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Tautomerism of Anthraquinones: VIII.* Tautomerism and Conformations of 1,4-Diamino-9,10-anthraquinone

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Abstract—The compound widely known as 1,4-diamino-9,10-anthraquinone is in fact an equilibrium mixture of 4,9-diamino-1,10-anthraquinone and tautomeric imino forms, 10-amino-9-hydroxy-1,4-anthraquinone 1-imine and its conformer, and 4-amino-1-hydroxy-9,10-anthraquinone 9-imine or 4,9-dihydroxy-1,10-anthraquinone diimine. Amino–imino tautomerism and rotational isomerism are responsible for fine structure of the π_l,π^*-absorption of the title compound.

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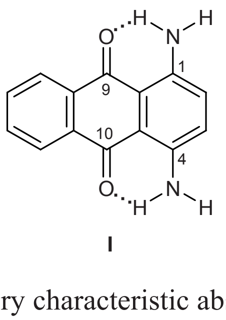
1,4-Diaminoanthraquinone (**Ia**) is one of the most important compounds in the chemistry of quinones, and it was the subject of hundreds studies. 1,4-Diaminoanthraquinone (**Ia**) is a large-scale product which is manufactured in most developed countries. It has found various practical applications [2] as bright fast synthetic dye (Disperse Violet 1, C.I. 61100), nontoxic dye for cosmetics, absorber for liquid light filters in new lighting devices, reagent for extractive photometric determination of Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, fluorometric determination of vanadium(V), and quantitative determination of gold and osmium, and metal indicator in complexometric titration. On the other hand, 1,4-diaminoanthraquinone (**Ia**) is one of the most mysterious compounds, and hot discussions on its structure have not subsided over decades. It is invariably assigned the structure of 1,4-diamino-9,10-anthraquinone (**I**).



I

It displays a very characteristic absorption spectrum containing three π_l,π^* bands in the visible region. Two bands in the long-wave region have similar intensities, and the short-wave band is less intense (it often appears as a shoulder). Such electronic absorption spectrum may be regarded as a specific "business card" of a vast number of derivatives having (alkyl, aryl)amino groups in positions *1* and *4* of the anthraquinone core [3]. These three bands were reported for the first time as early as 1900 [4]. Fine structure of the long-wave absorption of 1,4-diaminoanthraquinone has become the subject of detailed studies since 1942 [5–7].

On the other hand, quantum-chemical calculations of the electronic absorption spectrum of diamine **I** by different methods (PPP, INDO/S, *ab initio* [3]) showed that only one π_l,π^*-band responsible for the color of **I** should appear in the visible region. Numerous attempts to interpret the experimental spectra and their inconsistency with the calculated spectrum were so far unsuccessful.

The two long-wave π_l,π^*-absorption maxima were assigned [7–9] to excitation into two ionic states where the positive charge is localized on the substituents. Possible contribution of canonical structures was considered and ruled out in [10]. An attempt was made to relate the intensity ratio of the two long-wave components to aggregation [11]. However, this assumption was disproved by Sinclair and McAlpine [10] who found that the above ratio depended on the purity of the sample and thickness of polymeric film.

No success was achieved in an attempt to interpret the available experimental data [3] on the assumption that interaction of two substituents in positions *1* and *4* of the anthraquinone core gives rise to a new chromo-

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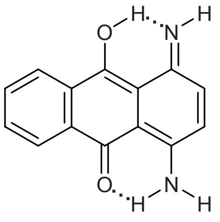
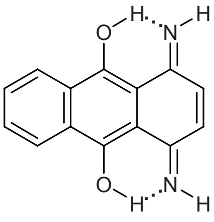
* For communication VII, see [1].

phore [7, 12] characterized by one π_l,π^*-absorption band with fine vibrational structure [13–15]. The two long-wave absorption bands of compound **Ia** are related to polarization along the long molecular axis, while the short-wave π_l,π^*-band, to polarization along the short axis [16]; therefore, they cannot be regarded as fine components of a single band. According to Kazankov [17], the deep color and fine structure of π_l,π^*-absorption of 1,4-bis[alkyl(aryl)amino]anthraquinones originate from contributions of canonical 1,10- and 1,4-anthraquinoid structures. As presumed in [3], these structures are anthraquinone imines. The results of studies on electronic absorption spectra and quantum-chemical calculations showed [15] that 1,4-bis(*p*-tolylamino)anthraquinone exists as tautomeric 9,10- and 1,4-quinoid forms.



II



III

Our studies on the tautomerism of hydroxyanthraquinones [1, 18–21] revealed that these compounds cannot be considered to be exclusively substituted 9,10-anthraquinones. It was also presumed that the same also applies to aminoanthraquinones [3]. In the present article we report the results of the first systematic study on the tautomerism of amino-substituted anthraquinone. Prototropic amino–imino tautomerism of diamine **I** was expected to give rise to 1,10- and 1,4-quinone imine derivatives **II** and **III**. We have collected and analyzed 237 electronic absorption spectra of **I** in 120 different media, including our measurements. These data were given in part in [12].

