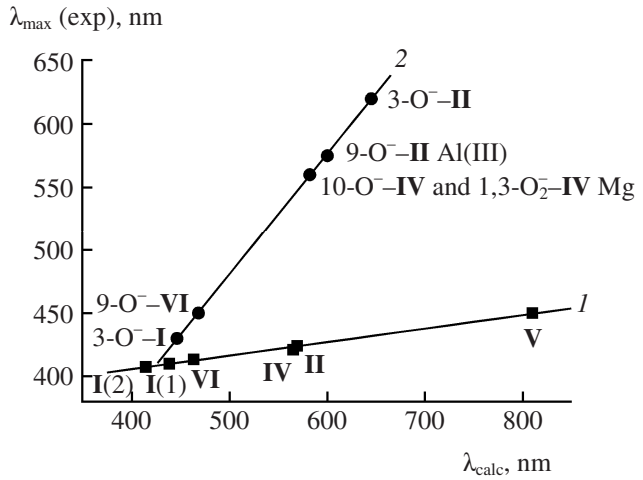
Another feature of anthragallol is that two $\pi_l,\pi^*$ bands were experimentally observed for tautomer **I** only. For other tautomers, no other bands but long-wave $\pi_l,\pi^*$ bands were detected.

Let us now consider the possible structures of anthragallol anions. In alkaline media, the first ionized hydroxy group can be those not involved into intramolecular hydrogen bonding. Our previous experience with hydroxyanthraquinone ionization shows that two negatively charged oxido groups in neighboring positions of the anthraquinone ring are energetically unfavorable and do not form.

It is unlikely that of the two possible monoanions of tautomer **I** 2-oxido derivative ($\lambda_{calc}$ 454 and 415 nm) is preferred over the anion containing a 3-oxido group (446 and 422 nm). Their $M$ values are 2.886 and 2.859, respectively, i.e. they differ less than by 1%. Both the monoanions are stabilized by a strong intramolecular hydrogen bond O–H···O$^-$. The most ionized product in a strongly alkaline medium should be the 1,3-dioxido derivative ($\lambda_{calc}$ 458 and 432 nm).

Two monoanions of tautomer **II**, the first containing a 3-oxido group ($\lambda_{calc}$ 627, 442 and 369 nm, $M$ 3.665) and the second, a 2-oxido group ($\lambda_{calc}$ 645, 436 and 371 nm, $M$ 3.638), too, are almost equally probable. They both are stabilized by a strong intramolecular hydrogen bond O–H···O$^-$. In strongly alkaline media, the intramolecular hydrogen bond 9-O–H···O=C may cleave to form either the 3,9- ($\lambda_{calc}$ 618, 465 and 372 nm, $M$ 3.508) or 2,9-dianion ($\lambda_{calc}$ 636, 458 and 377 nm, $M$ 3.482).

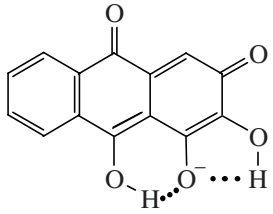
The monoanoin of tautomer **IV** is 10-oxido derivative which characteristically gives two $\pi_l,\pi^*$ bands at 585 ($f$ 0.492) and 407 nm (0.239) separated by a weak $\pi,\pi^*$ band at 436 nm (0.004). Formation of the 3,10-dianion, 608 (0.465), 447 (0.009) and 412 (0.267), and, in a strongly alkaline medium, of a trianion, 606 (0.499), 463 (0.005) and 422 (0.246) nm, is also possible.




Correlation of the experimental $\lambda_{max}$ values of (*1*) anthragallol and (*2*) its anions and metal complexes with the $\lambda_{calc}$ values obtained by the PPP method for tautomeric compounds.

Analogously, tautomer **IV** can form the 10-monoanion ($\lambda_{calc}$ 582, 464, and 384 nm), 3,10-dianion ($\lambda_{calc}$ 610, 469, and 389 nm) and a trianion ($\lambda_{calc}$ 598, 503, and 395 nm).

Tautomer **V** can form the 4-monoanion only, which is stabilized by two strong intramolecular hydrogen bonds.



