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LETTERS TO THE EDITOR

Determination of the Sequence of Tautomeric and Conformational Transformations of Organic Compounds

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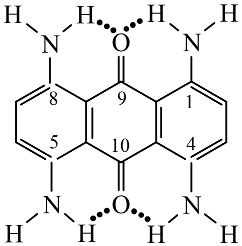
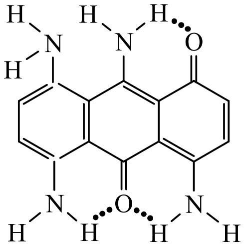
Studies of organic compounds tautomerism are usually aimed to establish their tautomeric transformations using a variety of methods. However, for compounds containing multiple substituents capable of tautomerism, whereby capable of forming various tautomers, the fact of existence of a certain type of tautomerism is not enough. Only a few tautomers are usually realized from the many formally possible.

Determination of the tautomeric content of the known compounds, which differ by the synthesis or purification methods, as well as by the nature of the environment in which they are located [1, 2], makes it possible to determine the sequence of actually occurring tautomeric transformations. Prior to our work a similar problem was not raised by the researchers. The isomers are known to have differing reactivity. The managing tautomeric equilibria allows to achieve improvement in the key technologies. The establishment of the tautomeric content and sequence of the tautomeric transformations are the necessary steps in this direction. The solution to this problem will show on an example of compounds, which is commonly attributed to the structure of 1,4,5,8-tetraamino-9,10-anthraquinone **I**.



I



II

Typical for it a prototropic amino-imino tautomerism may lead to a variety of ways in tautomeric transformations depending on thesequence of migration of different active hydrogen atoms involved into the intramolecular hydrogen bonding. According to the different authors, the experimental electronic absorption spectra contain from 1 to 3 π_l,π *-bands responsible for the substance color. Only their combined consideration makes possible to determine overall picture of the real tautomeric transformations sequence. The linear dependence between the ν_{max} values and σ_A-constants sums of the substituents, free or connected by the intramolecular hydrogen bonds, calculated for different tautomeric structures (equation) shows that the compound is neither individual compound or substituted 9,10-anthraquinone. It exists as the dynamic equilibrium mixtures of 4,5,8,9-tetraamino-1,10-anthraquinone **II** and its tautomers: 1,4,8-triamino-5-hydroxy-9,10-anthraquinone-10-monoimine **III**, 4,8,9-triamine-10-hydroxy-1,5-anthraquinone-5-monoimine **IV**, 5,8-diamino-4,9-dihydroxy-1,10-anthraquinone-1,10-diimine **V** and 8,10-diamino-5,9-dihydroxy-1,4-anthraquinone-1,4-diimine **VI**. Differences in the electronic spectra of its different samples, measured in the identical media, are caused by the different tautomeric content.

$$\nu_{max} = (858\pm8)\Sigma\sigma^A + (19764\pm33)\ \text{cm}^{-1}.$$

The tautomers number $N = 5$, the correlation coefficient $r = 0.99986$, the standard deviation $s = 17$ cm^{-1}. Solvent ethanol.

The monoimine **III** and diimine **V** exist as the conformers **IIIc4** and **Vc4** containing the 4-substituent, which is free from the intramolecular hydrogen bonds. Identification of the specific tautomers, really formed by the tautomerism, allows to establish, what and in what sequence the tautomeric transformations occur in the tetraamine **II**.

IV ← II → IIIc4 → Vc4 → V → VI
562 635 598 607 645 nm

The diimine **V** is formed only as an intermediate product. Its conformer **Vc4** is included into the tautomeric content of the known samples of the compound. Note that the direction of tautomeric transformations is determined not only by the stability in the alternative tautomers solutions.

The above equation makes it possible to calculate the position of π_l,π^*-bands for all the possible tautomers of tetraamine **II** and their conformers, that allows us to predict the electronic spectra in the case, when the tautomeric transformations will go in another direction under the influence of external factors.

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