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 not by similarity between the calculated and experimental values but by the existence of a linear correlation between them [22]. The Dewar version of the Pariser–Parr–Pople (PPP) π-electron method [23] with the use of variable β approximation [24] remains so far the only semiempirical quantum-chemical method which was shown to reliably simulate structural variations in numerous anthraquinone derivatives [1, 3, 18–21].

Compound **Ia** is usually synthesized from 1,4-dihydroxyanthraquinone (quinizarin) via reduction to leucoquinizarin, treatment of the latter with concentrated aqueous ammonia under pressure, and oxidation of 1,4-diaminoanthrahydroquinone thus formed [25]. On the other hand, we recently showed [20] that quinizarin is a mixture of 9,10-, 1,10-, and 1,4-quinoid tautomers and conformers existing in dynamic equilibrium and that its chemical transformations, such as ionization and complex formation are accompanied by shifts of those equilibria [26]. Rearrangements of quinoid structures in the course of chemical reactions are well known [25]. For example, the reduction of diamine **Ia** to its leuco derivative and the formation of boron-containing complex are accompanied by rearrangement into 1,4-quinone diimine tautomers. Therefore, the synthesis of diamine **I** may be accompanied by formation of isomers **IV** and **V**, and each of the latter could undergo amino–imino tautomerism. So far unknown aminotropic tautomerism involving migration of amino group also cannot be ruled out *a priori*. If rearrangements implying migration of acyl and aryl groups do occur [25], there are no arguments against the possibility in principle for migration of other substituents that are larger than proton. Then compound **Ia** could formalistically give rise to ten tautomers **I**–**X** rather than three (**I**–**III**).

PPP quantum-chemical calculations of structures **I**–**X** (Table 1) showed that amino tautomers **I** and **V** are spectrophotometrically indistinguishable and that the λ_{max} value calculated for tautomer **IV** is lower by

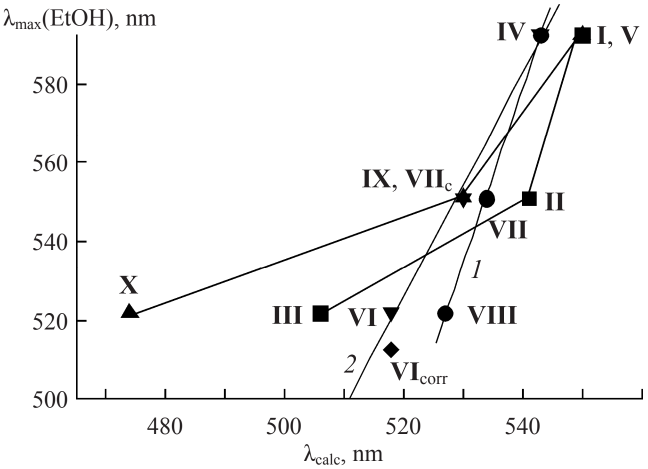
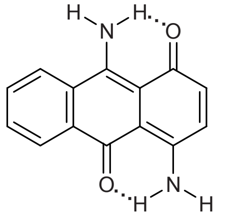
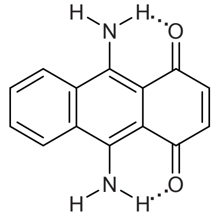


Fig. 1. Correlations between the experimental (λ_{max}) and calculated (λ_{calc}) absorption maxima of 1,4-diaminoanthraquinone. The point numbering corresponds to tautomer numbers; **VII**$_c$ stands for conformer of tautomer **VII**, and **VI**$_{corr}$ denotes the corrected value for **VI**.



IV



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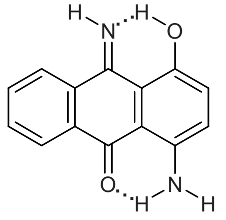
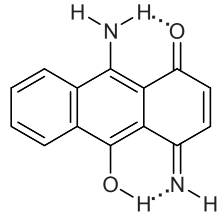
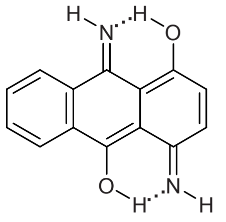


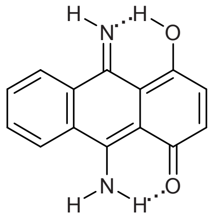
VI



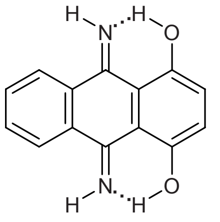
VII



VIII



IX



X

7 nm. Such spectral patterns of isomeric aminoanthraquinones are inconsistent with the experimental data on π_l,π^*-absorption of diamine **Ia**, which disproves the assignment of three π_l,π^*-bands to amines **I**, **IV**, and **V**. According to the calculations, the imino tautomers absorb at shorter wavelengths as compared to amino. Therefore, the π_l,π^*-band appearing at the longest wavelength should be assigned to amino form. In each spectrum, π_l,π^*-bands may be assigned to only one of the three diamines and to the corresponding imino tautomers. Insofar as no aminotropic tautomerism occurs, diamines cannot exist in equilibrium with "foreign" imino tautomers. If equilibrium involved all 10 tautomers, the numbers of π_l,π^*-bands in the spectra recorded in different media would be different. However, this number is almost always constant.

