



# Effect of donor terminal group and polymethine chain length on structure of merocyanine dyes in the crystal state



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## ABSTRACT

X-ray diffraction study of the merocyanine series with different sign of solvatochromism but of the same structural type revealed the effects of donor-acceptor properties of terminal groups and polymethine chain length on their electronic structure in the solid state. The bond length alternation in the negatively solvatochromic dyes corresponds to the dipolar polyene limiting structure, contribution of which, in contrast to solutions, increases for higher vinylogues. Conversely, the nonpolar polyene structure prevails for the positively solvatochromic merocyanines, its contribution increases for higher vinylogues in both solid state and solutions. The DFT (*in vacuo* and PCM) calculations reproduce tendencies observed for the positively solvatochromic merocyanines but do not reflect the dipolarity growth in higher vinylogues of the negatively solvatochromic ones. The calculations results can be improved taking explicitly into account intermolecular interactions in the crystal.

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## 1. Introduction

Development of new organic materials for light energy conversion, information storage and processing involves design of novel functional dyes with a certain set of physical-chemical properties. Among these, merocyanines and other donor-acceptor-substituted conjugated systems (D- $\pi$ -A) attract probably the most profound interest [1–8]. Depending on the donor-acceptor properties of the terminal groups and the conjugated chromophore system extension their electronic structure can vary from neutral polyene (A1) to ideal polymethine (A2) and then to dipolar polyene (A3) [8,9] (see Scheme 1), which results in a wide range of photophysical and photochemical properties variations, as well as strong solvatochromism of merocyanines.

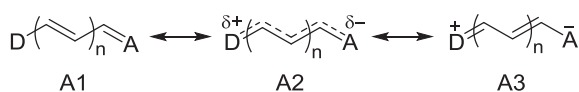
The regularities of A1–A2–A3 polyene–polymethine variations in merocyanines have been investigated mostly in solutions. Similar regularities have not been obtained so far in the absence of a solvent, e.g. in crystal state. Their determination should provide better insight into the electronic structure of D- $\pi$ -A conjugated systems and give an additional reference point for quantum-chemical modelling of conjugative systems.

The latter task is eminently topical for negatively solvatochromic merocyanines. Thus, Brooker's merocyanine **1** (see Scheme 2), which is one of the most comprehensively studied polymethines, is characterized by negative solvatochromism, i.e. its electronic structure is highly dipolar and change toward the structure A3 in high-polarity solvents. However, its quantum-chemical calculations in vacuum assumed the structure A1 with "normal" bond length alternation (BLA) [10–12], contrary to the X-ray diffraction data [13]. This contradiction was explained by the presence of the crystallization water in the merocyanine **1** packing, which, forming strong hydrogen bonds with the carbonyl group, facilitates the structure A3 realization. Indeed, when the crystallization water was taken into account in the quantum-chemical simulation, the dipolar structure A3 was achieved [11,12]. Analysis of the molecular structure of Brooker's merocyanine di-*tert*-butyl analogue **2**, whose crystals, unlike **1**, do not contain solvent molecules [14], would seem to confirm this suggestion.

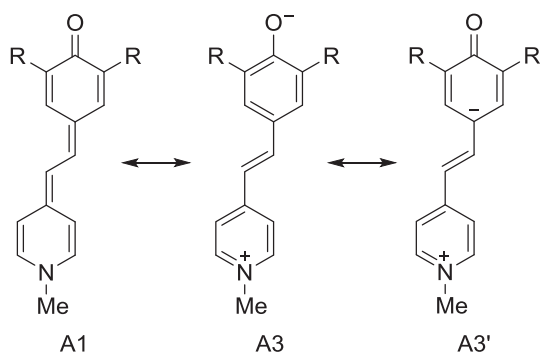
The authors in Ref. [14], comparing only the C–O bond lengths, came to the conclusion that in molecule **2** the BLA is closer to the neutral quinone (A1) rather than to the betaine (A3) limiting structure, like in **1**, thus explaining the deeper colouring of crystals of the former. Later, M. Rezende referred to these data as to an argument in favour of the lower electron accepting ability of the 3,5-di-*tert*-butyl substituted 4-oxocyclohexa-2,5-dienylidene

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**Scheme 1.** Three virtual limiting structure of merocyanines.



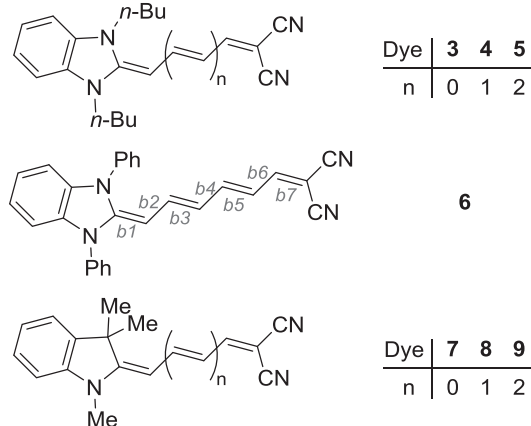
**Scheme 2.** Resonance structures of Brooker's merocyanine (**1**, R = H) and its di-*tert*-butyl analogue (**2**, R = *tert*-Bu).

residue compared to the unsubstituted one [15,16].

