ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 9, pp. 1558–1566. © Pleiades Publishing, Ltd., 2012.
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1,10-Quinoid Structure and Prototropic Amino-Imine Tautomerism of α-Aminoanthraquinones

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 July 7, 2011

Abstract—Structure and amino-imine tautomerism of α-aminoanthraquinones, 1,5- and 1,8-diaminoanthraquinones, as well as 1,4,5-triamino-9,10-anthraquinones was studied. We found that in the study of properties of the compounds prone to tautomeric transformation the tautomeric composition should be taken into account.

DOI: 10.1134/S1070363212090186

Aminoanthraquinones occupy an important place in science and technology [1]. Generally, their structure is regarded as that of substituted 9,10-anthraquinones. At the same time, the chemistry of anthraquinones, which was developed for many years as the chemistry of 9,10-anthraquinone, in recent years is considered actively as the chemistry of isomeric anthraquinones, existing not independently, but in close connection with each other.

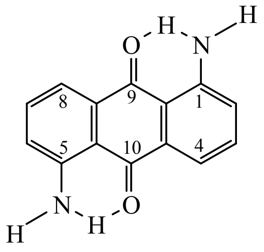
The phenomenon of tautomerism discovered and explained by Butlerov in the eighteen sixties consists in the existence of a number of substances forming an equilibrium mixture of two or more isomers, which easily transform into each other. We have previously shown that, contrary to traditional views, some α-aminoanthraquinones are neither individual compounds, nor substituted 9,10-anthraquinones. They are characterized by the prototropic amino-imine tautomerism, and they exist as dynamic equilibrium mixtures of amines and respective tautomeric imines, whose qualitative composition depends on the methods of their preparation and purification, as well as on the structure of the solvates. There are 1-amino-9,10- and 9-amino-1,10-anthraquinones (**I**), each is in a tautomeric equilibrium with imines [2]. The dye 1,4-diamino-9,10-anthraquinone exists as an equilibrium mixture of 4,9-diamino-1,10-anthraquinone (**II**) with imines of the 1,10- and 1,4-quinoid structure [3]. The substance, to which is assigned the structure of 1,4,5,8-tetraamino-9,10-anthraquinone, is actually an equilibrium mixture of 4,5,8,9-tetraamino-1,10-anthraquinone (**III**) with related tautomeric mono- and diimines [4]. It was important to reveal whether these structural features are common to the α-aminoanthraquinones.

The existence only of the fact of amino-imine tautomerism is not enough for this group of substances. It is necessary to reveal which quinoid structure is typical for each amine and imine structure. In the presence of several amino groups the tautomeric transformations can occur in different directions. Therefore it is important to know which of the many formally possible tautomers and in what sequence are formed in a certain case. This issue was not considered prior to our studies. Experimentally, the problem is solved by means of correlation analysis of electron absorption spectra (EAS) of samples of known compounds [4, 5]. An EAS is not an impersonal set of bands that characterize a compound, as it is commonly perceived. The number and position of π_l,π^*-bands responsible for the color of a compound have an objective content: they indicate the number of tautomers which are in dynamic equilibrium, and characterize the structure of each of them [3, 6]. In this paper we studied tautomeric conversion of industrially important products, known as 1,5- (**IV**), 1,8-di- (**V**) and 1,4,5-triamino-9,10-anthraquinones (**VI**), and compared the data on the structure of different α-aminoanthraquinones.

Formally, the first of these substances can have three isomeric quinoid structures: 1,5-diamino-9,10- (**IV**), 5,9-diamino-1,10- (**VII**), and 9,10-diamino-1,5-anthraquinone (**VIII**).

The tautomeric transformations of diamine **IV** may lead to monoimine **IX** and diimine **X**, of diamine **VII**, The results of PPP calculations for a-aminoanthraquinones **I–XXIV**