Figure 1 illustrates a typical example of correlation analysis of the experimental π_l,π^*-absorption data for compound **Ia**. The values λ_{max} 592.5, 551, and 522 nm (shoulder) in ethanol [8] should be assigned to 4,9-diamino-1,10-anthraquinone (**IV**) and the corresponding imino tautomers **VII** and **VIII** rather than to diamines **I** and **V** and the corresponding imines which do not fit a straight line. Correlation *1* in Fig. 2 is described by Eq. (1):

$$\lambda_{max} = (4.416\pm0.132)\lambda_{calc} - (1806\pm71)\text{ nm};$$
$$N = 3,\ r = 0.9995,\ s = 1.6\text{ nm}. \qquad (1)$$

This assignment is confirmed by the fact that isomer **IV** is characterized by the largest solvatochromic coefficient *M* (Table 1) among three possible diamines

Table 1. Calculated absorption maxima (λ_{calc}), energies of formation (ΔH), solvatochromic coefficients (M), σ- and π-bond energies (E_σ, E_π), and energies of frontier molecular orbitals (E_{HOMO}, E_{LUMO}) of 1,4-diamino-9,10-anthraquinone (**I**) and its isomers and tautomers **II**–**X**

Compound	λ_{calc},[a] nm (f)	ΔH, eV	M, eV	E_σ, eV	E_π, eV	E_{HOMO}, eV	E_{LUMO}, eV
1,4-Diamino-9,10-anthraquinone (**I**)	550 (0.429)	146.561	3.821	73.926	29.203	–7.562	–2.726
4-Amino-9-hydroxy-1,10-anthraquinone 1-imine (**II**)	541 (0.588)	145.673	3.444	73.841	27.989	–7.666	–2.960
9,10-Dihydroxy-1,4-anthraquinone diimine (**III**)	506 (0.394)	145.216	1.764	73.740	27.222	–7.983	–2.840
4,9-Diamino-1,10-anthraquinone (**IV**)	543 (0.605)	146.303	4.821	73.896	28.975	–7.535	–2.888
9,10-Diamino-1,4-anthraquinone (**V**)	550 (0.499)	146.287	4.352	73.875	28.980	–7.563	–2.803
4-Amino-1-hydroxy-9,10-anthraquinone 9-imine (**VI**)	518 (0.368)	146.088	2.649	73.855	28.390	–7.823	–2.745
9-Amino-10-hydroxy-1,4-anthraquinone 4-imine (**VII**)	534 (0.448)	145.757	3.030	73.808	28.106	–7.752	–2.825
4,9-Dihydroxy-1,10-anthraquinone diimine (**VIII**)	527 (0.586)	145.158	2.165	73.797	27.107	–7.820	–3.020
9-Amino-4-hydroxy-1,10-anthraquinone 10-imine (**IX**)	530 (0.554)	145.795	3.639	73.842	28.110	–7.724	–2.948
1,4-Dihydroxy-9,10-anthraquinone diimine (**X**)	474 (0.314)	145.602	1.524	73.781	27.567	–8.168	–2.759

[a] *f* is the oscillator strength.

I, **IV**, and **V**. The error in determination of the position of two long-wave absorption maxima usually does not exceed 1 nm, whereas the corresponding error for the short-wave shoulder is considerably larger. The above correlation makes it possible to correct its position. For this purpose, a straight line in Fig. 1 is drawn through two reliable points **IV** and **VII**, and the position of π_l,π^*-band for tautomer **VIII** is calculated using refined Eq. (1a): λ_{max} = 519 nm instead of 522 nm according to [8].

$$\lambda_{max} = 4.611\lambda_{calc} - 1911.3 \text{ nm}. \qquad (1a)$$

Nevertheless, it was impossible to assign all π_l,π^*-bands to the corresponding tautomers in most spectra. As we showed previously for hydroxyanthraquinones [20], this means that not only different tautomers but also rotational isomers (i.e., conformers formed as a result of rotation of one or two hydroxy groups with rupture of intramolecular hydrogen bonds) are involved in equilibrium. Insofar as the PPP approximation cannot be used to calculate different conformers, we proposed to study such equilibria with the aid of substituent constants σ^A [20]. To perform calculations for amine **Ia**, unknown constants σ^A for amino group were required for 1,10- and 1,4-quinoid forms. They were calculated from the linear relations between constants σ^A for free (OH) and H-bonded hydroxy groups (OH*), and oxido groups (O^-) for different quinoid tautomers (Fig. 2).

