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# Tautomeric Composition and Tautomeric Transformation Sequence of 1,4-Bis(alkylamino)anthraquinones

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**Abstract**—Compounds widely known as 1,4-bis(alkylamino)-9,10-anthraquinones are in fact neither individual substances nor substituted 9,10-anthraquinones but equilibrium mixtures of tautomers. Their amino–imine tautomeric transformations follow the sequence 4,9-bis(alkylamino)-1,10-anthraquinones ↔ 9-alkylamino-4-(alkylimino)-10-hydroxy-1,4-dihydroanthracen-1-ones ↔ $N^1$,$N^{10}$-dialkyl-4,9-dihydroxy-1,10-dihydroanthracene-1,10-diimines.

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Tautomerism implies that a substance with a definite composition and molecular weight exists as an equilibrium mixture of two or more isomers which are readily converted into each other. From this definition it follows that tautomeric compounds are not individual substances but dynamic equilibrium mixtures of tautomers. Their structure cannot be represented by a single formula.

Tautomerism of organic compounds is usually studied with a view to determine by different methods he type of their tautomeric transformations. However, the fact of the existence of a certain type of tautomerism is quite insufficient. Each potentially tautomeric compound could give rise to a definite number of formally possible isomers. Not all of these are necessarily involved in real dynamic equilibria. Tautomeric equilibria may be displaced by the action of external factors, and the number and nature of tautomers constituting a compound under study may change. This prompted us to introduce the term *tautomeric composition* as an independent parameter of a particular sample of a substance existing under certain conditions [1] rather than of a substance per se. Widespread views implying that different samples of the same substance synthesized or purified by different methods should necessarily be identical in structure and differ only by the nature and amounts of impurities are erroneous.

Determination of tautomeric compositions of known samples of such compounds makes it possible to ascertain the sequence of real tautomeric transformations [2]. This problem was not raised prior to our studies. Nevertheless, it is known that isomers exhibit different reactivities. Getting control over tautomeric equilibria could provide a tool for achieving essential improvement of the technologies for the preparation of many industrially important compounds.

An excellent method for the determination of tautomeric compositions is correlation analysis of electronic absorption spectra. Contrary to generally accepted views, electronic absorption spectra characterize a particular sample of a substance rather than that substance in a certain medium. If different samples of the same substance or similar samples under different conditions have qualitatively different tautomeric compositions, their electronic absorption spectra are also different [3]. Just that factor is responsible for differences in the electronic absorption spectra of the same compounds recorded in the same or similar media. Electronic absorption spectrum is not a featureless set of bands. The number and position of the experimental $\pi_l$,$\pi^*$-bands reflect the number of tautomers occurring in equilibrium and characterize the structure of each of them. Determination of tautomeric composition of compounds becomes an important theoretical and practical problem. Study of their properties without consideration of tautomeric composition could lead to serious errors.

In the present work we studied tautomeric compositions of a large series of compounds which

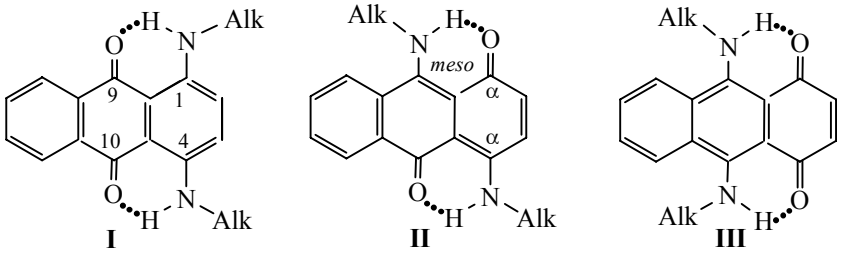
were permanently assigned the structure of 1,4-bis (alkylamino)-9,10-anthraquinones. These compounds are very important from the practical viewpoint as disperse and reactive dyes for plastics, polymeric fibers, and liquid crystalline materials, intermediate products for the synthesis of cationic dyes for poly (acrylonitrile) fiber, components of antibacterial, antiviral, and antitumor drugs, etc. [4].

