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Electronic properties of polymethine systems. 11. Absorption spectra and nature of electron transitions in cationic oxystyryl and their neutral derivatives

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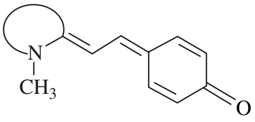
Abstract

Complex quantum-chemical and spectral study of the features of the electron transitions and absorption spectra of the both oxystyryls and related merocyanines containing the pyridinium, quinolinium, indolium and benz[*c*,*d*]indolium end residues has been performed. It was shown that the relative long wavelength absorption of the neutral merocyanines, in comparison with the cationic dyes, is caused by considerable redistribution of the electron density within the chromophore upon excitation, not by equalizing of the carbon–carbon bond lengths as it was predicted in the framework of the conception "cyanine limit". The opposite sign change of the dipole momentum in the excited state in the cationic and neutral dyes depends noticeably on the basicity of the donor end groups and causes the opposite solvatochromism which increases additionally the distance between the absorption bands of these dyes of the different types.

Keywords: Merocyanines; Oxystyryls; Electron structure; "Cyanine limit"; Absorption spectra; Quantum-chemical calculation

1. Introduction

Merocyanine **1** are typical high polarizable donor–acceptor molecules which can be considered as neutral derivatives of cationic oxystyryls **2**.



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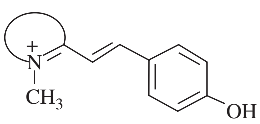

2

Notwithstanding that these two related types of the linear conjugated systems differ from each other insignificantly in the chemical constitution, first of all, by a number of atoms bonded by σ-bonds and by hybridization of the oxygen atom, they exhibit the electron–structural similarity: oxystyryls **2** and merocyanine **1** contain the same number of the π-electrons. However, there is a principal distinction between π-electron systems of the compound **1** and **2** which is connected with a total charge: oxystyryls **2** are charged conjugated systems while merocyanine **1** are neutral molecules. It causes the sharp difference in the electron structure and spectral properties, in particular, in shape and position of the long wavelength absorption band [1,2]. In the contrast to the neutral cyanine bases absorbing in the shorter spectral region than the corresponding cationic cyanine [3], the absorption band is shifted bathochromically from charged oxystyryls **2** to their neutral merocyanines **1** [1,2].

As donor–acceptor π-electron molecules, the compounds **1** are well-known highly sensitive sensors on the solvent polarity [4] as well as they are used as the suitable model for the wide quantum-chemical study of the

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solvatochromism [5,6]. The theoretical model was based on the fact that **1** similarly to other types of the merocyanines consist of an electron donor residue (D) and an electron-acceptor group (A) linked by the polymethine chain, so that their highly polarizable π-electron structure can be described in terms of the resonance between a neutral form **3** and a charge-separated form **4**:

$$\underset{\mathbf{3}}{\mathrm{D-(CH=CH)}_n\mathrm{-A}} \leftrightarrow \underset{\mathbf{4}}{\mathrm{D^+=(CH-CH)}_n\mathrm{=A^-}}$$

The contribution of each resonance form depends self-evidently on solvent polarity. It was postulated that by providing the equal weights of two forms, there arises the so called cyanine-like structure which is, first of all, characterized by the minimum bond length alternation and the maximum in the wavelength of the first absorption band [6].

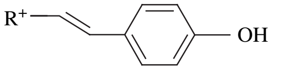
The growing interest in the merocyanines in the last two decades is connected with use of these compounds as non-linear optical materials (see review [7] and references therein). It was found that the higher hyper-polarizibilities, β_o and χ_o, are unambiguously determined by the donor and acceptor strengths of the terminals groups or, more correctly, by difference in the dipole moments in the excited (μ_e) and ground (μ_g) states: $\Delta\mu = \mu_e - \mu_g$, which, in turn, depends on the alternation of the lengths of the carbon–carbon bonds in the conjugated chain, so called parameter BLA [7,8]. Increasing of the BLA upon the increasing of the difference in the donor strength and acceptor strength causes the growth of the second hyperpolarizibility, β_o, but only to the crucial magnitude; thereafter parameter β_o decreases because of the decreasing of the overlap of the ground and excited state functions, $<\Psi_g|\Psi_e>$, and hence decreasing of the transition momentum, μ_{ge} [7].

Also, it was found in the framework of the topological (Hückel) approximation [8] that the BLA value can be both negative and positive, depending on the donor and acceptor strengths of the end residues (or Coulomb and resonance integrals of the terminal heteroatoms in the model donor–acceptor conjugated molecule). Providing the fixed difference in the electron donor–acceptor ability, BLA = 0 and "cyanine limit" can be reached. However, investigations in the approximations taking correctly into consideration an electron interaction have shown that the merocyanines could exhibit some features in the dependence of the electron structure on the nature of the end groups [6]. So, cyanine-like structure (BLA = 0) is not reached in the merocyanine $(H_3C)_2N-(CH=CH)_2-CH=O$, even in the extremely polar media. In contrast, in the meroform of the pyridoxystyryl, the charge-separated resonance structure prevails and parameter BLA is negligible which leads to the inversion of the solvatochromism, as compared with the merocyanines [6].

One can assume that properties of the meroforms should strongly depend on the donor strength of the nitrogen-containing end residue, as well as on the extending of the π-electron system of the total chromophore at the conjugation with own π-system of the end group. In this paper, we present the results of the quantum-chemical and spectroscopic study of the oxystyryls **5** and merocyanine **6** with the various heterocyclic donor residues which simulate decrease of the donor strength regularly.

2. Objects and methodology

The formulae of the oxystyryls **5** and their neutral derivatives, merocyanines **6**, investigated are following:



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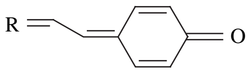
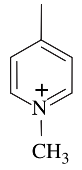


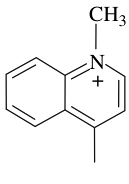
6

where R is end group. In present article, the following heterocyclic residues were used as end groups:

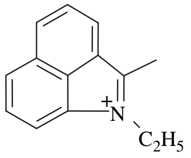
R+:



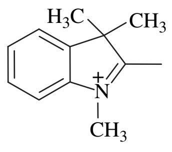
5-Py



5-Qu

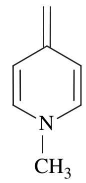


5-BIn

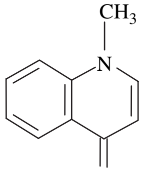


5-In

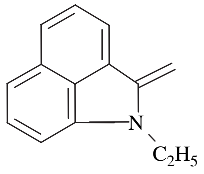
R :



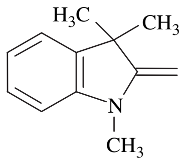
6-Py



6-Qu



6-BIn



6-In