Comp. no.	Compound	λ_{calc}, nm	ΔH, eV	M, eV
I	9-Amino-1,10-anthraquinone	491	137.037	3.813
II	4,9-Diamino-1,10-anthraquinone	543	146.303	4.821
III	4,5,8,9-Tetraamino-1,10-anthraquinone	609	164.209	6.892
IV	1,5-Diamino-9,10-anthraquinone	467	146.634	3.802
IX	5-Amino-9-hydroxy-1,10-anthraquinone-1-imine	505	145.562	3.270
X	9,10-Dihydroxy-1,5-antraquinonediimine	565	144.468	2.800
VII	5,9-Diamino-1,10-anthraquinone	497	146.271	4.887
XI	5-Amino-1-hydroxy-9,10-anthraquinone-9-imine	450	146.154	2.720
XII	9-Amino-10-hydroxy-1,5-anthraquinone-5-imine	551	145.196	4.479
XIII	5,9-Dihydroxy-1,10-antraquinonediimine	495	145.030	2.186
VIII	9,10-Diamino-1,5-anthraquinone	533	145.947	6.179
XIV	9-Amino-5-hydroxy-1,10-anthraquinone-10-imine	490	145.781	3.788
XV	1,5-Dihydroxy-9,10-antraquinonediimine	395	145.674	1.632
V	1,8-Diamino-9,10-anthraquinone	490	146.647	3.754
XVII	8-Amino-9-hydroxy-1,10-anthraquinone-1-imine	534	145.276	2.912
XVI	8,9-Diamino-1,10-anthraquinone	517	145.930	4.422
XVIII	8-Amino-1-hydroxy-9,10-anthraquinone-9-imine	460	146.098	2.568
XIX	9-Amino-8-hydroxy-1,10-anthraquinone-1-imine	528	145.457	3.224
VI	1,4,5-Triamino-9,10-anthraquinone	563	155.692	4.691
XX	4,5,9-Triamino-1,10-anthraquinone	552	155.481	5.792
XXV	5,9-Diamino-10-hydroxy-1,4-anthraquinone-4-imine	550	154.665	3.759
XXVI	4,9-Diamino-10-hydroxy-1,5-anthraquinone-5-imine	608	154.188	5.048
XXVII	4,5-Diamino-1-hydroxy-9,10-anthraquinone-9-imine	530	155.233	3.566
XXVIII	8-Amino-4,9-dihydroxy-1,10-antraquinonediimine	551	154.048	2.828
XXIX	8-Amino-5,9-dihydroxy-1,10-antraquinonediimine	565	153.908	2.740
XXI	4,8,9-Triamino-1,10-anthraquinone	560	155.178	5.399
XXX	1,5-Diamino-4-hydroxy-9,10-anthraquinone-10-imine	524	155.156	3.472
XXXI	5,9-Diamino-8-hydroxy-1,10-anthraquinone-1-imine	562	154.533	4.123
XXXII	5,10-Diamino-9-hydroxy-1,4-anthraquinone-1-imine	543	154.612	3.681
XXXIII	5-Amino-4,9-dihydroxy-1,10-antraquinonediimine	532	154.216	3.063
XXXIV	10-Amino-4,9-dihydroxy-1,5-antraquinonediimine	600	153.605	3.762
XXII	5,8,9-Triamino-1,10-anthraquinone	580	155.031	5.352
XXXV	1,4-Diamino-5-hydroxy-9,10-anthraquinone-10-imine	556	155.153	3.505
XXXVI	4,9-Diamino-8-hydroxy-1,10-anthraquinone-1-imine	565	154.708	4.262
XXXVII	4,10-Diamino-9-hydroxy-1,5-anthraquinone-1-imine	592	154.175	5.039
XXXVIII	4-Amino-5,9-dihydroxy-1,10-antraquinonediimine	551	154.276	3.143
XXXIX	10-Amino-5,9-dihydroxy-1,4-antraquinonediimine	545	154.170	2.582
XXIII	5,9,10-Triamino-1,4-anthraquinone	555	155.162	5.032
XXIV	4,9,10-Triamino-1,5-anthraquinone	582	154.855	6.564



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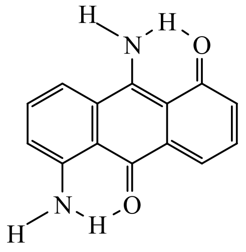

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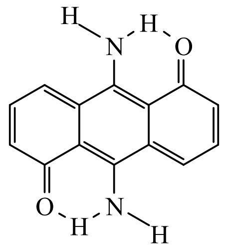

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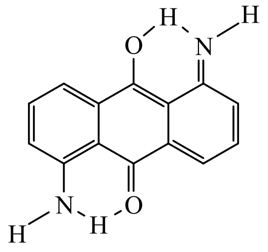

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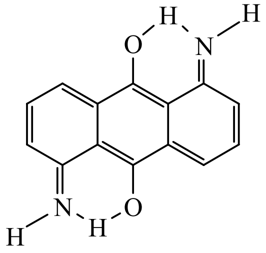

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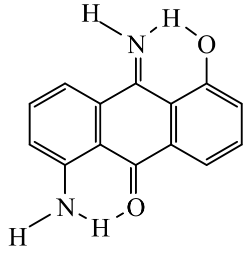

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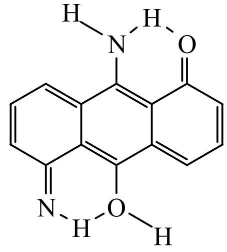

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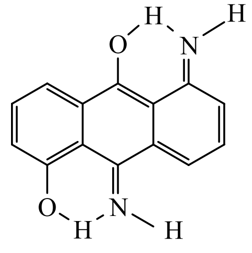

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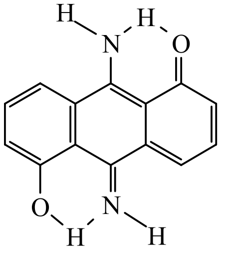
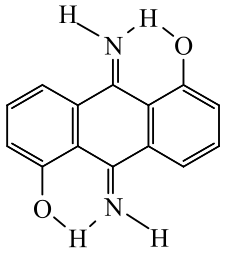


XIV



XV

to monoimines **XI, XII** and diimine **XIII**, of diamine **VIII**, to monoimine **XIV** and diimine **XV** (see the table).