The electronic absorption spectra of anthraquinones, calculated by different quantum-chemical methods (including high-level *ab initio* calculations), include only one $\pi_l,\pi^*$-band which determines their color [5]. However, experimental absorption spectra of most anthraquinones contain several absorption bands, and there are considerable discrepancies in the number of bands reported by different authors for the same compounds in similar media [5, 6]. Attempts to rationalize these contradictions in terms of the 9,10-quinoid structures were unsuccessful. Our previous studies (see, e.g., [7–11] showed that traditional views on the structure of anthraquinones need to be seriously revised.

The mere fact of tautomerism of aminoanthraquinones, which were studied by many authors with the aid of various physicochemical methods, is beyond doubt, and no additional proofs for each compound are necessary. Our studies on the tautomerism of 1,4-diamino- [10] and 1-amino-4-hydroxyanthraquinones [11] produced on a large-scale in developed countries showed that these compounds are not 9,10-anthraquinone derivatives since none of the tautomers constituting their known samples has 9,10-quinoid structure.

1,4-Bis(alkylamino)anthraquinones display in the visible region of the electronic absorption spectra two maxima with similar intensities and a short-wave shoulder [7, 8 ]. Such spectral pattern may be regarded as a specific "business card" of this group of compounds. The presence of three $\pi_l,\pi^*$-bands indicate the existence of three isomers, but it remains unclear which of the ten formally possible isomers participate in tautomeric equilibria. There are three probable reasons for the appearance of three $\pi_l,\pi^*$-bands.

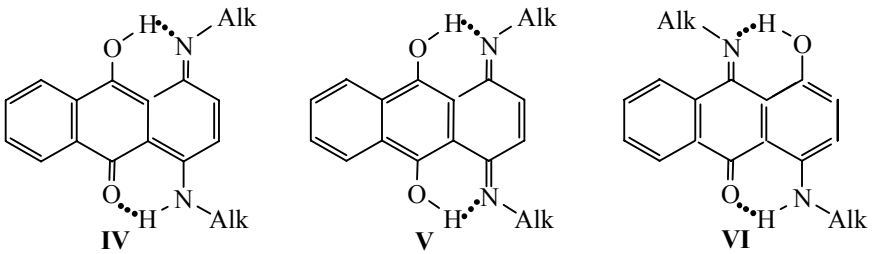
(1) Formation of three isomers during the synthesis. 1,4-Bis(alkylamino)anthraquinones are generally synthesized by reduction of 1,4-dihydroxyanthraquinone (quinizarin) to leucoquinizarin, followed by reaction of the latter with alkylamine and oxidation of 1,4-bis(alkylamino)anthrahydroquinone thus obtained [12]. As we showed previously [8], quinizarin is an equilibrium mixture of 9,10-, 1,10-, and 1,4-quinoid tautomers and conformers, and its chemical transformations are accompanied by shifts of the tautomeric and conformational equilibria [8, 13]. Therefore, 1,4-bis(alkylamino)-9,10- (**I**), 4,9-bis(alkylamino)-1,10- (**II**), and 9,10-bis(alkylamino)-1,4-anthraquinones (**III**) may be present in solution simultaneously.