Table 2. Constants σ^A of hydroxy, oxido, and amino groups in tautomeric anthraquinones

Constant σ^A	9,10	1,4	1,10
σ^A_α(OH)	–0.49	–0.66	–0.67
σ^A_α(OH*)	–0.62	–0.81	–0.81
σ^A_α(O^-)	–1.01	–1.25	–1.23
σ^A_α(NH_2)	–0.99	–1.23	–1.21
σ^A_{meso}(OH)	–	–0.58	–0.60
σ^A_{meso}(OH*)	–	–0.71	–0.72
σ^A_{meso}(O^-)	–	–1.10	–1.09
σ^A_{meso}(NH_2)	–	–1.08	–1.07

$$\sigma^A_{meso}(1,4) = (0.882\pm0.004)\sigma^A_\alpha(9,10) - (0.0035\pm0.0037); \qquad (2)$$

$$\sigma^A_{meso}(1,10) = (0.876\pm0.005)\sigma^A_\alpha(9,10) - (0.012\pm0.004); \qquad (3)$$

$$\sigma^A_\alpha(1,4) = (1.133\pm0.005)\sigma^A_\alpha(9,10) - (0.106\pm0.004); \qquad (4)$$

$$\sigma^A_\alpha(1,10) = (1.077\pm0.000)\sigma^A_\alpha(9,10) - (0.14\pm0.00); \qquad (5)$$

for all Eqs. (2)–(5): $N = 3$, $r = 1.00000$, $s = 0.00$.

The calculated values of σ^A are collected in Table 2. Each tautomer and conformer is characterized by the

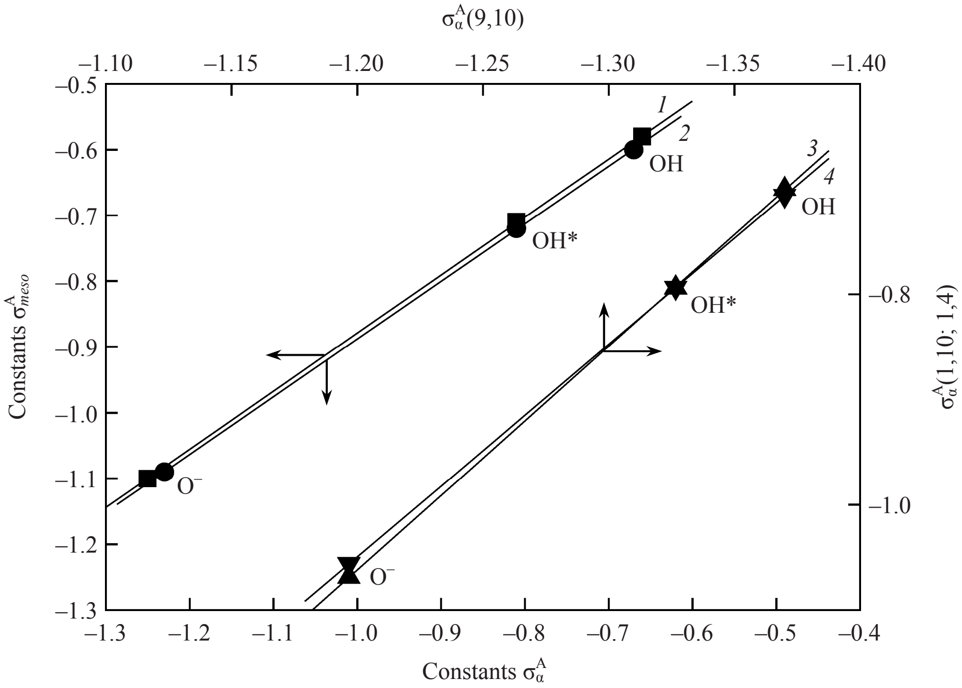


Fig. 2. Linear correlations between the constants (*1*, *2*) σ^A_α and σ^A_{meso} and (*3*, *4*) $\sigma^A_\alpha(9,10)$ and $\sigma^A_\alpha(1,10/1,4)$ for (*1*, *3*) 1,4-anthraquinones and (*2*, *4*) 1,10-anthraquinones.

