



Solvatochromic fluorescence of 4-alkoxybenzoic acid liquid crystals: Ground and excited state dipole moments of monomer and dimer structures determined by solvatochromic shift methods



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ABSTRACT

The absorption and fluorescence spectra of 4-ethoxybenzoic acid (4EOBA), 4-propoxybenzoic acid (4POBA) and 4-butoxybenzoic acid (4BOBA) liquid crystals have been recorded and evaluated comprehensively in a series of organic solvents. The fluorescence is observed as highly sensitive to solvent polarity, giving a synthetic rainbow of emission in different organic solvents. The ground state (μ_g) and excited state (μ_e) dipole moments of the monomer and dimer structures of the 4-alkoxybenzoic acid liquid crystals are determined by means of Bilot–Kawski, Lippert–Mataga, Bakhshiev, Kaski–Chamma–Viallet and Reichardt solvatochromic shift methods based on dielectric constant and refractive index function. Excited state dipole moments are found as larger than the ground state dipole moments both in monomer and dimer forms. Ground state dipole moments of dimer structures are observed to be higher than that of monomer structures. Consistency between experimental and theoretically computed ground state dipole moments indicates that molecules exist in dimer form. Solute–solvent interactions are analyzed by means of linear solvation energy relationships (LSERs) using Kamlet–Taft and Catalan parameters. Kamlet–Taft solvatochromic model indicates that dispersion–induction interaction has the stronger effect compared to dipolar–orientation interaction in controlling solute–solvent interactions. It is also found that solvatochromic behavior is dominantly controlled by hydrogen bond donor ability. Catalan model displays that the solvent of basicity is relatively affective to refer to the solvatochromic behavior. Both Kamlet–Taft and Catalan models designate positive solvatochromism for absorption and fluorescence spectra. HOMO, LUMO, molecular electrostatic potential (MEP) and solvent accessible surface (SAS) of monomer and dimer 4-alkoxybenzoic acids are calculated by using DFT-B3LYP method.

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1. Introduction

Liquid crystals (LCs) have an important potential for functional molecular systems because of their self-organized dynamic structure and their prospective optical characteristics [1–3]. LCs take place in many applications such as displays in digital watches, calculators, cell phones and laptops [4–9]. Hydrogen-bonded liquid crystals have attracted a great deal of interest, due to their structural and dynamic properties as they play significant roles in many chemical and biological systems [10,11]. 4-Methoxybenzoic acid was also observed as a degradation compound of dibenzenotiofeno [12], which belongs to the class of the polycyclic aromatic hydrocarbons (PAHs), being considered an environmental pollutant mainly due to their mutagenic and carcinogenic potentials. 4-Alkoxybenzoic acids have been studied as tyrosinase inhibitors in the food chemistry [13].

4-Alkoxybenzoic acid liquid crystals are the only examples of mesogens with one ring. Generation of liquid crystal phases is known

as required at least two rings. Although a single molecule cannot have a long species or lath-like shape, dimerization via hydrogen-bonding leads to molecule has long lath-like structure with a three-ring core and two flexible terminal chains [14]. Alkoxybenzoic acids have attracted a lot of attention and show that hydrogen-bonding gives a strong contribution for generating the novel LC materials due to dimerization of either symmetrical dimers or asymmetrical dimers [15–17]. Liquid crystals are strongly stabilized by forming hydrogen bond and depending on thermodynamic conditions; they can exist as mixtures of various compositions of monomer, or open or closed dimer [18]. Earlier studies reported that increasing the terminal alkyl group gives rise to supramolecular hydrogen-bonded complexes with 4-alkoxybenzoic acid liquid crystal which has lower melting point, greater mesophase and thermal stability. Additionally, alkyl chain length is a very important parameter which influences the properties of mesogen molecules [19,20]. Depending on the detailed literature investigation of alkoxybenzoic acid and 4-alkoxybenzoic acid liquid crystals, it seems that most of the studies are focused on liquid crystal properties and crystal structure [21–25,15], and thermodynamic and spectroscopic properties [26–31,17,18].

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Taking into account the abovementioned applications and properties of 4-alkoxybenzoic acid liquid crystal derivatives, we have proposed a research project aiming to investigate the ground and excited state dipole moments and solvatochromic behaviors. To the best of our knowledge, there is no reported works include the dipole moment and solvatochromic behaviors on 4-alkoxybenzoic acid liquid crystals in the literature so far.

2. Materials and methods

2.1. Theoretical background

2.1.1. Bilot–Kawski method

Kawski and co-workers [32–35] obtained a simple quantum mechanical relation for absorption ($\tilde{\nu}_a$) and fluorescence ($\tilde{\nu}_f$) band shifts in different solvents of varying permittivities (ϵ) and refractive indexes (n). According to this formulism, the difference and sum of absorption, $\tilde{\nu}_a$, and fluorescence maxima, $\tilde{\nu}_f$ (in cm^{-1}) can be expressed by the following independent equations:

$$\tilde{\nu}_a - \tilde{\nu}_f = m^{(1)}f(\epsilon, n) + \text{constant} \quad (1)$$

$$\tilde{\nu}_a + \tilde{\nu}_f = -m^{(2)}[f(\epsilon, n) + 2g(n)] + \text{constant} \quad (2)$$

where $m^{(1)}$ and $m^{(2)}$ are the slopes obtained from Eqs. (1) and (2), respectively.