Each of these compounds exists also as the *trans* conformer which does not contain one or two intramolecular hydrogen bonds. We have previously drawn attention to the fact that the ability of compounds to get a geometry providing the possibility of formation of the intramolecular hydrogen bond does not mean indispensable existence of just such a structure [7, 8].

Calculation of the diamine **IV**, its isomers, and tautomers by the π-electron method of Pariser-Parr-Pople (PPP) allowed us to establish how the tautomeric transformations affect their EAS and stability (see the table). The PPP method in the Dewar version [9] that uses the approximation of the varied β [10] is still the single semiempirical quantum chemical method which on numerous examples has demonstrated the ability to adequately and accurately simulate the results of the structural changes in anthraquinones. Modern non-empirical quantum-chemical methods are less accurate [11] and give worse results when applied to anthraquinones [12]. We have calculated all α-aminoanthraquinones and their tautomers; the table comprises just some of the results.

At the tautomeric transformations of diamine **IV** the λ_{calc} values grow in the sequence: diamine < monoimine < diimine. Therefore in the experimental EAS the short-wavelength π_l,π^*-band should belong to the diamine form. The stability of compound in the vapor state is determined by the values of the formation energy ΔH, in a solution, by the value of solvation coefficient M. In both phases, the stability of the compounds in this series decreases. If the diamine has 1,10-quinoid structure, the magnitude of λ_{calc} grows in the series: **XI** < **XIII** < **VII** < **XII**. One of the long-wavelength bands of the experimental EAS should be assigned to the diamine **VII**. If the diamine structure is expressed by 1,5-quinoid structure **VIII**, then the band of the longest wavelength must belong to it. The consideration of these patterns allows an unambiguous assignment of the experimental π_l,π^*-bands to the corresponding isomers.

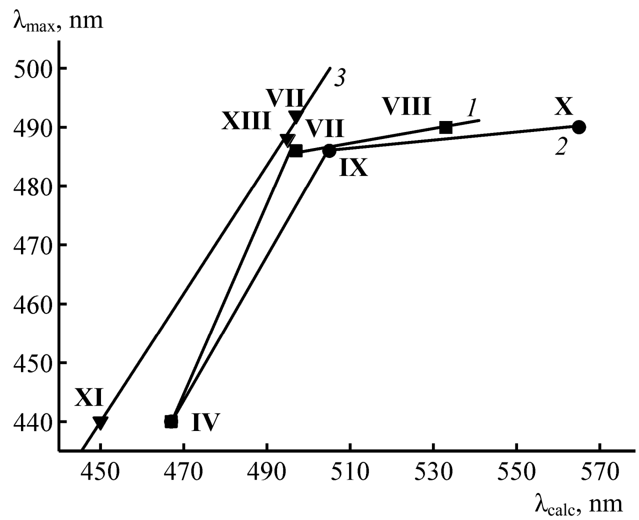


Fig. 1. Comparison of experimental values of λ_{max} of the compound known as 1,5-diaminoantraquinone, with λ_{calc} values found by PPP calculation for the isomeric diamines (*1*), 9,10- (*2*), and 1,10- (*3*) quinoid diamines and imines.

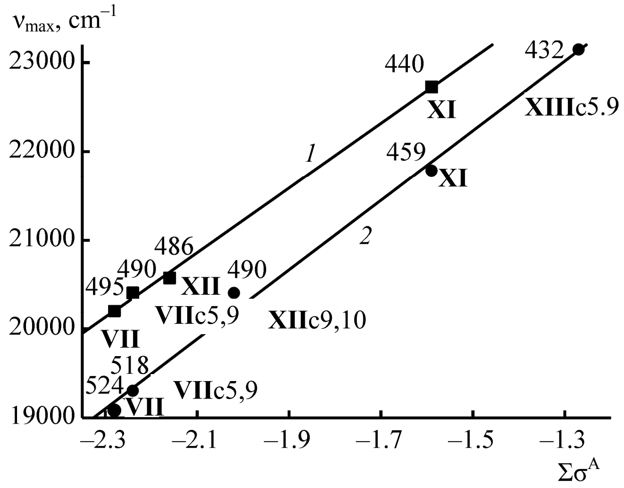


Fig. 2. The linear relationship of the experimental ν_{max} values of the compound known as 1,5 diaminoantraquinone, with the sums of the σ^A constants of substituents: (*1*) in ethanol solution, (*2*) in solid ethanol matrix at 77 K.

