

Asymmetry in ground and excited states in styryls and methoxystyryls detected by NMR (^{13}C), absorption, fluorescence and fluorescence excitation spectroscopy

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ABSTRACT

Combined quantum-chemical and spectral study of electron structure features of styryls and their oxyanalogues containing benzothiazolium, benzooxazolium, indoleninium, pyridium, quinolinium residues has been fulfilled. It showed that asymmetry degree of molecular geometry and charge distribution in the chromophore of styryls and methoxystyryls considerably differ in the ground and excited states. It was established that two the lowest transitions in styryls are splitting and involve both donor levels, similarly to symmetrical cyanines. If compare with methoxystyryls the long-wave high intensive absorption band is shifted bathochromically due to considerable interaction between the donor quasi-local chromophores. In contrary, because of the low position of a lone electron pair of oxygen in methoxystyryls, only one donor quasi-local chromophore is effective, hence such unsymmetrical dyes absorb appreciably higher.

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1. Introduction

Unsymmetrical cyanine dyes, including styryls and their methoxyanalogues, continue to be used widely, in parallel with corresponding symmetrical dyes, in numerous applications; they are widely used objects due to their unique electronic and spectral properties which form a basis for the design of new effective materials connected with the light conversion, i.e. spectral sensitization, molecular probing in biology, active and passive components for tuneable lasers, non-linear media exploring excited state absorption, etc. [1–4]. Also, symmetrical and unsymmetrical cyanine molecules remain convenient objects for developing of new theoretical concepts and quantum-chemical models [5–9]. Going from symmetrical dyes to unsymmetrical ones causes significant changes in distribution of the total positive charge in the polymethine chromophore, molecular geometry and hence in spectral properties [1,4,10–12].

The styryls were usually considered as unsymmetrical cyanines with an extremely high degree of asymmetry because of the low basicity of the *p*-dimethylaminophenylene residue as a terminal group. Nevertheless, the nature of the lowest electron transition is similar to the nature of the one in symmetrical cyanines. Inser-

tion of an alkyloxy group with a high electronegative oxygen atom instead of amino group into styryls is likely to lead to more considerable change in the molecule electron structure of the dyes and in the nature of the electron transitions. It is expected that the spectral effects should depend on the difference in donor strengths of other terminal groups. So, we use absorption and fluorescence spectra or, more correctly, electron transitions, for studying the asymmetry of the excited state, whereas the degree of the asymmetry in the ground state can be obtained from NMR spectra. Also the quantum-chemical calculations give the information about the asymmetry in the charge distribution and molecular geometry in both ground and excited states.

This paper presents the results of the simultaneous quantum-chemical simulations and spectral measurements of the absorption spectra of unsymmetrical styryls and methoxystyryls.

2. Experimental

2.1. Objects and methodology

The general structures of investigated styryls **1** and corresponding methoxystyryls **2** containing indoleninium (In), benzothiazolium (BT), benzooxazolium (Ox), pyridium (Py) and quinolinium (Qu) residues are presented in Fig. 1. Also, as reference dyes, the symmetrical cyanines **3–5** will be considered. Methods of the syn-

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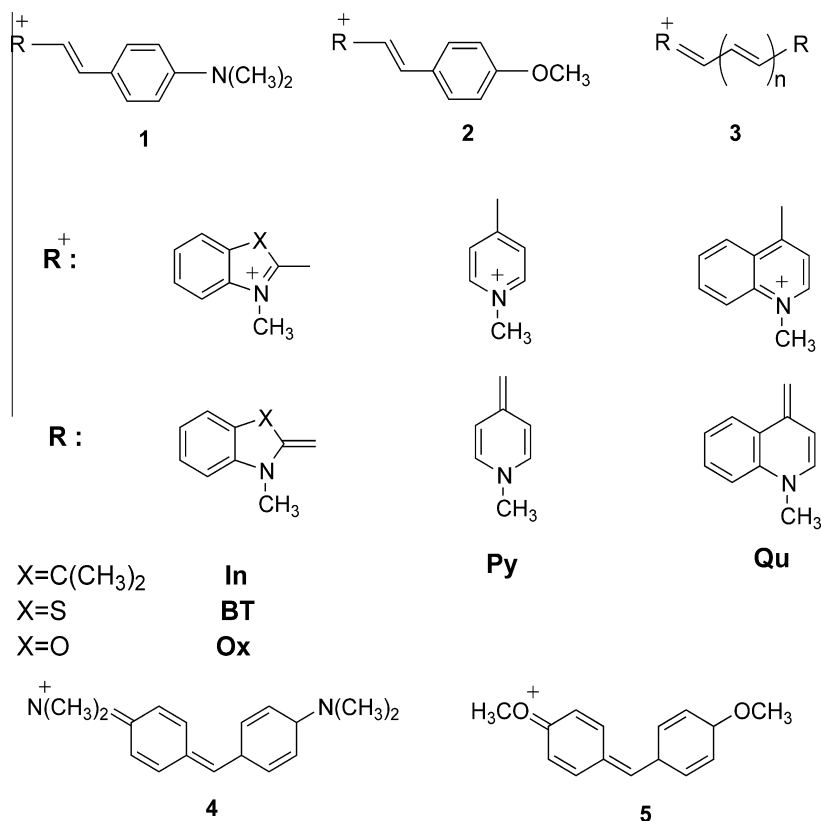