These relations can be used for estimating ground and excited state dipole moments of solute molecules. If the polarizability of the solute can be considered as isotropic and with the condition $2\alpha/a^3 = 1$ [36] where α is the polarizability and a is the Onsager cavity radius of the solute, $f(\epsilon, n)$ and $g(n)$ can be described as:

$$f(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \quad (3)$$

$$g(n) = \frac{3}{2} \left(\frac{n^4 - 1}{(n^2 + 2)^2} \right). \quad (4)$$

According to Onsager's reaction field theory:

$$m^{(1)} = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (5)$$

and

$$m^{(2)} = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (6)$$

where μ_g and μ_e are the dipole moments in the ground and excited states, respectively, h the Planck's constant (6.63×10^{-34} J s), c the velocity of light in vacuum (3.0×10^8 ms^{-1}), and a the Onsager's interaction radius of solute. The parameters $m^{(1)}$ and $m^{(2)}$ can be obtained from the slopes of straight lines correlating the difference and sum of absorption and fluorescence band maxima (Eqs. (1) and (2)). Considering that the symmetry of the investigated solute molecule remains unchanged upon electronic transition and that ground and excited state dipole moments are parallel, the following expressions are obtained on the basis of Eqs. (5) and (6) [37,38].

$$\mu_g = \frac{m^{(2)} - m^{(1)}}{2} \left(\frac{hca^3}{2m^{(1)}} \right)^{1/2} \quad (7)$$

$$\mu_e = \frac{m^{(2)} + m^{(1)}}{2} \left(\frac{hca^3}{2m^{(1)}} \right)^{1/2} \quad (8)$$

and

$$\mu_e = \frac{m^{(1)} + m^{(2)}}{m^{(2)} - m^{(1)}} \mu_g \text{ for } (m^{(2)} > m^{(1)}). \quad (9)$$

Generally, the dipole moments μ_g and μ_e are not parallel to each other but make an angle φ given by Eq. (10):

$$\text{Cos}\varphi = \frac{1}{2\mu_g\mu_e} \left[(\mu_g^2 + \mu_e^2) - \frac{m^{(1)}}{m^{(2)}} (\mu_e^2 - \mu_g^2) \right]. \quad (10)$$

The short-range specific interactions between solvent and solute molecules, such as hydrogen bonding, which are observed as deviations from the dielectric solvatochromic plot $f(\epsilon, n)$, are not taken into consideration in the abovementioned theory.

2.1.2. Lippert–Mataga, Bakhshiev and Kawski–Chamma–Viallet methods

Experimental excited singlet-state dipole moments were also determined by the solvatochromic methods, using the equations proposed by Lippert–Mataga (Eq. (11)) [39,40], Bakhshiev (Eq. (12)) [41] and Kawski–Chamma–Viallet (Eq. (13)) [33,42].

$$\tilde{\nu}_a - \tilde{\nu}_f = m_{L-M} F_{\text{Lippert–Mataga}}(\epsilon, n) + \text{constant} \quad (11)$$

$$\tilde{\nu}_a - \tilde{\nu}_f = m_B F_{\text{Bakhshiev}}(\epsilon, n) + \text{constant} \quad (12)$$

$$\frac{\tilde{\nu}_a + \tilde{\nu}_f}{2} = -m_{K-C-V} F_{\text{Kawski–Chamma–Viallet}}(\epsilon, n) + \text{constant} \quad (13)$$

where

$$m_{L-M} = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (14)$$

$$m_B = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (15)$$

$$m_{K-C-V} = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (16)$$

$\tilde{\nu}_a$ and $\tilde{\nu}_f$ are the absorption and fluorescence maxima wavenumbers (in cm^{-1}), respectively. $F_{\text{Lippert–Mataga}}(\epsilon, n)$, $F_{\text{Bakhshiev}}(\epsilon, n)$, and $F_{\text{Kawski–Chamma–Viallet}}(\epsilon, n)$ are the solvent functions given by Eqs. (17), (18), and (19), respectively; m_{L-M} , m_B and m_{K-C-V} are the slopes found by linear curve fitting corresponding to Eqs. (17), (18), and (19), respectively.

$$F_{\text{Lippert–Mataga}}(\epsilon, n) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (17)$$

$$F_{\text{Bakhshiev}}(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (18)$$

$$F_{\text{Kawski–Chamma–Viallet}}(\epsilon, n) = \left[\frac{2n^2 + 1}{2(n^2 + 2)} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \right]. \quad (19)$$

2.1.3. Molecular-microscopic solvent polarity parameter (E_T^N)

The empirical solvent polarity parameter, E_T^N , proposed by Reichardt correlates better with spectral shift than the traditionally used bulk solvent polarity functions involving dielectric constant (ϵ) and refractive

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