The EAS of a substance described in [13] typically contain one or two π_l,π^*-bands, the position of the their maxima in the case of identical environments differ markedly in the measurements of different authors. Thus, for the ethanol solutions different authors obtained only the π_l,π^*-band with maxima at 486, 490 or 495±2 nm and, for example, in [14] two π_l,π^*-bands, a band at 492 nm and shoulder at 440 nm. The difference in the positions of absorption maxima is in the range of 9 nm, that is too large to be reliably attributed to measurement errors. Previously these differences did not attract attention, probably because the researchers trusted only their own measurements, and the published data different from them were discarded as erroneous. In the solid ethanol matrix at 77 K five π_l,π^*-bands: 432, 459, 490, 518, 524 nm were measured [15]. Quantum-chemical calculations of aminoanthraquinones by different methods predict the existence of a single π_l-π^*-transition [16]. These contradictions are still not explained. Based on the results of our previous work they can be attributed to the differences in the tautomeric composition of different samples of the substance. The overall picture of the sequence of actual tautomeric transformations can be revealed only by the joint analysis of different data.

The criterion of reliability of the λ_{max} values of the corresponding tautomers characterized by the values of λ_{calc} is not the maximal similarity of these values, but their linear correlation [17]. The linear dependence of the experimental values of λ_{max} values on the λ_{calc} of the isomers **IV**, **VII**, **VIII** is lacking (Fig. 1, curve *1*). This means that these compounds are not tautomers, and each of them can exist in equilibrium with a “stranger” imines. For the diamines and their tautomeric imines, a linear relationship occurs only for 1,10-quinoid isomer **VII** [Fig. 1, curve *3*; Eq. (1)]. The most common band at 490 nm is attributed to diamine **VII**, and the bands at 440 and 486 nm, to monoimine **XI** and diimine **XIII,** respectively. This indicates the 1,10- but not 9,10-quinoid structure of the diamine.

$$\lambda_{max}(\text{ethanol}) = (1.088 \pm 0.034)\lambda_{calc} - (50 \pm 17). \quad (1)$$

Number of isomers $N = 3$, correlation coefficient $r = 0.9995$, standard deviation $s = 1.3$ nm.

Analysis of the linear relationship of the experimental ν_{max} values and the sums of σ^A constants of substituents proposed for anthraquinones [17] and calculated for the isomeric quinoid structures [3] shows that not only the diamine **VII** may be involved in the equilibrium, but also respective *trans*-conformers, for example, **VII,** conf. 5,9 [Fig. 2, curve *1*; Eq. (2)]. Here the Arabic numerals denote the position of the substituents, whose rotation destroys the intramolecular hydrogen bonds. Perhaps this causes the difference in the measurements of the band around 490 nm. The observation was confirmed [18] that the correlation between the sum of σ^A constants of substituents was a more subtle instrument of assignment of bands to tautomers than the comparison with the PPP calculated values.

$$\nu_{\max} = (3646 \pm 111)\,\Sigma\sigma^{A} + (28\,516 \pm 232)\ \text{cm}^{-1}, \quad (2)$$
$$N = 4,\ r = 0.9991,\ s = 62\ \text{cm}^{-1}.$$

In the solid ethanol matrix at 77 K a part of the tautomers involved in equilibrium includes the *trans* conformers [Fig. 2, curve *2*; Eq. (3)].

$$\nu_{\max} = (3966 \pm 67)\,\Sigma\sigma^{A} + (28\,148 \pm 127)\ \text{cm}^{-1}, \quad (3)$$
$$N = 4,\ r = 0.9992,\ s = 58\ \text{cm}^{-1}.$$

With accounting for the fact that the point for the conformer (**XII,** conf. 9,10) slightly deviates from the straight line due probably to inaccurate measuring, the value of $r = 0.9973$. This pattern allows us to refine the position of π_l,π^*-band of this conformer: 495 nm. The values of the slopes in the Eqs. (2), (3) show a slight (10%) increase in sensitivity of π_l,π^*-bands toward tautomerization with decreasing temperature.

Lowering the medium temperature promotes participation in equilibrium of more tautomers and *trans*-conformers, in good agreement with the results obtained for the other anthraquinone derivatives [15]. This explains the cause of formation at 77 K of the EAS with more π_l,π^*-bands than observed at room temperature. Lowering the temperature leads to a red shift of the bands, and the numerical coincidence of some $\lambda_{\max}$ values with those measured at room temperature does not imply their identity.