Table 3. Sums of constants σ^A and calculated absorption maxima λ_{calc} for 1,4-diaminoanthraquinone tautomers and conformers

Tautomers		Conformers[a]		
comp. no.	$\sum\sigma^A$	comp. no.	$\sum\sigma^A$	λ_{calc}, nm
I	–1.98	–	–	–
II	–1.93	**II**$_c$	–1.81	535
III	–1.42	**III**$_c$	–1.16	461
		III$_{c9}$	–1.29	482.5
IV	–2.28	–	–	–
VII	–1.79	**VII**$_c$	–1.66	530
VIII	–1.53	**VIII**$_c$	–1.27	479
		VIII$_{c1}$	–1.39	500
		VIII$_{c10}$	–1.41	504
VI	–1.61	**VI**$_c$	–1.48	514
V	–2.16	–	–	–
IX	–1.88	**IX**$_c$	–1.74	524
X	–1.24	**X**$_c$	–0.98	435
		X$_c$	–1.11	453.5

[a] Structures **III**$_{c9}$, **VIII**$_{c1}$, **VIII**$_{c10}$, and **X**$_{c1}$ are conformers in which one hydroxy group (in position *9*, *1*, or *10*) is turned.

respective sum of substituent constants σ^A. From the linear relations between the wave numbers ν_{calc} and $\sum\sigma^A$ we calculated λ_{calc} for all possible conformers (Table 3), and the calculated values were used to determine tautomeric and conformational composition of amine **Ia** in different media.

Correlation analysis of a large number of electronic absorption spectra of amine **Ia** did not allow us to assign π_l,π^*-bands to tautomer **I** or **V** or the corresponding imino forms. The long-wave π_l,π^*-band always turned out to belong to diamine **IV**. However, the second and third π_l,π^*-bands could not be assigned unambiguously. As follows from the data in Table 1, among three imino tautomers of diamine **IV**, the π_l,π^*-band of quinone monoimine **VI** appears at the shortest wavelength and has the lowest intensity. Therefore, it might be expected that that the third band belongs to tautomer **VI**. Correlation analysis of the known spectra, some examples of which are given in Tables 4–6, confirmed that in most cases the third band does correspond to structure **VI**. Only in a few spectra it may be assigned to 4,9-dihydroxy-1,10-anthraquinone diimine **VIII**. The second band should be assigned to one of the three structures, imine **VII**, its conformer **VII**$_c$, or diimine **VIII** (Tables 4–6).

Let us consider a typical example of correlation analysis of π_l,π^*-bands with a view to distinguish between the above structures. Provided that the second and third π_l,π^*-bands in the spectrum of **Ia** in ethanol correspond to structures **VII$_c$** and **VI**, correlation *2* in Fig. 1 would be characterized by the parameters $r = 0.997$ and $s = 4.0$ nm, which are considerably worse than those of the correlation given by Eq. (1). In this case, the straight line passing through two reliable points **IV** and **VII$_c$** is described by the equation

$$\lambda_{max} = 3.192\lambda_{calc} - 1141 \text{ nm}. \qquad (1b)$$

The value $\lambda_{calc} = 512.5$ nm, calculated for the short-wave shoulder (**VI**$_{cor}$) by Eq. (1b), differs from the experimental value ($\lambda_{max} = 522$ nm) more strongly than does that calculated by Eq. (1a). Thus the assignment of the second and third bands to tautomers **VII** and **VIII** much better simulates the experimental spectrum, as compared to structures **VII**$_c$ and **VI**.

In most cases correlation analysis ensures unambiguous assignment of absorption bands. If two possible

Table 4. π_l,π^*-Absorption maxima of 1,4-diaminoanthraquinone tautomers in neutral media and parameters of the corresponding correlations

Medium	**IV**	**VII**$_{c.}$	**VIII**	**VI**	Reference	*r*	*s*, nm
Gas phase	525		492	470	[6]	0.9990	1.8
Hexane	575	535		500 sh	[6]	0.99988	0.8
Decane	575	535		500	[6]	0.99988	0.8
Cyclohexane	576		534	509	[10]	0.99989	0.7
Carbon tetrachloride	576	540		508	[6]	0.99994	0.5
Benzene	578	542		512	[10]	0.9997	1.1
Chlorobenzene	580	545		516 sh	[8]	0.9995	1.4
Trichlorobenzene	584	547		509 sh	[12]	0.9995	1.6

Table 5. π_l,π^*-Absorption maxima of 1,4-diaminoanthraquinone tautomers in proton-acceptor media and parameters of the corresponding correlations

Medium	**IV**	**VII**$_{c.}$	**VIII**	**VI**	Reference	*r*	*s*, nm
Methyl acetate	580	545		510	[5]	0.9997	1.1
Nitrobenzene	580	545		510	[6]	0.9997	1.1
Anisole	582	545		510	[6]	0.99998	0.4
Methyl ethyl ketone	583	546		515	[10]	0.9996	1.3
Acetone	584		543	518	[10]	0.9998	1.0
Dioxane	585	547		510 sh	[27]	0.99988	0.8
Phenyl acetate	585	547		510	[6]	0.99988	0.8
Carbon disulfide	587	550		515	[6]	0.99998	0.3
Dimethylformamide	593	553		520	[10]	0.9995	1.7
Polyethylene terephthalate	594		547	520	[10]	0.99998	0.3
Pyridine	595	556		520 sh	[12]	1.00000	0.0

