LETTERS TO THE EDITORS

FLUORESCENCE OF SOLUTIONS OF 8-AZASTEROIDS WITH $\alpha$-ACYL-$\beta$-AMINOVINYL CARBONYL AND IMINO GROUPS

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Experiments on observation of the luminescence of 8-azasteroid derivatives and its regularities are carried out for the first time. Strong solvent and excitation wavelength dependences are observed for fluorescence spectra of the compounds investigated, whereas their fluorescence excitation spectra depend only weakly on the fluorescence emission wavelength. An analysis of the data obtained points to the complex character of the electronic structure, important role of intramolecular dynamics, and multicenter character of the behavior of these systems upon absorption of light.

Key words: 8-azasteroids, fluorescence, multicenter character, conjugation.

Investigations of the physical, chemical, and biological properties of azines, in particular, alkaloids, purines, and azasteroids, are important both from the standpoint of revealing the regularities of the electronic structure of the molecules in this large class of organic compounds, and determining the interrelations of the spectroscopic properties of the molecules with their properties as bioregulators of natural and artificial origin.

Taking into account the polyfunctional character of the 8-azasteroids, the regularities in the fluorescence spectra observed in the present work should be considered within the framework of the concept of the multicenter character of molecular systems and, in particular, the conjugation concept [1, 2]. At present, the concepts of cross-conjugation [3], conjugation configurations [4], and mesomeric tautomerism [5] are used in the interpretation of these spectral phenomena.

The concept of cross-conjugation as a particular case of conjugation as a whole was formulated quite recently [6]. For the first time, this phenomenon was observed in an investigation of branched polyenes (2-vinylbutadiene or 3-methylene-1,4-pentadiene) [6]. Later, the model was extended to various $p-\pi$ and $\pi-\pi$ molecular systems: 1,3-divinyl ketones, 2-arylidene-1,3-dicarbonyl and enol derivatives of $\beta$-tricarbonyl compounds [7-9], and many others.

The concepts of conjugation configurations [4], which are the result of systematic studies of over last few years, in essence offer an alternative view of the electronic nature of the substances specified.

The viewpoint expressed by the authors of the present study — the concept of the mesomeric tautomerism of cross-linked donor-acceptor molecular fragments [5] — takes an intermediate position between the two above-mentioned ones and resolves their disagreements by assuming a dynamic rather than static nature of their electronic

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structure.

The assumption on the transfer of interaction between electron-donor and electron-acceptor functions or, more generally, between $\pi$ or $\pi-\pi$ electronic fragments of molecules via alternating C–C, C=C, or C–X bonds (where X is a heteroatom, in particular, N), constitutes the basis of the concept. The geometric parameters of equivalent fragments participating in conjugation (lengths of C–C, C=C, and C–X bonds), values of the dipole moments, and other molecular parameters serve as the conjugation criteria of the electronic systems specified.

The data available on the properties of $\alpha$-acyl-$\beta$-aminovinylcarbonyl compounds as typical representatives of cross-linked $\pi-\pi$ and $\pi-\pi$ electron systems (8-azasteroids Ia and Ib) [10, 11]:

provide statistically sound evidence of the realization of a kind of electronic tautomerism in this series — mesomeric tautomerism — which corresponds to the combination of cis-($\cdot$) and trans-($\cdot$) conjugation configurations (see formula Ia). Since the process, as well as conjugation and its variations (cross-conjugation and conjugation configurations), is realized on the level of electronic interactions and is characterized by rather short lifetimes and low energy barriers of direct and reverse transitions, one should assume that spectroscopic methods are most useful with respect to information content and conclusive power.

In the present work, we present the results of investigations of two compounds of the 8-azasteroid class: 16,16-dimethyl-8-aza-D-homogone-1,3,5(10),13-tetraene-12,17a-dione (Ia) and 16,16-dimethyl-12-methyleneimino-2,3-dimethoxy-8-aza-D-homogone-1,3,5(10),13-tetraene-17a-one hydrochloride (Ib) and discuss the regularities of their fluorescence parameters.

The fluorescence spectrum of compound Ia changes (rather substantially) in the polar solvent acetonitrile (Fig. 1, curves 1 and 2) with an increase in the wavelength of the exciting radiation, whereas in a neutral solvent (cyclohexane), the fluorescence spectrum has the form of a narrow band and is independent of the excitation wavelength. In both cases, the fluorescence excitation spectrum does not undergo substantial changes with variations in the emission wavelength within the limits of the emission spectrum ($\lambda_{em} = 400$ and 550 nm). Relaxation processes in the excited electronic state are responsible for the changes in the fluorescence spectra of Ia in polar media.

It is noteworthy that the fluorescence spectrum of Ib in hexane also has the form of a narrow band, is located close to that of Ia, and has similar parameters ($\lambda_{max} = 300$ nm, Fig. 2, curve 1). At the same time, the spectral manifestations of fluorescence of Ib acquire specific regularities. Thus, compound Ib fluoresces in the region of 400-600 nm. The wavelength of the fluorescence maximum is $\lambda_{max} = 450$ nm in acetonitrile, (curve 2) and 500 nm in ethanol (curve 3). Such a difference between the luminescence spectra in the two solvents cannot be explained within the framework of universal interactions.

For ethanol, $n = 1.36$, $\epsilon = 24.3$, and the dipole moment $\mu = 1.69$ D; for acetonitrile $n = 1.34$, $\epsilon = 36.2$, and $\mu = 3.92$ D. According to the universal interaction functions, the fluorescence spectrum in acetonitrile should lie at longer wavelengths than in ethanol [12]. The reverse picture is observed in the experiment (see curves 2 and 3 in Fig. 2). The reasons for these discrepancies in spectral parameters can be connected with the intramolecular dynamics and hydrogen bonding-type donor–acceptor intermolecular interactions. Ethanol is a stronger protic solvent. It is known that adding HCl to a protic solvent blocks hydrogen bonding [13]. This should be manifested by a short-wave shift of the fluorescence spectra, which was indeed observed experimentally (Fig. 2, curve 4). The C=O carbonyl groups and N atom in the $\pi-\pi$ conjugation system are the most likely proton acceptors in protic solvents.