Of the eight formally possible imines **IX**–**XV,** only three actually exist in ethanol medium: the monoimines **XI**, **XII** and diimine **XIII**. As far as each stage of the tautomeric transformations is associated with the migration of one of the active hydrogen atoms involved in the intramolecular hydrogen bonding, there is the following sequence of transformations:

XI ⇄ **VII** ⇄ **XII** ⇄ [**XIII**] ⇄ [**XIII**c9] ⇄ **XIII**c5,9
⇅ ⇅
VIIc5,9 ⇄ **VII**c9 [**XII**c9] ⇄ **XII**c5,9

Conformers, whose numbers are enclosed in brackets, are involved in equilibria as intermediates, and they were not yet found in the EAS. We failed to distinguish the conformers with one substituent free of intra-H-bond IHB in a position 5 or 9.

Equation (2) makes it possible to calculate the position of π_l,π^*-bands for all possible tautomers of the diamine **VII** and respective *trans*-conformers, which allows the prediction of the EAS when the tautomeric transformations occur in another direction due to the external influence.

Analysis by the above two methods of the EAS measured in hexane (460, 482 sh [19], 473 nm [20]) or toluene (467, 488 sh [19], 476 nm [21]) showed a difference in the tautomeric composition in these solvates. In toluene, in the tautomeric transformations, along with the diamine **VII** and monoimine **XI,** the mono-imine **XII** is involved [Eq. (4)], and in hexane its *trans* conformer (**XII,** conf. 9,10) [Eq. (5)]:

$$\lambda_{\max}(\text{toluene}) = (1.088 \pm 0.034)\lambda_{\text{calc}}\,(50 \pm 17), \quad (4)$$
$$N = 3,\ r = 0.9991,\ s = 0.6\ \text{nm};$$

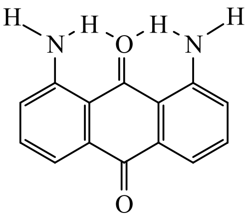
$$\nu_{\max}(\text{hexane}) = (1433 \pm 35)\Sigma\sigma^{A} + (24\,022 \pm 69), \quad (5)$$
$$N = 3,\ r = 0.9997,\ s = 17\ \text{cm}^{-1}.$$

At room temperature, in the neutral hexane and toluene, and in the amphiprotic ethanol, the tautomeric conversion of diamine **VII** is possible in both possible directions: formation of monoimines with 9,10- (**XI**) and 1,5-quinoid structure (**XII**). Less stable diimine (**XIII,** conf. 5, 9) is formed only at 77K.

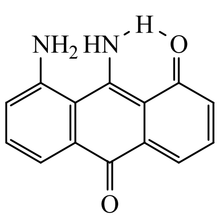
XI ⇄ **VII** ⇄ **XII** ⇄ [**XII**c9] ⇄ **XII**c9,10
⇅
[**XIII**] ⇄ [**XIII**c9] ⇄ **XIII**c5,9

The values of the slopes in the Eqs. (2) and (5) indicate that the sensitivity of π_l,π^*-bands toward tautomerization is 3646:1433 ≈ 2.5 times higher in ethanol than in hexane.

The substance known as 1,8-diamino-9,10-anthraquinone **V** probably has isomeric structure 8,9-diamino-1,10-anthraquinone **XVI**:

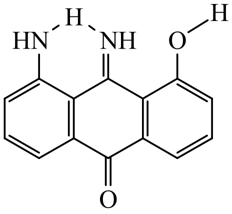


V

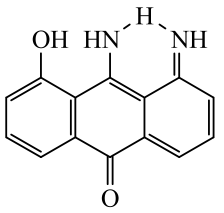


XVI

The diamine **V** can exist as two *trans*-conformers: (**V,** conf. 8) and (**V,** conf. 1,8); diamine **XVI** can have only one *trans*-conformer (**XVI,** conf. 9). Tautomeric transformations can only lead to monoimine structures **XVII–XIX**, each can form the corresponding *trans*-conformer.