Table 6. π_l,π^*-Absorption maxima of 1,4-diaminoanthraquinone tautomers in proton-donor and amphiprotic solvents and parameters of the corresponding correlations

Solvent	**IV**	**VII**	**VII**$_c$	**VIII**	**VI**	Reference	*r*	*s*, nm
Methanol	590		550		515	[10]	0.99988	0.8
Ethanol	588	548		521		[10]	0.99993	0.6
Ethanol	592.5	551		522 sh		[8]	0.9996	1.5
Propan-1-ol	590	550		520		[10]	0.99995	0.5
Butan-1-ol	592	551		520		[10]	0.99997	0.4
Pentan-1-ol	592	552		526		[10]	0.9988	2.3
Propan-2-ol	595		550		507 sh	[9]	0.99991	0.8
Acetic acid	590		550		510	[6]	0.9997	1.3
Propionic acid	590		550		510	[6]	0.9997	1.3
Acetaldehyde	588		555		521	[10]	0.9995	1.5
Water	585		546		508 sh	[28]	0.99988	0.8
Butylamine	595		555		517	[6]	0.99997	0.5
Diethylamine	595		552		510	[6]	0.99998	0.4

correlations have similar parameters, preference should be given to more stable structures. The stability of a compound in the gas phase is characterized by its energy of formation ΔH, and in solution, by the solvation coefficient M. The ΔH and M values given in Table 1 indicate that in both cases quinone monoimines are more stable than diimines. Therefore, equilibrium involving two monoimines **VII**$_c$ and **VI** is preferred to participation of quinone diimine **VIII**.

As follows from the data collected in Tables 4–6, the π_l,π^*-bands observed in most media must be assigned to structures **IV**, **VII**$_c$, and **VI**. On the other hand, λ_{calc} for tautomers **VII**, **VII**$_c$, and **VIII** are fairly similar (Tables 1, 3). Therefore, even small experimental errors resulting from different purities of samples of **Ia** and solvents could lead to different assignments of the second and third bands, and our assignments should be regarded as preliminary. A very large array of data, extremely high correlation coefficients *r*, and small standard deviations *s* leave no doubt that the above correlations are valid despite minimal number of points included thereinto.

Correlation analysis of five π_l,π^*-bands observed in a solid ethanol matrix at 77 K (λ_{max} 602.4, 590.3, 559, 523.8, and 486.8 nm [13]) allowed us to determine tautomeric and conformational composition of diamine

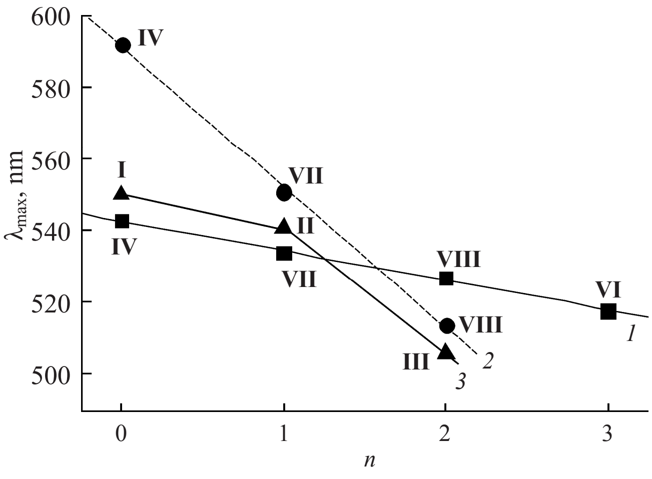


Fig. 3. Correlations of λ_{max} for 1,4-diaminoanthraquinone and the number of protons *n* involved in tautomeric transformations: (*1*) λ_{calc} for **IV** and the corresponding imino tautomers, (*2*) experimental λ_{max} in ethanol, and (*3*) λ_{calc} for tautomer **I** and the corresponding imino forms.

Ia under these conditions: the equilibrium includes structures **IV**, **VII**$_c$, **VI**, **VIII**$_{c1}$, and **VIII**$_c$:

$$\lambda_{max} = (1.856 \pm 0.039)\lambda_{calc} - (403 \pm 20)\text{ nm}; \quad (6)$$
$$N = 5,\ r = 0.9993,\ s = 2.0\text{ nm}.$$

Thus both mono- and diimine tautomers exist at 77 K, and most hydroxy groups are not involved in intramolecular hydrogen bonds but are involved in intermolecular hydrogen bonds.