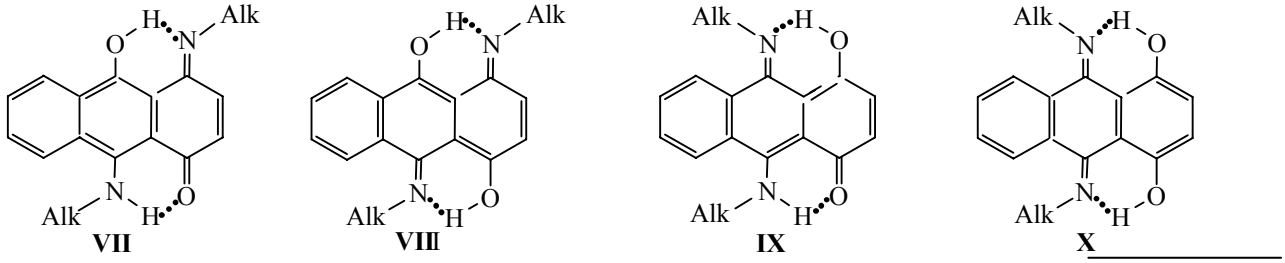



(2) Prototropic amino–imino tautomerism [10, 11]. Each isomeric bis(alkylamino)anthraquinone may exist as mono and/or diimino tautomers.

(3) Rotational isomerism involving rupture of one or both intramolecular hydrogen bonds [9]. Such isomerism is possible for each structure **I**–**X**.

Three $\pi_l,\pi^*$-bands observed in the electronic absorption spectra of a compound widely known as






1,4-diaminoanthraquinone ($\lambda_{max}$ 588, 548, and 521 nm; EtOH) were assigned, respectively, to 4,9-diamino-1,10-anthraquinone, 10-amino-9-hydroxy-1,4-anthraquinone 1-imine, and 4,9-dihydroxy-1,10-anthraquinone diimine [10]. 1,4-Bis(methylamino)anthraquinone in ethanol displayed absorption maxima at λ 646.2, 595.0, and 558.2 nm [14]. The $\lambda_{max}$ values of these two compounds are linearly related to each other [Fig. 1, *1*; Eq. (1)].

$$\lambda_{max}(\text{methylamino}) = (1.311\pm0.023)\lambda_{max}(\text{amino}) - (124\pm13)\ \text{nm}, \quad (1)$$

Number of tautomers $N = 3$, correlation coefficient $r = 0.99985$, standard deviation $c = 1.1$ nm.

The above data suggest similar tautomeric compositions of the examined samples. The slope of the dependence given by Eq. (1) indicates that the position of the $\pi_l,\pi^*$-band of the methylamino derivatives is more sensitive to tautomeric transformations by 30% as compared to 1,4-diaminoanthraquinone.

Experimentally observed $\pi_l,\pi^*$-bands may be assigned to particular tautomers by calculating absorption maxima for each tautomer [7–11]. 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 [15]; for this purpose, at least three bands are necessary. The Dewar version of the Pariser–Parr–Pople (PPP) π-electron method [16] with the use of variable β approximation [17] remains so far the only semiempirical quantum-chemical method which was shown to reliably simulate structural variations in anthraquinone derivatives [5, 7–11]. *Ab initio* calculations ensure considerably lower accuracy [18, 19].

The results of PPP calculations of all possible tautomers of 1,4-bis(methylamino)anthraquinone are given in Table 1). These data allowed us to reveal some general relations between their structure and color. Insofar as α-substituents affect the color of anthraquinones to a greater extent than do those in the *meso* positions, 9,10-quinoid structure **I** should absorb at the longest wavelength. The $\pi_l,\pi^*$-absorption maximum shifts blue in going from alkilamino to imino and then to diimino tautomers. Therefore, the experimental $\pi_l,\pi^*$-band appearing at the longest wavelength was assigned to alkylamino tautomer. Diimino tautomers of 9,10- and 1,4-anthraquinones and monoimino tautomers of 1,10-anthraquinones are characterized by the lowest intensity of the $\pi_l,\pi^*$-bands.

