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## An insightful approach for understanding solvatochromic reversal

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## ABSTRACT

Several studies have shown that organic dyes may show solvatochromic reversal with respect to the solvent polarity. This controversial non-monotonic behavior is still not well understood. This has been analyzed here using the merocyanine of Brooker as the working example. Associating a continuous variable to model the solvent polarity a solvatochromic reversal is obtained with a single solute without aggregation. This reversal is in excellent agreement with the experimental results and is shown to be the outcome of a competition between structural change and intramolecular charge transfer.

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## 1. Introduction

The position, intensity and shape of the UV–Vis absorption spectrum of organic molecules in solvents depend on the chemical structure and physical properties of the chromophore and on the solvent polarity [1–12]. In particular, among several organic compounds, the merocyanine dyes have been extensively studied [1–29] because of the sensitivity of the absorption spectra to solvents, causing higher negative or positive solvatochromism with the solvent change. Usually, the behavior of each absorption band has a well-defined tendency with increasing or decreasing solvatochromism with the solvent polarity. However, some dyes exhibit a solvatochromic reversal where the solvatochromism changes from positive to negative. This phenomenon is still controversial, sometimes being attributed to self-aggregation [30]. In spite of this, some works discard the aggregation origin and point to structural changes of resonance hybrid between the neutral (quinoid) and the zwitterionic (benzenoid) canonical structures [1,6,7,13,17,18]. Also it is argued that the flow direction of the charge transfer in the merocyanine dye plays an important role [14]. A better understanding of the real possibility of solvatochromic reversal is both timely and relevant. A thorough theoretical investigation including explicit consideration of the solvent molecules is difficult for several reasons. One is that sophisticated and computationally demanding models such as QM/MM [1,20–22], should be used for many different solvents. It may be added to this the challenge of maintaining the same accuracy for the cal-

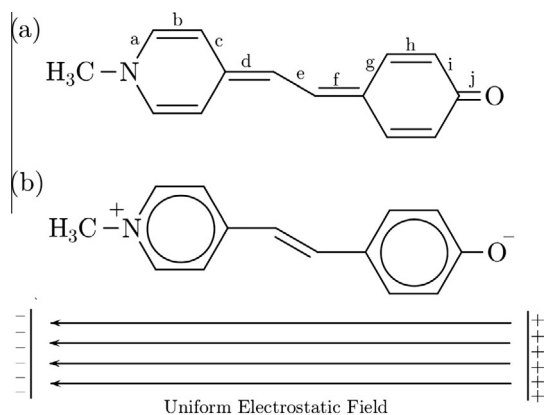
culations made in each one of these different solvents with different polarities. Hence a simpler model that could be used indistiguibly to any solvent polarity is needed at this stage. One such possibility is the use of a static electric field to mimic the solvent. This has been considered [31] before in another context. We will show that associating the field strength to the solvent polarity a solvatochromic reversal is obtained. Thus the reversal is possible for the single solvated molecule and it is obtained as the result of a competition between structural changes and charge transfer. As the working system for the application we have selected the stilbazolium betaine, also known as the merocyanine of Brooker (MB) that has been frequently studied [5–21,30–37] and reported to present a solvatochromic reversal [6,17] in the characteristic  $\pi \rightarrow \pi^*$  transition.

MB (Fig. 1a) has an electron donor ( $\text{CH}_3\text{N}$ ) and an acceptor (CO) group separated by aromatic chains and double conjugated bonds that facilitate the electron drift between the  $\text{CH}_3\text{N}$  and CO groups. So, the chemical environment that the molecule is exposed can induce charge transfer in the ground and the lowest excited state of the solute molecule. Also, the charge transfer can induce conformational changes in the solute molecule and these two combined effects cause large shifts in the absorption and in the emission bands. However, the individual contribution of each of these effects is not entirely understood.

The main focus of the present work is the understanding of the possibility of solvatochromic reversal. We present an analysis of the influence of the geometry relaxation and the charge transfer effects in the lowest absorption energy of MB. To separate these two effects in a controllable way, an electrostatic field with distinct intensities is applied in the parallel direction of the dipole moment

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**Fig. 1.** The schematic illustration of the merocyanine of Brooker in the canonical forms: (a) neutral (quinoid); (b) zwitterionic (benzenoid). Also shown are the bonds labels used in the structural analysis and the direction of the uniform electrostatic field used in the description of the solvent effect.

(c.f. Fig. 1) of the merocyanine dye to mimic the solvent effect influencing both the geometric and electronic properties of the MB. This allows the separation of the total effect in essentially two different contributions: the influence of the structure changes and the intramolecular charge transfer in the absorption spectra of the several forms of MB. A solvatochromic reversal is clearly obtained and interpreted in terms of the change in regime of the combined and competitive effects of charge transfer (that causes a blue shift) and structural changes (that causes a red shift). To complement this study the NMR shielding constant of  $^{13}\text{C}$  of the  $\text{C}=\text{O}$  group is also analyzed.