The assignment of π_l,π^*-bands of **Ia** to 1,10-anthraquinone tautomer **IV** and the corresponding imino forms was confirmed by a series of independent correlations. The calculated (λ_{calc}) and experimental values (λ_{max}) were found to be linearly related to the number of migrating protons *n* [Fig. 3; Eqs. (7), (8)]. The position of the point for tautomer **VI** on straight line *1* at $n = 3$ suggests that imine **VI** is formed from diimine **VIII** rather than directly from diamine **IV**. No analogous relation was found for λ_{calc} for tautomers **I** and **V** and the corresponding imino forms (plot *3* in Fig. 3 is bent).

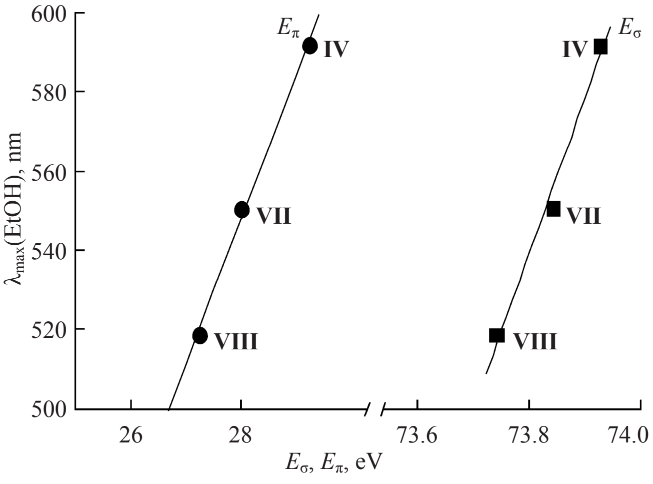


Fig. 4. Correlations between λ_{max} of 1,4-diaminoanthraquinone and (*1*) σ- and (*2*) π-bond energies.

$$\lambda_{calc} = (542.8 \pm 0.5) - (8.20 \pm 0.28)n\text{ nm}; \quad (7)$$
$$N = 4,\ r = 0.9988,\ s = 0.6\text{ nm};$$

$$\lambda_{max}(\text{EtOH}) = (591.3 \pm 1.5) - (39.00 \pm 1.15)n\text{ nm}; \quad (8)$$
$$N = 3,\ r = 0.9996,\ s = 1.6\text{ nm}.$$

We previously studied prototropic 9,10–1,10–1,4-quinoid tautomerism of quinizarin [18] and found that the experimental λ_{max} values of quinizarin and diaminoanthraquinone **Ia** in a neutral solvent (hexane) are linearly related to each other [Eq. (9)]. This indicates similar mechanisms of tautomeric transformations of these compounds and confirms prototropic character of tautomeric transformations of **Ia**.

$$\lambda_{max}(\mathbf{Ia}) = (1347.8 \pm 10.9)$$
$$- (1.631 \pm 0.022)\lambda_{max}(\text{quinizarin})\text{ nm}; \quad (9)$$
$$N = 3,\ r = 0.99991,\ s = 0.7\text{ nm}.$$

The slope of correlation (9) is negative, for prototropic amino–imino tautomerism of diamine **IV** leads to a blue shift of λ_{max}, whereas keto–enol tautomerism of quinizarin gives rise to a red shift. The π_l,π^*-band of **IV** is more sensitive to tautomeric transformations than λ_{max} of quinizarin by a factor of 1.6.

The above correlation becomes poorer in going to proton-acceptor and amphiprotic solvents; for example, the correlation in ethanol is characterized by $r = 0.997$ and $s = 4.5$ nm. This may be due to difference in the mechanisms of solvation of amphiprotic amine **Ia** and proton-acceptor quinizarin in which both hydroxy groups form intramolecular hydrogen bonds with the neighboring carbonyl groups but are not involved in intermolecular hydrogen bonding [3]. Thus the proposed methodology makes it possible to compare on a quantitative level two types of prototropic tautomerism in the anthraquinone series, keto–enol tautomerism of hydroxy-substituted anthraquinones and amino–imino tautomerism of amino-substituted anthraquinones.

The effect of solvent on the position of the long-wave π_l,π^*-band of amine **Ia** is described by the

Kamlet–Taft, Koppel'–Pal'm, and Bakhshiev equations [3]. Proportional sensitivity of λ_{max} to solvent nature was found for diamine **IV** and the corresponding imino tautomers:

$$\lambda_{max}(\mathbf{VII_c}) = (0.748 \pm 0.051)\lambda_{max}(\mathbf{IV}) + (110 \pm 30)\text{ nm}; \quad (10)$$
$$N = 18,\ r = 0.965,\ s = 1.1\text{ nm};$$

$$\lambda_{max}(\mathbf{VIII}) = (0.839 \pm 0.042)\lambda_{max}(\mathbf{IV}) + (52 \pm 24)\text{ nm}; \quad (11)$$
$$N = 6,\ r = 0.995,\ s = 2.3\text{ nm};$$

$$\lambda_{max}(\mathbf{VI}) = (0.721 \pm 0.035)\lambda_{max}(\mathbf{IV}) + (92 \pm 20)\text{ nm}; \quad (12)$$
$$N = 21,\ r = 0.98,\ s = 2.2\text{ nm}.$$

