Estimation of the basicity of the donor strength of terminal groups in cationic polymethine dyes

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ABSTRACT

The well-known conception of the basicity of the terminal groups in the cationic polymethine dyes showing their donor properties is examined (considered) in detail. The various approachs are proposed to quantitative quantum-chemical estimation of a donor strength of the terminal groups in cationic polymethine dyes: shift of the frontier levels upon introducing terminal residues in comparison with unsybstituted polymethine cation; transferring of the electron density from the terminal groups to the polymethine chain and hence manifested itself as a redistribution of total positive charge between molecular fragments; changes of the charge alternation at carbon atoms along the chain. All approach correlate between them and agree with the concept of the basicity as a capability of terminal hetero-cycles to show its donor properties in the polymethine dyes.

The results of the fulfilled calculations of numerous examples are presented; the proposed parameters point correctly the tendency in the change donor strength upon varying of the chemical constitution: the dimension of cycle, introducing of various heteroatoms, linear or angular annelating by benzene ring; as well as direct to take into consideration the existence of local levels.

1. Introduction

The polymethine dyes (PDs) are well known for more than a century, however, their investigations are still continued due to permanent extension of their application areas (see, for example, monography [1] and reviews [2–5] and references therein). Besides traditional use of PDs as fluorescence probes and labels in chemistry and biology, initiators for polymerization reaction, active and passive components for tunable dye lasers [6–11], in the last decades they have shown a great potential for applications in nonlinear optics as optical materials [12,13].

In the other hand, PDs with their simple chromophore represent suitable model compounds for the testing of new theoretical concepts, beginning from the Hueckel method [14–18] to the theory of solitonic charge waves [19–24]. One of the most important problems of the color theory of PDs is the investigation of charge distribution between molecular fragments and its redistribution upon

excitation [1,2,25]. So, it was established for the cationic PDs that the considerable alternation of atomic charges exists along polymethine chromophore; the excitation causes the appreciable transferring of the electron density from the carbon atoms in the odd positions to the atoms in the neighbouring positions [1,25]. Also, the experimental and quantum-chemical study has shown that the values of the atomic charges in both ground and excited state depend immediately on donor properties of terminal groups in the symmetrical dyes as well as on an asymmetry degree in the unsymmetrical dyes [1,25–29].

The many theoretical approaches were proposed for the quantitative estimation of the donor propreties or donor strengths of the terminal groups in the PDs; the analysis of the can be found in the review [25]. However, these approaches were mainly based on the simple Hueckel approximation, which provides an acceptably accurate taking into account of the molecular topology of the conjugated molecules. But they did not take into consideration the electron interaction, while the PDs are ionic π-electron systems. Recent detailed investigations of cationic PD have shown that there appear some specific electron and spectral features of these

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compounds, particularly, nature and symmetry of the higher excited state, drastic distortion of the cyanine-like shape of the long-wavelength band in the absorption spectra in polar solution at 1000 nm (see, for example, review [4] and refers therein), which can be correctly interpreted only upon taking into consideration the electron interaction in the ionic conjugated systems.

It was established that a charge (positive or negative) injected in a high polarizable collective system of the π-electrons of the PDs is not located on some individual atom as well as it is not delocalized uniformly along all atoms, but becomes autolocalized as solitonic-like charge wave of the alternated partial atomic charges [19–24]. Also, the injection of charge mentioned above leads to an appearance of specific electron levels: so-called soliton level or level of the charge [19]. Numerous quantum-chemical investigations according to various methods have shown that going from the neutral π-system to its cation or anion causes a substantial shift of electron levels down or upwards, correspondingly [24]. Such fundamental transformation of the electron levels in the ionic PDs in comparison with neutral polyenes provokes a principal change of the relative disposition of the levels of the different fragments in the PD molecules.

This paper presents a new approach for the estimation of donor strength of the terminal groups in the PDs, based on the correct analysis of the electron interaction by non-empirical methods: HF/6–31 (d,p) and DFT/CAM-B3LYP/6–31 (d,p). The package Gaussian03 [28] was used for the calculations. Both methods (HF and DFT) are known [29,30] to give the serious divergence between the calculated and experimental characteristics of the electron transition, however, we will optimistically propose that they provide reliable picture of the electron distribution and level spectrum for the series of the PDs containing the complex terminal groups with own conjugated system.