Fig. 1. Formulae of the dyes.

thesis of dyes **1–3** were described earlier [10,13,14]; the spectral characteristics of the known compounds correspond to data in these papers. The spectral data of new dyes change regularly upon the change of the chemical constitution.

2.2. NMR spectra, absorption spectra, fluorescence spectra, fluorescence excitation spectra, fluorescence excitation anisotropy spectra

NMR (nuclear magnetic resonance) spectra. All NMR measurements were carried out on Varian GEMINI 2000 spectrometer with ¹H and ¹³C frequencies of 400.07 and 100.61 MHz, respectively at 293 K. Tetramethylsilane was used as a standard for δ (NMR chemical shifts) scale calibrating. ¹H NMR spectra were recorded with spectral width 8000 Hz and numbers of points 32,000; ¹³C NMR spectra were recorded with spectral width 30,000 Hz and numbers of points 128,000. ¹H–¹H COSY [15] spectra were acquired into 2048 (F2) and 512 (F1) time-domain data matrix and 2048 (F2) \times 2048 (F1) frequency-domain matrix after zero-filling. NOESY [16] spectra were acquired, if necessary, with parameters similar to COSY spectra. Mixing times were determined preliminary from T₁-measurement experiment for each sample by a conventional inversion-recovery method. Heteronuclear chemical shift correlation (HETCOR) [17] was used to determine ¹H–¹³C attachment with 2048 (F2) \times 256 (F1) time-domain matrix and 2048 (F2) \times 1024 (F1) frequency-domain matrix after zero-filling. The average value of one bond constant J_{CH} was set to 140 Hz. HETCOR for determination long range correlation had very similar parameters and average value of multibond C–H coupling constant was set to 8 Hz.

Absorption spectra were recorded on spectrophotometer Speord UV VIS in ethanol.

Fluorescence spectra and **Fluorescence excitation spectra** were recorded on Varian Cary Eclipse fluorescence spectrophotometer.

Fluorescence excitation spectra were measured upon various concentrations. They showed that an increasing of concentration leads to splitting of the band, which is the result of reabsorption. So we used for measurements such concentrations that fluorescence excitation spectra reproduced absorption spectra.

Fluorescence excitation anisotropy spectra were recorded on fluorescence spectrophotometer CM2203 in glycerin. They were recorded to find out the transition $S_0 \rightarrow S_2$ when it is orthogonally polarized to the first electron transition $S_0 \rightarrow S_1$.

2.3. Quantum-chemical calculations

To study the dependence of the electron structure and electron transitions on molecular constitution quantum-chemical calculations were performed. The equilibrium geometry and charge distribution in the ground state were calculated by DFT B3LYP (6-31G**) method (packages GAUSSIAN03) [18]. The electron transition characteristics were calculated by ZINDO/S method using, as a rule, all π -electron single excited configurations. There are some problems in the correlation between the calculated and the experimentally observed energies both for the first and for higher electron transitions, which have been discussed in detail earlier [19]; here we have used the same methodology.

3. Results and discussion

3.1. Ground state

3.1.1. Optimized molecular geometry

The performed calculations of the equilibrium molecular geometry give the conjugated part of all unsymmetrical molecules, **1** and **2**, and symmetrical cyanines **3**, to be planar that is typical for π -electron systems [20]. Only methyl groups in the indolenine resi-

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