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LETTERS TO THE EDITOR

Tautomeric Composition as a Compound Characteristic

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The electronic absorption spectra (EAS) of organic compounds that are capable of tautomeric transformations, when measured by the different authors, often differ significantly not only in the range of π_l,π^*-bands responsible for the color of the compound, but also in the number of the bands. For example, electronic spectrum in ethanol of a popular reagent for metal analysis, quinalizarin, the 1,2,5,8-tetrahydroxy-9,10-anthraquinone, contains by different data 1, 2, 3, or 5 π_l,π^*-bands, and the position of the longwave band varies from 510 to 550 nm [1]. For a long time no proper significance was attracted to such differences, despite their frequent occurrence: the researchers discarded the published data as erroneous if they were not consistent with their own measurements. However, these substances are not individual compounds, but dynamic mixtures of tautomers and conformers.

The π_l,π^*-bands are a valuable information source on the tautomeric and conformer composition of the substances [2]. The electronic absorption spectrum calculated by the quantum-chemical methods and containing a single π_l,π^*-band characterizes one tautomer. The experimental spectrum is not an impersonal set of the bands that characterize the compound. The number and position of the π_l,π^*-bands have objective sense: they indicate the number of tautomers that are in dynamic equilibrium, and characterize the structure of each of them.

For each substance capable of tautomeric transformations there are a number of formally possible tautomers. They are not all necessarily involved in a real dynamic equilibrium. Under the influence of external factors the tautomeric equilibrium can be shifted. As a result, the number and nature of the tautomers included in the test substance may be changed. The correlation analysis of π_l,π^*-bands developed by the example of anthraquinone derivatives [1–3] is an excellent tool for investigating the tautomeric composition of substances.

There is a necessity to revise the ingrained idea that different samples of the same substance obtained or purified by different methods are structurally identical and differ only by the nature and content of impurities. The substance, for which a tautomerism is typical, under various conditions can have qualitatively and quantitatively different tautomeric composition and different electronic spectra. One should discard the general view of the EAS as a constant in a certain environment characteristic of any substance. For compounds that are capable of tautomeric transformations, electronic absorption spectra characterize not the substance in general, but its specific sample under the specific conditions.

Chemical reactions of substances are usually accompanied by a shift of tautomeric equilibrium. The study of reactions without taking this into account may lead to serious errors. Such errors were revealed by us, for example, in the works, which explored the ionization, protonation, complexation, and esterification of hydroxyanthraquinones. It was found that a number of known analytical methods is not based on the proper reactions with reagents, but on the shifts of tautomeric equilibrium accompanying them [4]. The study of any reaction of a substance capable of tautomerism is correct only if the tautomeric compositions of the starting material and the reaction products are established.

It is known that the tautomers differ in their reactivities. The way to significant improvement of the synthesis technologies for many industrially important substances is the ability to control the tautomeric equilibrium.

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