XVIII



XIX

According to quantum-chemical calculations, if the diamine has the 9,10-quinoid structure **V**, then a short-wavelength π_l,π^*-band in the experimental EAS should belong to it, or if its structure is 1,10-quinoid **XVI,** then the middle of the three possible π_l,π^*-bands corresponds to it. In most solvents EAS contain only one π_l,π^*-band [22]. For example, in ethanol by different authors were given the values of λ_{max} 502, 504, 505, 507, 508 and 510 nm. Such values cannot belong to 9,10-quinoid diamine **V**, which absorbs at shorter wavelengths than diamine **VII**. Therefore, it is expected that a substance to which the structure **V** is assigned is actually 8,9-diamino-1,10-anthraquinone **XVI,** like other α-aminoanthraquinones. The 8 nm spread of the λ_{max} values is too great to be explained by the inaccuracy of the measurements, and it is probably the consequence of the existence of samples of this substance in the form of the *trans*-conformer (**XVI,** conf. 9). The effect of the nature of 15 solvents on the values of ν_{max} is perfectly described by the Kamlet–Taft and Koppel–Palm equations with high values of r = 0.993 [17]. This indicates the identical structure of the different solvates of amine **XVI**. However, there are also evidence of a dynamic equilibrium with the imine form **XIX**: in some neutral solvents (hexane, CCl_4, benzene) the EAS contain a long-wavelength shoulder, and in dioxane [23] three π_l,π^*-bands were recorded at 435, 458, and 490 nm. According to other reports, in the spectrum of a dioxane solution there is a sole π_l,π^*-band at 490 [24] or 493 nm [25], which should be attributed to the 1,10-diamine **XVI**. The correlation of ν_{max} values with $\Sigma\sigma^A$ required to assign the band at 435 nm to imine **XVIII**, and that at 458 nm, to imine **XIX**. The imino group in the compound **XVIII** can form the intra-H-bond with hydroxy or amino group. The correlation analysis using the variables $\Sigma\sigma^A$ does not allow us to assign the 435 nm band to the structures containing the intra-H-bond OH···N=H, but also does not allow us to determine reliably whether the NH···N=H intra-H-bond is formed. Thus, in the absence of both intra-H-bonds:

$$\nu_{max} = (3425 \pm 265)\Sigma\sigma^A + (27\,913 \pm 489), \quad (6)$$
$$N = 3,\ r = 0.997,\ s = 148\ \text{cm}^{-1}.$$

In the presence of the intra-H-bond NH···N = H the r value decreases to 0.994.

The data obtained suggest the following sequence of tautomeric and conformeric transformations: (**XVI,** conf. 9) **XVI** $\rightleftarrows$ **XVIII** $\rightleftarrows$ **XIX**.

Among all the α-aminoanthraquinones the greatest tautomeric potential has the compound known as 1,4,5-triamino-9,10-anthraquinone **VI**. The following quinoid isomers may correspond to it: 4,5,9- (**XX**), 4,8,9- (**XXI**) and 5,8,9-triamino-1,10- (**XXII**), 5,9,10-triamino-1,4- (**XXIII**) and 4,9,10-triamino-1,5-anthraquinones (**XXIV**). Each can be in dynamic equilibrium with the corresponding imines. For example, the triamine **XXII** is capable of forming three monoimines, **XXXV-XXXVII,** and two diimines, **XXXVIII** and **XXXIX**. Each tautomer may exist in 2 to 7 conformeric *trans*-forms where the 1-3 intra-H-bond does not exist. For example, to the tautomer **XXXV** correspond *trans*-conformers (**XXXV,** conf. 1), (**XXXV,** conf. 4), (**XXXV,** conf. 5), (**XXXV,** conf. 1,4), (**XXXV,** conf. 1,5), (**XXXV,** conf. 4,5), and (**XXXV,** conf. 1,4,5). The relative simplicity of the experimental EAS suggests that many of the formally possible tautomers and conformers actually formed only in a very small amount, and it is important to establish which one and in what sequence.

The known EAS in different environments contain from one to three π_l,π^*-bands. For example, in ethanol: 535 (log ε 3.18), 564 (3.31), 590 (3.29) nm [14] or 535 sh, 570, 610 [26], in 2-propanol 538 sh, 568, 607 nm [26]. The EAS of nylon colored with this dye: 535sh, 573, 617 nm [26]. In [14, 26] the information about the methods of its production and purification is not given. The lack of correlation of λ_{max} with the λ_{calc} indicates that isomers **VI**, **XXXXIV** are not tautomers and cannot exist in equilibrium with the “stranger” imines.

If we assume that 564 and 570 nm is the same band measured with different accuracy, then four different π_l,π *-bands [14, 26] form a single straight line (r = 0.9991) only in the case when the band 590 nm belongs to the 5,8,9-triamine **XXII**, and other bands, to its imine forms. This indicates that the sample [26] does not contain a triamine, the equilibrium involves only

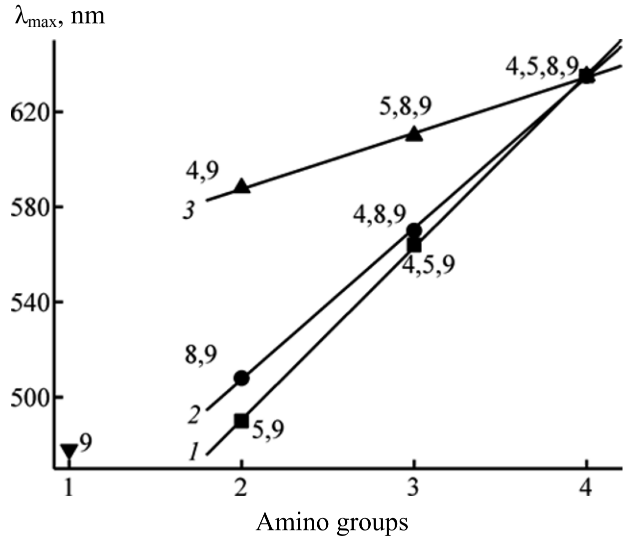


Fig. 3. Dependence of the λ_{max} values of the amino-substituted 1,10-anthraquinones in ethanol on the number of amino groups. Numbers indicate the positions of the substituents.