The stability of a compound in the gas phase is determined by the energy of formation $\Delta H$ which decreases in the series 9,10 > 1,10 > 1,4-anthraquinone. In keeping with the solvation coefficients *M*, the stability series of the same tautomers in solution is as follows: 1,10 > 1,4 > 9,10. Thus, as with hydroxyanthraquinones [7–9], solvation increases the probability for the formation of tautomeric quinoid compounds. The alkylamino structure is more stable than monoimino, and the latter is more stable than diimino, in both gas phase and solution. The stability

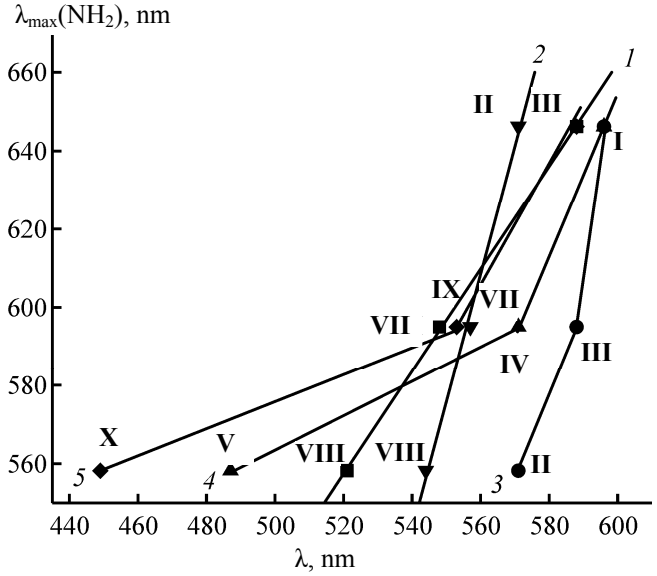



**Fig. 1.** Correlations of $\pi_l,\pi^*$-band maxima of 1,4-bis(methylamino)anthraquinone in ethanol with $\lambda_{max}$ of (*1*) 1,4-diaminoanthraquinone [$\lambda = \lambda_{max}(NH_2)$] and (*2–5*) $\lambda_{calc}$ for isomeric bis(methylamino)anthraquinones and their imino tautomers [$\lambda = \lambda_{calc}(NH_2)$].

**Table 1.** Calculated parameters of 1,4-bis(methylamino)-9,10-anthraquinone and its possible tautomers

| Comp. no. | Compound | $\lambda_{calc}$, nm (*f*) | $\Delta H$, eV | *M*, eV | $E_{HOMO}$, eV | $E_{LUMO}$, eV | $E_{\sigma}$, eV | $E_{\pi}$, eV |
|---|---|---|---|---|---|---|---|---|
| **I** | 1,4-Bis(methylamino)-9,10-anthraquinone | 596 (0.478) | 165.353 | 4.916 | –7.047 | –2.544 | 73.938 | 29.961 |
| **IV** | 10-Hydroxy-1-methylamino-4-methylimino-4,10-dihydroanthracen-9-one | 571 (0.516) | 164.791 | 3.722 | –7.217 | –2.626 | 73.839 | 29.295 |
| **V** | 9,10-Dihydroxy-$N^1$,$N^4$-dimethyl-1,4-dihydroanthracene-1,4-diimine | 487 (0.326) | 164.602 | 1.136 | –7.620 | –2.333 | 73.747 | 28.924 |
| **II** | 4,9-Bis(methylamino)-1,10-anthraquinone | 571 (0.610) | 165.252 | 5.991 | –7.098 | –2.657 | 73.908 | 29.899 |
| **VI** | 4-Hydroxy-1-methylamino-10-methylimino-9,10-dihydroanthracen-9-one | 544 (0.366) | 165.199 | 2.848 | –7.320 | –2.428 | 73.871 | 29.625 |
| **VII** | 10-Hydroxy-9-methylamino-4-methylimino-1,4-dihydroanthracen-1-one | 557 (0.449) | 164.894 | 3.246 | –7.283 | –2.505 | 73.825 | 29.381 |
| **VIII** | 4,9-Dihydroxy- $N^1$,$N^{10}$-dimethyl-1,10-dihydroanthracene-1,10-diimine | 542 (0.593) | 164.444 | 1.428 | –7.288 | –2.613 | 73.797 | 28.709 |
| **III** | 9,10-Bis(methylamino)-1,4-anthraquinone | 588 (0.519) | 165.170 | 5.604 | –7.121 | –2.647 | 73.898 | 29.814 |
| **IX** | 4-Hydroxy-9-methylamino-10-methylimino-1,10-dihydroanthracen-1-one | 553 (0.462) | 164.977 | 4.049 | –7.315 | –2.662 | 73.854 | 29.401 |
| **X** | 1,4-Dihydroxy- $N^9$,$N^{10}$-dimethyl-9,10-dihydroanthracene-9,10-diimine | 449 (0.245) | 165.026 | 0.989 | –7.847 | –2.273 | 73.791 | 29.341 |

