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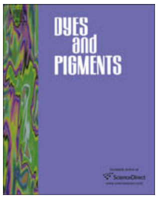

Quantitative evaluation of solvation and packing effects on the visible absorption of anthraquinone derivatives

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ABSTRACT

The solvatochromism of five anthraquinone compounds was evaluated at the TD-B3LYP level using the 6-31G(d,p) basis set whilst packing effects were investigated via an approach that combined semi-empirical and ab initio methods, namely ZINDO/TD-B3LYP/6-31G(d,p). This enabled calculation of the colourant's λ_{max} with an average accuracy of 0.14 eV. The packing effects induced large changes in the UV/VIS spectra of the anthraquinones; large bathochromic and hyperchromic displacements were observed.

1. Introduction

Anthraquininoid compounds constitute one of the most popular classes of dyes and pigments, representing ~30% of global colourant production. These compounds owe this popularity due to their abilities to provide a broad range of colours and a capacity to show long wavelength absorption bands. For instance, 9,10-anthraquinone (AQ) **1** (Fig. 1) derivatives can give rise to a large panel of shades, depending on the nature of the side groups. In addition, AQ derivatives also enter the composition of well-known vegetals and can be used to design new drugs. As a consequence, there is an intensive research aiming at designing new AQs, and rationalizing their properties. The organic pigments, especially carbonyls, are in general characterised by larger colour strengths and brightnesses than the inorganic class of pigments, though the former suffer fickle fastness properties [1,2].

The electronic excitation responsible for the colour of anthraquinones is mainly associated to a HOMO–LUMO transition, and presents the π–π^* nature that is typical of conjugated organic molecules. It can be considered that the C=O groups are the active chromophores for which the zwitterionic limiting structures (C^+–O^-) predicted by resonance structure theory have a larger weight in the excited state [3]. The magnitude of the charge separation as well as its stabilisation is directly related to the position and the height of the absorption band. Several factors that would favour a zwitterionic structure can be assessed. For instance, by grafting amino auxochromes in 1,4,5 or 8 positions of AQ, one stabilizes the C^+–O^- form due to hydrogen bonds formation [4]. Apart from these auxochromic effects, the visible spectra of AQ may be strongly affected by the nature of the surroundings of the molecule. In this work, we particularly focused on the solvent (the dielectrical medium stabilizes the excess charge of the carbonyl moeities) and the packing effects (introducing stronger specific intermolecular interactions) on the visible spectra of AQ.

While the methodology used for the evaluation and prediction of the maximum wavelength of absorption (λ_{max}) of AQ dyes in solution is now well established [5–7], there is, to our knowledge, still no consistent procedure designed to evaluate the λ_{max} (in the visible spectrum) of AQ pigments. We have therefore established a supermolecular approach to mimic the model crystal behaviour. The scheme allows to take into account the specific effects due to the intermolecular interactions but suffers important computational costs, which inevitably imply to resort to semi-empirical approaches. Indeed, our supermolecule technique combines the ZINDO [8,9] and the TD-DFT [10–16] schemes to quantify the crystal packing effects on the visible spectra of 1,4-diOH-AQ, 1,4-diNH$_2$-AQ, 1-NHMe,2-Me-AQ, 1-OH,4-NH(*p*-tolyl)-AQ, and the 1-NH$_2$,4-NHPh-AQ for which the experimental pigments spectra are available [17]. Difficulties could arise when extrapolating the results obtained from clusters of finite size to the conceptually infinite crystal, although we show that a proper description using 1- D components (constituted by clusters of 2 unit cells) is already sufficient to evaluate semi-quantitatively the packing effects on the λ_{max}.

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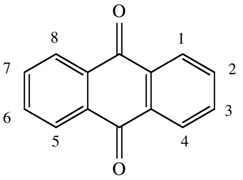

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Fig. 1. Sketch of the anthraquinone (AQ) and numbering.

2. Computational procedure

All calculations have been performed with the Gaussian 03 [18] suite of programs and the computational scheme is organized in two parts.

2.1. Solvatochromism

In a first step, we evaluate solvatochromism effects by calculating the λ_{max} difference between the isolated and solvated dye. The UV/VIS spectra have been calculated at the TD-B3LYP/6-31G(d,p) level [19,20], which is recognized to be adequate for AQs [5–7]. For the isolated systems, we first perform a so-called gas-phase calculation on the molecules with the experimental crystal geometry whereas, for liquid-phase calculations, the ground state structures of the dyes have been optimized at the DFT/B3LYP level. Following each optimization, the vibrational spectrum has been determined and it has been systematically checked that all vibrational frequencies are real. The bulk solvent effects are taken care off in the TD calculations by using the non-equilibrium Polarizable Continuum Model (PCM) solutions [12,21,22]. In this model, the system is divided into a solute part (the dye) lying inside a cavity, and a solvent part represented as a structureless material and characterised by its dielectric constant as well as other macroscopic parameters. *i*-Propanol is the experimentally used solvent and as the characteristics of this solvent are not available in the standard Gaussian 03 version, we entered the relevant values for the relative dielectric constant, ε_r (EPS = 20.18) as well as the relative dielectric constant at infinite frequency, ε_∞ (EPSINF = 1.896), to stick to the experimental conditions [23].