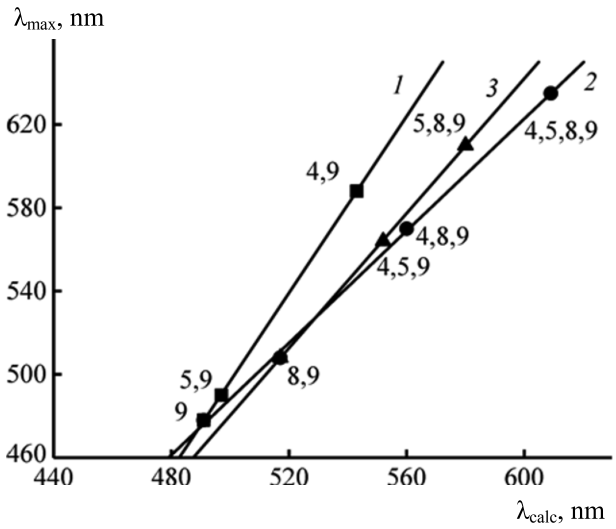


Fig. 4. Dependence of the λ_{max} values in ethanol of the amino-substituted 1,10-anthraquinones on the values of λ_{calc} calculated by the PPP method. Numbers indicate the positions of the substituents.

imine forms, that is unlikely since the amines are more stable than imines. Consequently, the amino specimens [14, 26] are isomers, but not tautomers.

The 1,10-quinoid structure of the α-amino-anthraquinone is confirmed by other independent correlation methods. Thus, in contrast to amino-9,10-anthraquinone, the values of λ_{calc} of amino-1,10-anthraquinones naturally increase with the number n of amino groups. This pattern is manifested in the form of three lines intersecting at a point for tetraamine. The pattern of the same nature occurs for the experimental values of λ_{max} measured in ethanol [Fig. 3, Eqs. (7)–(9)].

$$\lambda_{max}\text{ (line 1)} = (72.50 \pm 0.87)n + (245.5 \pm 2.7), \quad (7)$$
$$N = 3,\ r = 0.99993,\ s = 1.2\text{ nm};$$

$$\lambda_{max}\text{ (line 2)} = (63.50 \pm 0.87)n + (380.5 \pm 2.7), \quad (8)$$
$$N = 3,\ r = 0.99991,\ s = 1.2\text{ nm};$$

$$\lambda_{max}\text{ (line 3)} = (23.50 \pm 0.87)n + (540.5 \pm 2.7), \quad (9)$$
$$N = 3,\ r = 0.9993,\ s = 1.2\text{ nm}.$$

A similar pattern was found at comparing the values of λ_{max} and λ_{calc} for amino-1,10-anthraquinones [Fig. 4, Eqs. (10)–(12)], but not for the 9,10-quinoid isomers.

$$\lambda_{max}\ (1) = (2.121 \pm 0.013)\ \lambda_{calc} - (563.8 \pm 6.6), \quad (10)$$
$$N = 3,\ r = 0.99998,\ s = 0.5\text{ nm};$$

$$\lambda_{max}\ (2) = (1.346 \pm 0.030)\ \lambda_{calc} - (185 \pm 16), \quad (11)$$
$$N = 3,\ r = 0.9995,\ s = 2.7\text{ nm};$$

$$\lambda_{max}\ (3) = (1.618 \pm 0.012)\ \lambda_{calc} - (328.8 \pm 6.7), \quad (12)$$
$$N = 3,\ r = 0.99997,\ s = 0.5\text{ nm}.$$

The same conclusion was obtained at correlating the values of ν_{max} of the amine forms with the sums of σ^A constants of substituents. For example, for the amines **I**, **III**, **XVI**, and **XXI**:

$$\nu_{max} = (1523 \pm 75)\ \Sigma\sigma^A + (22\,898 \pm 238), \quad (13)$$
$$N = 4,\ r = 0.998,\ s = 195\text{ cm}^{-1}.$$

These observations allowed us the assignment of the experimental π_l,π^*-band to the isomeric triamines: 564 nm to 4,5,9-, 570 nm to 4,8,9-, 610 nm to 5,8,9-triamines. Therefore the EAS [14] describes 4,5,9-triamine **XX** in equilibrium with the respective tautomeric imines, and EAS [26] can be attributed to dynamic mixtures of 4,8,9- or 5,8,9-triamines with respective imines. The comparison of EAS [14] with the values of λ_{calc} shows that the imine forms have a structure of 9,10-monoimine **XXVII** and 1,10-diimine **XXIX**, and among the two possible interpretations of the spectrum [26] the one where the 570 nm band is attributed to the 4,8,9-triamine **XXI**, 535 nm to 9,10-monoimine **XXX**, and 610 nm to 1,5-quinoid diimine **XXXIV** is preferred as a much more accurate.

$$\lambda_{max} = (0.9871 \pm 0.0080)\ \lambda_{calc} + (17.6 \pm 4.5), \quad (14)$$
$$N = 3,\ r = 0.99997,\ s = 0.4\text{ nm}$$

We do not know an EAS which could be attributed to 5,8,9-triamine **XXII** with λ_{max} 610 nm.