of the imino forms decreases in the series 9,10 > 1,4 > 1,10 (gas phase) and 1,10 > 1,4 > 9,10 (in solution). These relations ensure unambiguous assignment of the experimental $\pi_l$,$\pi^*$-bands to particular tautomers.

The lack of linear correlation between $\lambda_{max}$ and $\lambda_{calc}$ of isomers **I**–**III** (Fig. 1, *3*) indicates that these isomers are not present in solution. It also follows that isomeric bis(methylamino)anthraquinones cannot exist in equilibrium with "foreign" *N*-methylimines and that the tautomeric transformations are limited to those represented by curves *2–5* in Fig. 1. It is seen that 1,10-quinoid structure **II** and the corresponding tautomeric methylimines give rise to a linear correlation between the experimental and calculated (PPP) $\pi_l$,$\pi^*$-band maxima [Fig. 1, *2*; Eq. (2)].

$$\lambda_{max}(\text{ethanol}) = (3.264 \pm 0.238)\lambda_{calc} - (1220 \pm 133)\ \text{nm}; \quad (2)$$
$$N = 3,\ r = 0.997,\ s = 4.5\ \text{nm}.$$

These findings clearly indicate 1,10- (but not 9,10)-quinoid structure of the tautomer characterized by the longwave absorption maximum, though this band is invariably assigned in the literature to 9,10-anthraquinone derivative. The described procedure did not allow us to assign with certainty the shortwave band to structure **VI** or **VIII** because of insignificant difference in the $\lambda_{calc}$ values.

The above assignment of the experimental absorption bands to isomer **II** and its imino tautomers is also confirmed by the dependence of $\lambda_{max}$ upon the number of transferred protons *n* [Eq. (3)]. No such dependence is observed for other isomers.

$$\lambda_{max} = (643.8 \pm 5.4) - (40.0 \pm 4.2)n\ \text{nm}. \quad (3)$$
$$N = 3,\ r = 0.996,\ s = 6\ \text{nm}.$$

The fractions of tautomers in the equilibrium mixture may be estimated on the basis of the absorption intensities. The ratio of the calculated oscillator strength *f* is **II**:**VII**:**VIII** = 1.00:0.73:0.97 against 1.00:0.99:0.92 in the experimental spectrum recorded in ethanol [14]. This means that monoimine **VII** is the major tautomer and that diimine **VIII** is the minor one.

Each tautomer or conformer may be characterized by the sum of substituent constants $\sigma^A$ calculated for isomeric anthraquinones [10, 15]. Missing constants for the methylamino group were calculated from the linear correlations between the $\sigma^A$ values [10] (Table 2). Correlations between $\nu_{max}$ for $\pi_l$,$\pi^*$-bands and the sums of substituent constants $\sigma^A$ confirmed our assignment:

a linear dependence was observed only for 1,10-quinoid structure **II** and methylimino forms **VII** and **VIII** assuming that the latter exists conformer **VIIIc9** with broken hydrogen bond $O^9$–H···N [Fig. 2, *2*; Eq. (4)]; no analogous linear relation was found for isomers **I** and **III** with the corresponding imino tautomers.