2.2. Solid-state effects

The evaluation of the pigments λ_{max} follows a two-step methodology:

(1) The crystal structures of the compounds are available in the Cambridge Structural Database (CSD Version 5.28, 11/2006). The ref codes corresponding to 1,4-diOH-AQ; dihydrated 1,4-diNH$_2$-AQ; 1-NHMe,2-Me-AQ; 1-OH,4-NH(*p*-tolyl)-AQ; and 1-NH$_2$,4-NHPh-AQ are DHXANT (*Z*, the number of molecules in the unit cell is 4 and the space group is P21/a) [24]; GICXOF (*Z* = 4, *Pnma*) [25]; XAPBIZ (*Z* = 2, P-1) [26]; WISKIS (*Z* = 4, P21) [27]; and FUFDUF (*Z* = 4, P21/c) [28], respectively. For all five systems, the *R* factor is lower than 0.07, ensuring the reliability of the crystallographic structures [29]. As an example, Fig. 2 depicts the orientation of the *a*, *b*, and *c* crystallographic axes for the (2H$_2$O)1,4-diNH$_2$-AQ and 1,4-diOH-AQ unit cell (UC). Note that most H atoms can generally be located in difference Fourier maps after refinement. The remaining H atoms are calculated geometrically (using the SHELXL97 software [30]) and restrained to ride on their parent atoms.

(2) The evolution of the pigment λ_{max} is provided on the energetic scale (i.e., in eV) by the relation:

$$\lambda_{\text{max}}^{\text{pigment}}(n,m) = \lambda_{\text{max}}^{\text{TD-DFT}}(0,0) \pm \Delta\lambda_{\text{max}}^{\text{ZINDO}}(n,m) \qquad (1)$$

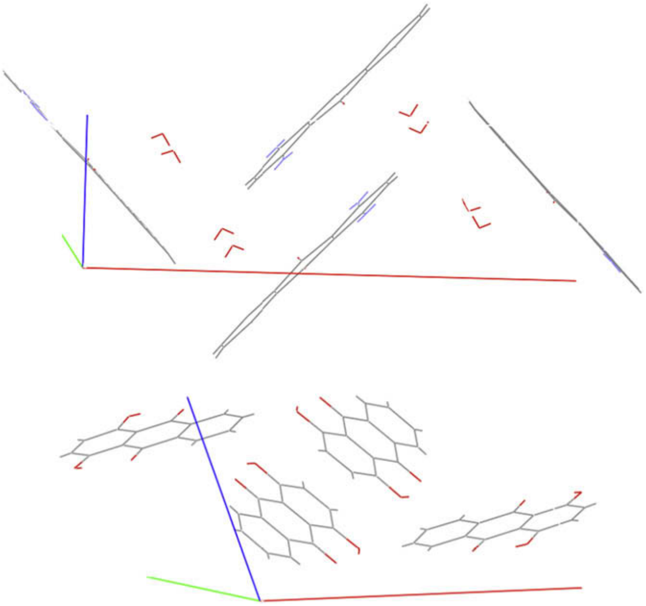

Fig. 2. Crystallographic axes *a* (in red), *b* (in green), and *c* (in blue) associated to the *Pnma* (2H$_2$O) 1,4-diNH$_2$-AQ (top) and the P21/a 1,4-diOH-AQ (bottom) unit cell. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In this mixed ab initio/semi-empirical scheme, we calculate the displacement factor (DF) $\Delta\lambda_{\text{max}}$ (n,m) of the maximum wavelength of absorption induced by the increase of the cluster size. Because of the large cluster sizes considered, the DF is calculated at the semi-empirical level with ZINDO. The excitation energy of the pigment $\lambda_{\text{max}}^{\text{pigment}}$ is then obtained by adding the global $\Delta\lambda_{\text{max}}^{\text{ZINDO}}$ (n,m) to the gas-phase B3LYP λ_{max} (0,0) of the isolated molecule. In Eq. (1), the final sign of ± is + (−) when the global crystal packing effect is hypsochromic (bathochromic).

The description of 1D packing effects is noted by the growth index GI(n) (for a growth of the crystal following the *a* or *b* or *c* axis). More precisely, $n = 0$ corresponds to one isolated molecule, $n = 1$ is associated to one UC and $n = 3$ corresponds then to a 3 UCs cluster. The description of 2D packing effects is noted by the GI(m) (for a growth of the crystal following the *ab* or *ac* or *bc* planes). Note that in the 2D context, $m = 0$ corresponds to one isolated molecule. Fig. 3 illustrates the growth of a crystal following the *b* axis and the *bc* plane; this figure shows that $m = 1$ corresponds to four UCs. For n superior or equal to 2, the global packing shift is calculated using:

$$\sqrt{\left(\Delta\lambda_{\text{max}}^{\text{ZINDO}}(n)\right)_a^2+\left(\Delta\lambda_{\text{max}}^{\text{ZINDO}}(n)\right)_b^2+\left(\Delta\lambda_{\text{max}}^{\text{ZINDO}}(n)\right)_c^2} \qquad (2)$$

whereas for $m \geq 1$, the $\Delta\lambda_{\text{max}}^{\text{ZINDO}}$ is provided by:

$$\sqrt{\left(\Delta\lambda_{\text{max}}^{\text{ZINDO}}(m)\right)_{ab}^2+\left(\Delta\lambda_{\text{max}}^{\text{ZINDO}}(m)\right)_{bc}^2+\left(\Delta\lambda_{\text{max}}^{\text{ZINDO}}(m)\right)_{ac}^2} \qquad (3)$$

We provide in Fig. 4 a representation of our procedure: as an example, for a 1D growth of the crystal, the packing effects can be dissociated into three components (three vectors): $(\Delta\lambda_{\text{max}}^{\text{ZINDO}}(n))_a$, $(\Delta\lambda_{\text{max}}^{\text{ZINDO}}(n))_b$, $(\Delta\lambda_{\text{max}}^{\text{ZINDO}}(n))_c$. The resulting vector therefore corresponds to the global packing effects (dotted vector).

3. Results

3.1. Solvatochromism

A characteristic feature of the absorption spectra of numerous AQ derivatives is the existence (in the long wave band) of several