2. Basicity conception

For the first time, the problem of the estimation of the donor properties of terminal groups has arisen when the absorption spectra of the symmetrical and unsymmetrical cyanine dyes **1** presented in Fig. 1 were investigated in detail [26,35].

It was experimentally found that the maximum of the absorption band of unsymmetrical cyanines, $\lambda_{max, uns}$, are shifted hypsochromically in comparison with the arithmetical mean of the maxima of the parent symmetrical dyes, $\lambda_{max, 1}$ and $\lambda_{max, 2}$; the value of the shift, D, calculated by formula (1) was called as *deviation*.

$$D = (\lambda_{max, 1} + \lambda_{max, 2})/2 - \lambda_{max, uns}; \qquad (1)$$

It was established that the parameter D > 0 for the typical PDs
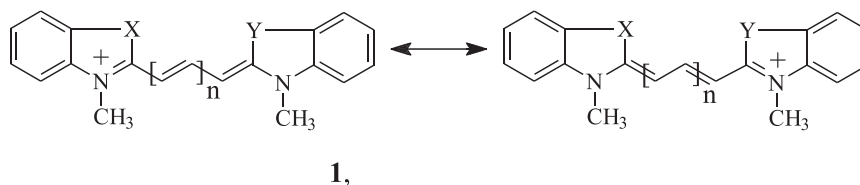
[26]. This spectral effect was treated to connect with the appearance of the alternation of the lengths of the carbon-carbon bonds along the polymethine chain of the unsymmetrical dyes, whereas the bond lengths in the corresponding symmetrical cyanines are significantly equalized, what is confirmed experimentally or quantum-chemically (see, for example, reviews [1–3,25] and refers therein). Based on detailed study of the serii of the symmetrical and unsymmetrical cyanines, Brooker has disposed the heterocyclic terminal residues in the series, so their donor strength regular decreases [26]. Also, he has proposed the parameter *basicity* as a characteristic of the donor properties of the terminal residues. Additionally to experimental estimation of the degree of asymmetry, there were proposed different theoretical increments taking into consideration of the asymmetry of the linear conjugated systems (their comprehensive examination was discussed in review [25]).

According to L.G.S. Brooker [26], the *basicity* can be treated as an additional stabilization of the dye molecule by the double bonds of the terminal groups: parameter ADBS (*additional double bond stabilization*). This parameter can be estimated quantitatively in framework of Valence structure theory by the ratio of the numbers of the Kerule's structure for the terminal group written in the electron acceptor (EA) form and electron donor (ED) form. For example, the unsymmetrical styryl **2** can be presented by two resonance structures, as it shows in Fig. 2.

In structure A, the pyridinium residue is in the electron acceptor form, while the *p*-aminophenylene residue is in electron donor form. In structure B, the types of the both terminal groups is opposite. The pyridinium heterocycle can be presented by 2 Kerule's structures in the EA-form and by only 1 Kerule's structure in ED-form; then ADBS = 2:1. As a result, the pyridinium residue could be treated as high basic terminal group. In the same time, the parameter ADBS = 1:2 for the *p*-aminophenylene residue, and hence this heterocycle could be treated as low basic terminal group.

Later, this approach was added by using of graph theory [31] when not only Kekule graphs (K-graphs) but also Cycle graphs (C-graphs) take into consideration, each graph having its weight.

The quantitative method of estimation of donor properties was also proposed by Platt [18]; he has written the formulae for the
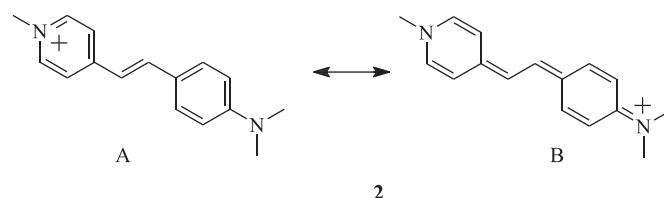
Fig. 2. Two resonance structure of pyridostyryl **2**.

1,

n = 1, 2, 3

X = C(CH₃)₂, S, Se, O, NCH₃, CH=CH

Y = C(CH₃)₂, S, O,   NCH₃, CH=CH

Fig. 1. Formulae of cyanine dyes **1.**