$$\nu_{max} = (2240 \pm 38)\Sigma\sigma^A + (21\,064 \pm 75)\ cm^{-1}; \quad (4)$$
$$N = 3,\ r = 0.99986,\ s = 29\ cm^{-1}.$$

1,10-Quinoid structure of the alkylamino form is also supported by the fact that isomer **II** in solution is the most stable among three possible bis(alkylamino) derivatives **I**–**III**, for it is characterized by the highest solvatation coefficient *M* (Table 1).

The PPP method cannot be applied to conformers. Conformational equilibria may be analyzed using the sums of substituent constants $\sigma^A$. The $\sigma^A$ values for the free methylamino group and that involved in hydrogen bond differ only slightly, by 0.01–0.02 (Table 2); this means that rotational isomerism in bis(alkylamino)-anthraquinones doe not contribute to the electronic absorption spectrum.

Analysis of more than 160 electronic absorption spectra of various 1,4-bis(alkylamino)anthraquinones in different solvents showed that the given tautomeric composition is typical of this group of compounds. Replacement of methyl group by other alkyls weakly affects the position of the $\pi_l,\pi^*$-band maxima and does not change the tautomeric composition. Likewise, no appreciable variations in the spectral pattern and tautomeric composition is produced by introduction of electron-donor substituents into the alkyl groups, e.g., as in 1,4-bis(2-hydroxyethylamino)anthraquinone (Disperse Blue 23, C.I. 61545). Examples are given in Table 3.

We previously found that $\lambda_{max}$ of 1,4-diamino-anthraquinone tautomers correlate with the energies of the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO). Therefore, it may be presumed that tautomeric transformations occur both in the ground and in the excited states and that the transformations in these states are qualitatively different [10]. Analogous pattern is observed for 1,4-bis(methylamino)anthraquinone. In ethanol, the ground-state tautomeric equilibrium between structures **II**, **VI**, and **VIII** (Fig. 3) is described by Eq. (5).

$$\lambda_{max}(EtOH) = (333 \pm 110)E_{HOMO} + (3009 \pm 795)\ nm. \quad (5)$$
$$N = 3,\ r = 0.95,\ s = 18.6\ nm.$$

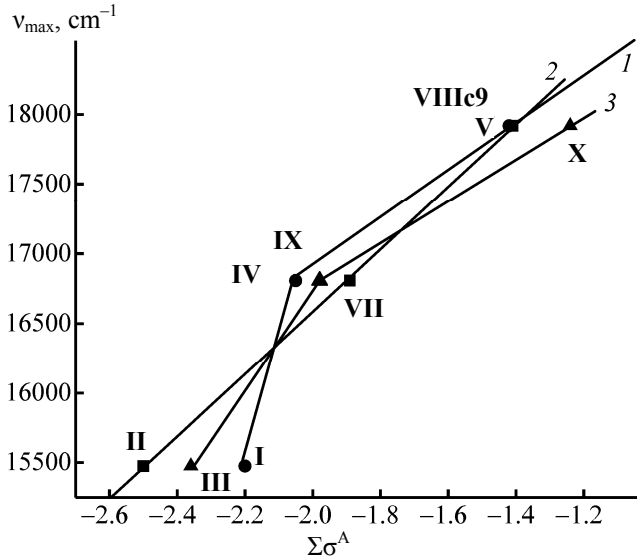



**Fig. 2.** Correlation of $\nu_{max}$ of 1,4-bis(methylamino)anthraquinone in ethanol with the sums of substituent constants $\sigma^A$ for isomeric bis(methylamino)anthraquinones and their tautomers. For (*1*)–(*3*) see the text.