The coefficients of correlations (10)–(12) are not high, for solvent-induced shifts of the absorption bands are small; as a result, even small experimental errors inevitably appearing while measuring the spectra by different authors become significant, especially in the determination of λ values for shoulders. These data suggest similar solvent effects on the position of π_l,π^*-bands of tautomers and conformers of **Ia**. As follows from the slopes of correlations (10)–(12), the imino tautomers are less sensitive to solvent than the amino tautomer.

We previously found that λ_{max} values characterizing tautomers of 1,2,4-trihydroxyanthraquinone (purpurin) correlate with the energies of their highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO). This means that tautomeric transformations occur in both ground and excited states and that the transformations in these states are qualitatively different [19]. Analogous pattern is observed for compound **Ia**. For example, equilibrium between tautomers **IV**, **VII**, and **VIII** in the ground state in ethanol conforms to Eq. (13):

$$\lambda_{max}(\text{EtOH}) = (234 \pm 45)E_{\text{HOMO}} + (2355 \pm 48)\text{ nm}; \quad (13)$$
$$N = 3,\ r = 0.982,\ s = 9.5\text{ nm}.$$

The equilibrium in the excited state involves structures **IV**, **VII**, and **VI**, for which correlation (14) exists:

$$\lambda_{max}(\text{EtOH}) = -(487 \pm 84)E_{\text{HOMO}} - (819 \pm 237)\text{ nm}; \quad (14)$$
$$N = 3,\ r = 0.985,\ s = 8.5\text{ nm}.$$

Poor values of r and large standard deviations s for correlations (13) and (14) indicate that each state taken separately cannot be responsible completely for tautomeric transformations. Excitation promotes rearrangement of diimine **VIII** into more stable quinone monoimine tautomer **VI**. The slopes of Eqs. (13) and (14) show that λ_{max} of the excited state is more sensitive to tautomeric transformations than the ground state by a factor of 487 : 234 ≈ 2.

Tautomeric shifts of λ_{max} for quinizarin are determined mainly by change in the σ-bond energies. For example, in ethanol:

$$\lambda_{max} = (67375 \pm 7478) - (889 \pm 99)E_\sigma\text{ nm}; \quad (15)$$
$$N = 3,\ r = 0.994,\ s = 3.8\text{ nm}.$$

No analogous correlation with E_π exists. The corresponding shifts of λ_{max} for diamine **Ia** in ethanol depend on the energies of both σ- and π-bonds (Fig. 4):

$$\lambda_{max} = (392.7 \pm 49.0)E_\sigma - (28443 \pm 3617)\text{ nm}; \quad (16)$$
$$N = 3,\ r = 0.992,\ s = 6.5\text{ nm};$$

$$\lambda_{max} = (36.84 \pm 2.03)E_\pi - (482 \pm 57)\text{ nm}; \quad (17)$$
$$N = 3,\ r = 0.9985,\ s = 2.9\text{ nm}.$$

In keeping with the slopes of Eqs. (16) and (17), λ_{max} is more sensitive to the energy of σ-bonds by a factor of 392.7 : 36.84 ≈ 10, as compared to the sensitivity to the energy of π-bonds. The sensitivity of λ_{max} of diamine **Ia** is weaker by a factor of 889 : 392.7 ≈ 2 than that of quinizarin.

Thus we were the first to demonstrate that diamine **Ia** is characterized by prototropic amino–imino tautomerism. Tautomerism and rotational isomerism are responsible for the appearance of three π_l,π^*-bands in the electronic absorption spectrum of this compound. In fact, the compound commonly referred to as 1,4-diamino-9,10-anthraquinone (**I**) is not a substituted 9,10-anthraquinone. Its structure cannot be represented by a single formula, for it is an equilibrium mixture of diamine **IV**, the corresponding imino tautomers, and conformers of the latter. The state of the equilibrium is determined by external factors.

It might be expected that analogous transformations would also be typical of other amino-substituted quinones. Correlation analysis of electronic absorption spectra is an excellent tool for studying tautomerism and rotational isomerism of not only hydroxy- but also amino-substituted quinones. Our results provide an additional proof for the assumption made in our previous studies: The chemistry of anthraquinones is not exclusively the chemistry of 9,10-anthraquinones, and studies on tautomeric transformations become a foreground line in the chemistry of quinones. The obtained data extend our views on the role of tautomeric and conformational transformations in organic chemistry, and they could form the basis for new developments in nanotechnology.

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