Among the two possible monoanions of tautomer **VI**, the most stable one is the 9-monoanion ($\lambda_{calc}$ 468 and 403 nm) stabilized by a strong intramolecular hydrogen bond 1-O–H···O$^-$. The 9,10-dianion ($\lambda_{calc}$ 489 and 406 nm) is also possible.

Ionization of anthragallol also occurs upon addition of complex-forming salts to its solution in a neutral medium. The metal cation substitutes a hydrogen atom in the five- or six-membered chelate ring, after which

the O–M bond is ionized. The absorption spectrum of the complex compound corresponds to the spectrum of a hypothetical anion of the ligand in which the only ionized is the hydroxy group forming the intramolecular hydrogen bond. The possible anions are the 1-anion of tautomer **I** (454), 9-anion of tautomer **II** (600, 459), 9-mono- (571, 405) and 3,9-dianions (590, 410) of tautomer **III**, 1-mono- (557, 497, 381) and 1,3-dianions (582, 504, 385) of tautomer **IV**, 3-anion of tautomer **V** (862, 448, 374), and 1-anion of tautomer **VI** (473, 401). The figures in parentheses are $\lambda_{calc}$, nm.

We found in the literature only scarce data on the positions of the $\pi_l,\pi^*$-absorption bands of anthragallol anions and complexes, nm: in alkaline water, 430, 510, and 620 sh [19]; in ethanol in the presence of sodium acetate, 450, in the presence of an aluminum salt, 575, and in the presence of magnesium acetate, 560; and in aqueous methanol in the presence of germanium(IV), 575 nm [10]. By our data, the absorption spectrum of anthragallol in ethanol in the presence of sodium hydroxide contains two $\pi_l,\pi^*$ bands at 430 and 560 nm.

Correlation of the experimental $\lambda_{max}$ and calculated $\lambda_{calc}$ values for anthragallol anions is illustrated by plot *2* in the figure and is described by Eq. (2).

$$\lambda_{max} = (0.9548\pm0.0056)\lambda_{calc} + (3.7\pm3.1),\ \text{nm}, \qquad (2)$$

$$N\ 6,\ r\ 0.99993;\ s\ 1.0\ \text{nm}.$$

The value 510 nm obtained in a very old study [19] and not confirmed by more recent measurements is the only experimental observation we failed to assign. By Eq. (2), it corresponds to $\lambda_{calc}$ 530 nm, but this value was not obtained in calculations for any of the anthragallol anions. The question whether the value 510 nm is correct and belongs, e.g., to a nonplanar anion still remains open.

As seen from the figure, the known anthragallol anions have the 9,10-, 2,3-, 2,9-, and 1,10-antraquinone structures. They all are monoanions, that is, the hydroxy groups involved in intramolecular hydrogen bonding are not ionized. In the case of tautomers **I** and **II**, among the two possible monoanions whose *M* values only slightly differ from each other, the actually existing are those containing 3-oxido groups and having slightly lower *M* values than the 2-oxido isomers. This value cannot serve as an unequivocal criterion of the direction of not only tautomerization but also of ionization.

Ionization can be accompanied with tautomeric transformations. In particular, the fact that the $\lambda_{max}$ values obtained for ethanol solution of anthragallol in the absence and in presence of sodium acetate are identical to each other [10] by no means implies that sodium acetate does not ionize anthragallol. In this case, the ionization is accompanied by the transformation of the 2,9-quinoid into 2,3-quinoid tautomer .

The ligand in aluminum(III) and germanium(IV) complexes of anthragallol has the 9,10-quinoid structure and in magnesium(II) complexes, the 2,9-quinoid structure. The magnesium(II) anthragallol complex in acidified ethanol (450 nm [10]) contains an unionized 2,9-quinoid ligand. Complex formation, too, can be accompanied by tautomeric transformations.

Comparison of the slopes of Eqs. (1) and (2) shows that ionized forms of anthragallol are more sensitive to tautomerization (0.9548:0.1063 = 9) than the neutral form.

To conclude, the structures of anthragallol and its anions and metal complexes cannot be represented by single structural formulas. These compounds characteristically exist as several tautomeric forms in dynamic equilibrium. The equilibrium can be shifted under external influence. Experimental evidence was obtained for the existence of anthragallol and its anons in one or two tautomeric forms and of anthragallol metal complexes, in a single form only. Anthragallol conformers with broken hydrogen bonds were not found.

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