The tautomeric equilibrium in the excited state involves tautomers **II**, **VI**, and **VII** [Eq. (6)].

$$\lambda_{max}(EtOH) = -(359 \pm 42)E_{LUMO} - (310 \pm 105)\ nm. \quad (6)$$
$$N = 3,\ r = 0.993,\ s = 6.9\ nm.$$

Qualitative difference in the tautomeric compositions indicates that excitation is accompanied by transformation of diimine **VIII** into more stable monoimine **VII**.

Unlike 1,4-diaminoanthraquinone whose tautomeric transformations are approximately equally contributed by the ground and excited states, tautomeric transformations of 1,4-bis(methylamino)anthraquinone involve mainly the excited states since the correlation coefficient for Eq. (6) is considerably higher than for Eq. (5). As follows from the slopes of linear correlations (5) and (6), the sensitivities of $\lambda_{max}$ for the excited states are ground states to tautomeric

**Table 2.** Constants $\sigma^A$ of methylamino group in isomeric anthraquinones

| Group[a] | 9,10 | 1,4 | 1,10 |
|---|---|---|---|
| $\sigma^A_\alpha(NHCH_3*)$ | –1.10 | –1.35 | –1.33 |
| $\sigma^A_\alpha(NHCH_3)$ | –1.08 | –1.33 | –1.32 |
| $\sigma^A_{meso}(NHCH_3*)$ | – | –1.18 | –1.17 |
| $\sigma^A_{meso}(NHCH_3)$ | – | –1.17 | –1.16 |

[a] Substituents involved in H-bonding with carbonyl group are marked with an asterisk.

**Table 3.** Assignment of $\pi_l,\pi^*$-bands in the electronic absorption spectra of 1,4-bis(alkylamino)anthraquinones to particular tautomers

| Alkyl group | Solvent | $\lambda_{max}$, nm (log ε) | | | Reference |
|---|---|---|---|---|---|
| | | **II** | **VII** | **VIII** | |
| Methyl | Hexane–dioxane, 4:1 | 632.7 (3.59) | 593.3 (3.61) | 532.5 (3.37) | 14 |
| Methyl | Dioxane | 644 (4.28) | 596 (4.24) | 555 sh (3.92) | 20 |
| Methyl | Ethanol, 22°C | 646.2 | 595.0 | 558.2 | 14 |
| Methyl | Ethanol | 641 (4.21) | 593 (4.16) | 550 sh (3.86) | 21 |
| Ethyl | Ethanol | 644 (4.21) | 593 (4.16) | | 22 |
| Propyl | Ethanol | 644 (4.30) | 593 (4.23) | | 22 |
| Isopropyl | 2-Methoxyethanol | 642 (4.29) | 594 (4.20) | 556 (3.86) | 23 |
| *sec*-Butyl | 2-Methoxyethanol | 643 (4.33) | 595 (4.24) | 560 sh (3.90) | 23 |
| Decyl | Ethanol | 641 (4.06) | 597 (3.98) | 556 sh (3.67) | 24 |
| Octadecyl | Ethanol | 642 (4.04) | 596 (3.99) | 554 sh (3.68) | 24 |
| Cyclohexyl | Ethanol | 644 (4.356) | 596 (4.230) | 558 sh (3.857) | 25 |
| 2-Hydroxyethyl | 2-Ethoxyethanol | 640 (4.28) | 594 (4.21) | 556 sh (3.91) | 23 |
| Diethylaminomethyl | Ethanol | 639 (4.25) | 593 (4.18) | 556 sh | 26 |
| 3-Dimethylaminopropyl | Ethanol | 638 (4.29) | 592 (4.21) | 558 sh | 26 |

transformations differ only slightly, by a factor of 359 : 333 = 1.08.