The obtained results allowed us the establishment of the sequence of the actual tautomeric transformations of triaminoantraquinones:

XX ⇄ **XXVII** ⇄ **XXIX**,

XXI ⇄ **XXX** ⇄ [**XXXIII**] ⇄ **XXXIV**.

The finding that triaminoantraquinone has 1,10-quinoid structure leads to a sequence which can be regarded as curious. Formally a single 1,4,5-triamino-9,10-anthraquinone **VI** is possible, but three isomeric triamino-1,10-anthraquinones, **XXXXII**, can exist. This means that in each of the investigations of our predecessors actually one of the isomeric 1,10-quinoid triamines was studied as amine **VI**, and it remains unknown which of the properties described belonged to a certain isomer, as the isomeric structure of the investigated samples was not determined.

The angular coefficient k in equations $\lambda_{max} = k\lambda_{calc} + \lambda_0$, which we obtained for different α-aminoanthraquinones, allows the quantitative comparison of the sensitivity of these substances to tautomerism in ethanol:

Antraquinine	k
4,9-diamino-	4.416±0.132
5,9-diamino-	1.088±0.034
4,5,9-triamino-	0.722±0.045
4,8,9-triamino-	0.9871±0.0080
4,5,8,9-tetraamino-	2.875±0.057

It increases in the order: 4,5,9 < 4,8,9 < 5,9 < 4,5,8,9 < 4,9, varying in a rather wide limits: 4.416:0.722 ≈ 6 times.

The methodology of determining the structure of substance by quantum-chemical analysis of the effect of tautomeric transformations on the EAS, followed by correlation analysis of experimental data has justified itself on many compounds. Hundreds of examples, the extremely high values of r and low values of s, the similarity in assignment at the use of independent correlation methods, leave no doubt in reliability of the found pattern, despite the objectively minimum number of points involved in some of correlations. The same conclusions obtained in the analysis of the substances whose EAS contain up to 6 π_l,π^*-bands, and the correlations involved up to 12 points [7, 8, 27, 28]. All the known values of λ_{max} of all the studied substances were assigned to the corresponding tautomers. This fact is indisputable evidence that the tautomeric transformations are responsible for a variety of previously unexplained π_l,π^*-absorption bands.

Thus, the structure of α-aminoanthraquinones cannot be reflected only by their structural formulas. These compounds are characterized by 1,10-quinoid structure, and they exist in a dynamic equilibrium with the tautomeric mixtures of imines. This view is fully consistent with the Butlerov's concept of tautomerism. The chemistry of quinones is much more complicated than it still is believed. It should be estimated yet which information on the properties of aminoanthraquinones need to be revised due to the changes in views about their structure articulated in this paper.

The concepts of tautomerism of α-aminoanthraquinones and their derivatives give rise to explanation of some of measurements performed by one of the authors many years ago. Thus, the replacement of certain substituents R in 1-amino-5-R-9,10-anthraquinone, not forming the itra-H-bond, by the other led to a very small shifts of π_l,π^*-bands in the methanol solution. The shifts are proportional to the values of σ^A constants (0.05 for R = SO_3H, 0.06 for COOH, and 0.08 for Cl): 470, 474 and 475 nm, respectively. For R = CH_3 an anomalous blue shift to 461 nm is observed [29], although the value of σ^A constants for the methyl group is almost the same (0.07) [17]. The correlation analysis of the ν_{max} values of these compounds showed that the 5-methyl-substituted has the structure of 9-hydroxy-5-methyl-1,10-anthraquinone-1-imine:

$$\nu_{max} = (3404 \pm 177)\,\Sigma\sigma^A + (24\,675 \pm 177), \qquad (15)$$
$$N = 4,\ r = 0.997,\ s = 26\ \text{cm}^{-1}.$$

This fact is consistent with the observation that the chemical reactions of substances, which are characterized by tautomeric equilibrium, are often accompanied by shifts in these equilibria [18]. The study of reactions without taking this fact properly into account has already led to numerous errors. Virtually in every our publication on tautomerism we identified and resolved the existing contradictions and erroneous conclusions. To avoid new errors, it should be brought into the common practice the determination of the tautomeric composition of substances used for the investigation of any of their properties.

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