## 2. Methodology

An external electrostatic field was used to control the geometry distortion and the charge transfer effect. The electrostatic field was applied in the parallel direction of the merocyanine dipole (c.f. Fig. 1) and was varied from zero to  $200 \times 10^{-4}$  atomic units (au) with intervals of  $5 \times 10^{-4}$  au.

The geometry distortion was analyzed using the bond lengths shown in Fig. 1 and the bond length alternation (BLA) parameters defined as the difference between the average length of the single bonds and the double bonds of the neutral (quinoid) form of the MB. The BLA parameters used were: [6] (i)  $e - (d + f)/2$ ; and (ii)  $(c + e + g + i)/4 - (b + d + f + h)/4$ . With these definitions, positive values mean that the structure is closer to the neutral structure (c.f. Fig. 1a) and negative values indicate that the structure is closer to the zwitterionic structure (c.f. Fig. 1b).

The charge transfer was analyzed using the atomic charges obtained with the natural bond order (NBO) [38,39] and the merocyanine dipole moment calculated using the Charges from Electrostatic Potentials using a Grid-based methodology (ChelpG). [40] All geometry optimizations, charges and dipole moments calculations were performed using the DFT BHandHLYP/6-311++G(d,p) level of theory. The absorption energies were calculated using the TD DFT BHandHLYP/6-311++G(d,p) method and the  $^{13}\text{C}$  magnetic shielding constants were calculated using DFT B3LYP/6-311++G(d,p) level with the gauge including atomic orbitals (GIAOs) method [41,42]. All quantum mechanical calculations were performed using the Gaussian 03 program [43].

To analyze separately the structural change and charge transfer effects on the absorption spectra, we use three distinct possibilities:

- 1- **Flexible geometry/no Field (FG/nF):** The geometry was optimized in the presence of the electrostatic field inducing structural changes in the solute; all properties were then calculated after removing the field and keeping the resonance hybrid geometries (distorted geometries). Therefore, in this case only the structural change was considered.
- 2- **Rigid geometry/with Field (RG(X)/wF):** The geometry was kept fixed at the gas phase closer to the neutral structure ( $X = n$ , without the electrostatic field) or at the distorted geometry closer to the zwitterionic structure ( $X = z$ , see results for details) and the electrostatic field was applied for the calculation of the electronic properties. In this case, the effect of intramolecular charge transfer was analyzed in two extreme geometries. Therefore, the charge transfer was considered in each geometry.
- 3- **Flexible geometry/with Field (FG/wF):** The geometry was optimized in the presence of the electrostatic field inducing the structural changes in the solute, as in case 1, above but the electronic properties were then calculated in the presence of the electrostatic field. Therefore, in this case, both effects (structural changes and the intramolecular charge transfer) were considered simultaneously.

Optimizing the molecular geometry in the presence of a static electric field requires some care because of the need to align the molecular dipole with the field direction. Hence the optimization is made in successive steps, particularly for the high field intensities.

## 3. Results

### 3.1. Structural effect

In Fig. 2, we show the bond lengths (left) and the corresponding BLA parameters (right) of the MB optimized in the presence of the electrostatic field. The results show that the single bonds ( $a$ ,  $c$ ,  $e$ ,  $g$  and  $i$ ) become shorter with the increase of the external electrostatic field. However, the double bonds ( $b$ ,  $d$ ,  $f$ ,  $h$  and  $j$ ) become longer with the increase of the external electrostatic field. It can be noted that the first geometry, RG(n), generated without electrostatic field ( $E = 0$ ), is a quinoid-like (neutral-like) structure, because the double bonds of the rings,  $b$  and  $h$  (1.35 Å), are shorter than the other bonds,  $c$ ,  $g$ , and  $i$  (between 1.44 and 1.46 Å). The last geometry, generated with  $E = 200 \times 10^{-4}$  au, is a benzenoid-like structure, as the bonds  $b$  and  $h$  are in the same range of the other bonds of the rings (between 1.39 and 1.42 Å). Additionally it can be noted that the CO bond  $j$  increases with respect to the electrostatic field from 1.22 and 1.29 Å, the CC double bonds of the aliphatic chain,  $d$  and  $f$ , increases from 1.37 and 1.48 Å and the CC single bond of the aliphatic chain,  $e$  decreases from 1.41 and 1.34 Å. All these four bond length variations induced by the electrostatic field are related with the structural change: quinoid  $\rightarrow$  benzenoid. However considering the typical single and double bond length [44]: 1.43 and 1.23 Å for CO and 1.54 and 1.34 Å for CC respectively, we could say that in the last geometry of MB all bonds assume an intermediate length between single and double bond. Therefore, this last geometry of MB in the electrostatic field, that represents a solution with high polarity, would be a benzenoid-like structure.

As it will be discussed in the next section, the structural change induced by the electrostatic field is associated with an intramolecular charge transfer that stabilizes the structural changes. In Fig. 3, we show the variation of the internal energy of MB ( $\Delta E$ ) due to the structural change induced by the electrostatic field. Using the geometry optimized in the presence of the field and calculating

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