Detailed analysis of the structural data of dyes **1** and **2** allows one to deduce that the authors' interpretation in Ref. [14] was not quite correct. The alternation of C–C bond lengths in the entire chromophore of molecule **2** indicates a significant contribution of the zwitterion resonance structure A3' in which the negative charge is chiefly localized on the nodal C-atom of the acceptor (see Scheme 2). So, merocyanine **2** becomes highly dipolar even in the absence of a crystallization solvent. However, in the crystal molecules **2** are arranged so that the oppositely charged sites (D and A) are stacked alternately. Hence, it can be assumed that the structure A3' is not characteristic of an individual molecule but is attained due to strong intermolecular interactions (IMIs) in the packing. So, one cannot deduce definitely which of the limiting structures A1–A3 prevails in the case of isolated **1** and **2** (or other highly polarizable molecules) from their X-ray crystallography data, since there electronic structure in the solid state is greatly affected by the polar (dipole-dipole) IMIs.

To reveal the regularities of polyene-polymethine alterations in the solid state of merocyanines, one has to study dye series of the same structural type, in which the donor-acceptor properties of terminal groups and the polymethine chain length change regularly. The former markedly affect the position of a merocyanine electronic structure on the scale A1–A2–A3, i.e. the alternation of bond lengths and  $\pi$ -charges in its chromophore, as well as the molecular dipole moment. The chain length has little effect on the relative contribution of the limiting structures A1, A2 and A3 [8,15,16], but molecular polarizability and dipole moment depend heavily on it [4,7]. At that, it is preferable to have the series of merocyanines with the opposite sign of solvatochromism to maximize the observed effects. In this case, their electronic structure will lie on either side of the structure A2. In addition, there should be no crystallization water (or other high-polarity solvent capable of influencing the electronic structure of D- $\pi$ -A molecules, as it was the case with Brooker's merocyanine). In light of this, the series of merocyanines **3–9**, with the malononitrile acceptor terminal group were chosen as objects of study [17–19] (see Scheme 3).

Dyes **3–6** are characterized by negative solvatochromism, which indicates a significant contribution of the form A3 to their electronic structure in the ground state [17,18]. Merocyanines **7–9**, derivatives of the less electron-donating indole, possess positive



**Scheme 3.** Structures of merocyanines **3–9**.

solvatochromism, characteristic for molecules falling within the A1–A2 range [19]. Since merocyanines **3–9** are of the same structural type, the influence of IMIs in the crystal on their molecular structure should be similar or change gradually and regularly, depending on their structure. For this study, the malononitrile residue as an acceptor has the advantage of lacking carbonyl groups. Hence, it is not prone to formation of strong hydrogen bonds with protic solvents [20], which reduces the probability of incorporation of solvent or water molecules into the crystal lattice of corresponding merocyanines.

## 2. Experimental section

X-ray quality crystals of dyes **3–6** and **8** were grown by slow evaporation of their ethanol solutions from the test tubes capped with Parafilm. For merocyanines **5** and **8**, ethanol contained acetonitrile (5 v/v %) and toluene (5 v/v %), respectively. X-Ray diffraction studies were performed on an automatic "X-calibur-3" diffractometer (graphite monochromated MoK $\alpha$  radiation, CCD-detector,  $\omega$ -scanning). The structures were solved by direct method using SHELXTL package [21]. The restrictions on the bond lengths for the butyl substituents (C(sp<sup>3</sup>)–C(sp<sup>3</sup>)) 1.54 Å) have been applied for the compound **5**. Positions of the hydrogen atoms were located from electron density difference maps and refined by "riding" model with  $U_{iso} = nU_{eq}$  of the carrier atom ( $n = 1.5$  for methyl groups and  $n = 1.2$  for other hydrogen atoms) in structures **3–5**. The hydrogen atoms in **6** and **8** were refined using isotropic approximation. The crystallographic data and experimental parameters are listed in Table 1. Final atomic coordinates, geometrical parameters and crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, 11 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). The deposition numbers are given in Table 1. X-ray diffraction data for compounds **7** and **9** were published elsewhere [22].

Quantum chemical calculations were performed using Gaussian-09 software package [23]. The geometry optimization of molecules **3–9** was carried out at the DFT level using four various hybrid functionals – B3LYP, CAM-B3LYP, wB97XD, and B97D3 – with the split-valence 6-31G(d,p) basis set. The CAM-B3LYP functional comprises the greater share of HF exchange over a long range than B3LYP, which can be of consequence for long highly polarizable molecules [24,25]. The wB97XD includes both long-range correction and Grimme's empirical dispersion [25]. The B97D3 functional [26], which includes the latest version of Grimme's dispersion was used to model intermolecular interactions

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