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LETTERS TO THE EDITOR

Isomeric Structure of α-Amino Substituted Anthraquinones

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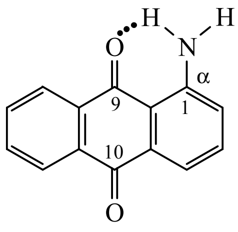
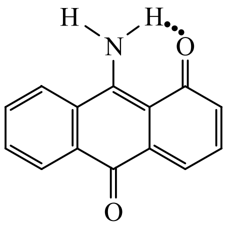
α-Amino substituted anthraquinones are the key compounds in the synthetic dyes chemistry. To their studying are devoted thousands of articles and patents, where they have been invariably considered as the substituted 9,10-anthraquinones. So long, as 1,4-diamino- [1] and 1-amino-4-hydroxyanthraquinones [2] were found to neither individual compounds or 9,10-anthraquinone derivatives. They are characterized by amino-imino [1, 2] and the keto-enol [2] tautomerism. They exist as equilibrium dynamic mixtures of tautomers of 1,10- and 1,4-quinoid structure. The question arises as to whether such structural features are common to the amino anthraquinones or they are inherent in 1.4-disubstituted derivatives only. The answer can be taken by the quantum chemical studying and correlation analysis of not the separate measurements of electronic absorption spectra, but of extensive collection of published data on the electronic spectra of α-amino anthraquinones.

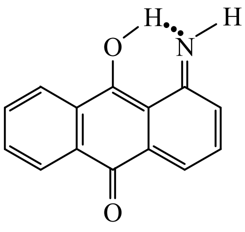
The influence of isomerization on the electronic spectra of 1-amino-, 1,5 - and 1,8-diaminoanthraquines was retraced by the quantum chemical calculations. In the visible field of the experimental spectra of 1-amino anthraquinone usually there are one or two π_l,π^*-bands responsible for the compound color. Their position found by the different authors is varied considerably, for example, in ethanol solution: 430, 441, 470, 475, 481, 490, 497 nm. Nonrandom nature of the extreme values in this series was confirmed by a number of the independent measurements in similar media, for example: 434 nm in 2-propanol or 488 nm in *o*-chlorophenols [3]. The correlation analysis of these data showed that the samples obtained by the different methods are not identical to each other and have different structures: 1-amino-9,10- (**I**) and 9-amino-1,10-anthraquinone (**II**), each of which is in an equilibrium with tautomeric imino-forms (**III**, **IV**). Some of them are able to exist as conformers, such as **IIa**, not containing intramolecular hydrogen bonds.



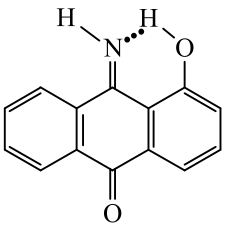
I



II



III



IV

$$\nu_{max}(9,10) = (18687.3\pm0.5) - (2389.6\pm0.7)\sigma^A \text{ cm}^{-1}.$$

The tautomers number $N = 3$, the correlation coefficient $r = 1.00000$, the standard deviation $s = 0.2$ cm^{-1}.

$$\nu_{max}(1,10) = (25308\pm41) + (4202\pm49)\sigma^A \text{ cm}^{-1},$$
$$N\ 4,\ r\ 0.99987,\ s\ 42 \text{ cm}^{-1}.$$

Similarly, according to the analysis data, 1,5- and 1,8-diamines are not substituted 9,10-anth-raquinones, as still believed. The first of these exists as the dynamic equilibrium mixtures of 5,9-diamino-1,10-anthraquinone, 5-amino-1-hydroxy-9,10-anthraquinone-9-imine, 9-amino-10-hydroxy-1,5-anthraquinone-5-imine and 5,10-dihydroxy-1,10-anthraquinone-1,10-diimine, some are the conformers that contain no intramolecular hydrogen bonds. The second contains the tautomeric mixture of 8,9-diamino-1,10-anthraquinone, 1-amino-

8-hydroxy-9,10-anthraquinone-9-imine and 9-amino-8-hydroxy-1,10-anthraquinone-1-imine.

Thus it is shown that α-amino anthraquinones like their hydroxy analogues [4] are not the individual compounds and not the substituted 9,10-anthraquinones only. Contrary to the conventional concept, their structure can not be presented by one structural formula. The results of study the reactions of quinoid rearrangements [5] and of our subsequent studying the quinones tautomerism suggest that the anthraquinone chemistry, one of the oldest and industrially important field of organic chemistry, now is not only the chemistry of 9,10-anthraquinone, but is formed as the chemistry of isomeric anthraquinones. It is need to revise the idea of two independently existing, disparate in size fields, the substituted 9,10-anthraquinones and compounds containing other arranged carbonyl groups in the anthracene core, united only by the rearrangements reactions. Isomeric anthraquinones are inseparably linked with each other.

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