As found previously for 1,4-diaminoanthraquinone, shifts of $\lambda_{max}$ in the tautomeric transformations of 1,4-bis(methylamino)anthraquinone are related to the energies of both σ- and π-bonds [Eqs. (7), (8)].

$$\lambda_{max} = (1004 \pm 135.0)E_\sigma - (73\,534 \pm 9985)\ \text{nm}; \quad (7)$$
$$N = 3,\ r = 0.991,\ s = 7.9\ \text{nm};$$

$$\lambda_{max} = (162.4 \pm 6.2)E_\pi - (4213 \pm 183)\ \text{nm}; \quad (8)$$
$$N = 3,\ r = 0.9993,\ s = 2.3\ \text{nm}.$$

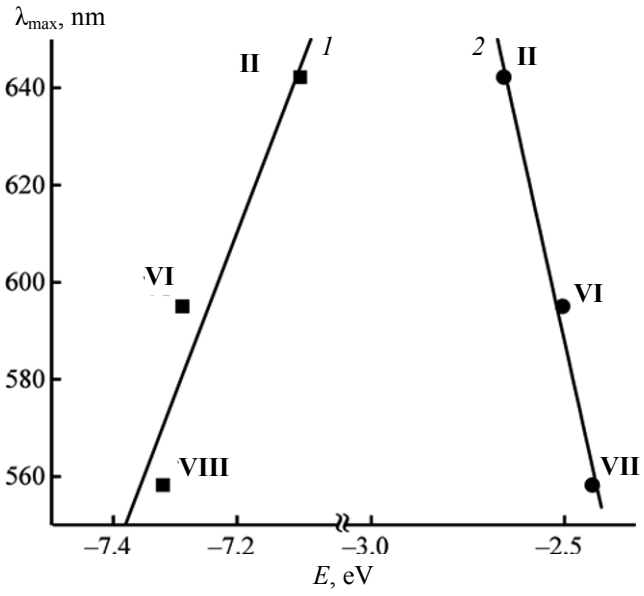



**Fig. 3.** Correlations of $\lambda_{max}$ of 1,4-bis(methylamino) anthraquinone in ethanol with the energies of (*1*) highest occupied ($E_{HOMO}$) and (*2*) lowest unoccupied molecular orbitals ($E_{LUMO}$).

The correlation with $E_\pi$ is much better than with $E_\sigma$. The slopes of Eqs. (7) and (8) indicate higher sensitivity of $\lambda_{max}$ to the energy of σ-bonds than to the energy of π-bonds (by a factor of 1004 : 162.4 ≈ 6). The $\lambda_{max}$ values of 1,4-bis(methylamino)anthraquinone are more sensitive to $E_\pi$ than $\lambda_{max}$ of 1,4-diaminoanthraquinone by a factor of 1004 : 392.7 ≈ 2.5.

Very large number of examples, high correlation coefficients *r*, and small standard deviations *s* leave no doubt of the reliability of the results of correlation analysis of $\pi_l,\pi^*$-bands, despite minimal number of points. This is also confirmed by the fact that all $\pi_l,\pi^*$-bands of all the examined anthraquinones, including polyhydroxy-substituted derivatives whose electronic absorption spectra contain five to six $\pi_l,\pi^*$-bands, were assigned to particular tautomers and conformers.

To conclude, by independent correlation analysis methods we unambiguously determined that compounds generally referred to as 1,4-bis(alkylamino)-9,10-anthraquinones, are not in fact 9,10-anthra-

quinone derivatives. They are dynamic equilibrium mixtures of tautomeric 4,9-bis(alkylamino)-1,10-anthraquinones, 9-alkylamino-4-alkylimino-10-hydroxy-1,4-dihydroanthracen-1-ones, and $N^1$,$N^{10}$-dialkyl-4,9-dihydroxy-1,10-dihydroanthracene-1,10-diimines. An elementary act of prototropic tautomerization involves migration of one proton. Therefore, the following tautomeric transformation sequence is typical of all known samples of compounds unjustifiedly assigned 9,10-quinoid structure **I**: **II ↔ VII ↔ VIII ↔ VIIIc9**.

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