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## Estimation of ground and excited state dipole moments of Oil Red O by solvatochromic shift methods



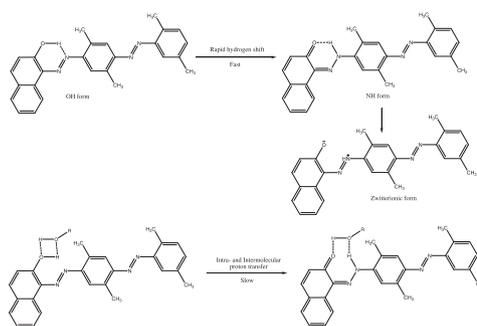
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### HIGHLIGHTS

- The ground and excited state dipole moments are determined by solvatochromic shift methods.
- For Oil Red O  $\mu_g > \mu_e$ .
- Absorption spectra do not sensitive to solvent change, while fluorescence spectra exhibit positive solvatochromism.
- Enol-keto tautomerism is not observed in the absorption and fluorescence spectra.

### GRAPHICAL ABSTRACT



Possible equilibrium structures of Oil Red O

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### ABSTRACT

Absorption and fluorescence spectra of Oil Red O (abbreviated as ORO) are recorded in various solvents with different polarity in the range of 250–900 nm, at room temperature. The solvatochromic shift methods have been used to determine the ground state ( $\mu_g$ ) and excited state ( $\mu_e$ ) dipole moments depending on dielectric constant and refractive index functions. It is observed that fluorescence spectra show positive solvatochromism whereas absorption spectra do not indicate sensitive behavior to solvent polarity. Excited state dipole moment is found as higher than those of ground state for all of the used methods and it is attributed to more polar excited state of ORO. Theoretical  $\mu_g$  has been determined by quantum chemical calculations using DFT and semi empirical methods. HOMO, LUMO, molecular electrostatic potential (MEP) and solvent accessible surface of ORO are calculated by using DFT-B3LYP method.

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### Introduction

Azo dyes are one of the most significant classes of colorants in term of their practical applications. Their importance comes from their use in the areas of textile, paper printing, food, toys, manufacture of drugs, nonlinear optical devices (NLO) and liquid crystalline displays (LCDs), optical data storage, a catalyzer in photo-catalytic reactions [1–13]. Oil Red O is used as a developer for fingerprints on wetted papers [14–17].

The optical properties and solvatochromic behavior of the azo dyes depend on the nature of electron donor/acceptor substituents, the *cis-trans* photoisomerization in azo chromophores, charge transfer (CT) mechanism and solute–solvent interactions. Azo dyes, especially those containing hydroxyl group in *ortho*-position can exist in three forms such as OH, NH and zwitterionic form. This tautomerism is generally observed in the solution phase. It is assumed that the tautomers in solution are stabilized by a strong intramolecular resonance assisted hydrogen bond (RAHB). The main structural characteristics are mainly due to the presence of at least one azo group ( $-N=N-$ ) connecting to phenyl rings

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(Ph–N=N–Ph) along with the donor/acceptor substituents located at *ortho*–*meta*–*para* positions on phenyl ring.

Zakerhamidi and co-workers determined the ground state and excited state dipole moments of some diazo Sudan dyes [18].

In this study, we have determined the ground state and excited state dipole moments of ORO by using Bilot–Kawski, Lippert–Mataga, Bakhshiev, Kawski–Chamma–Viallet and Reichardt solvatochromic shift methods. Solvent effects on absorption and fluorescence spectra are evaluated. Quantum chemical methods have been performed to calculate dipole moment, HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), molecular electrostatic potential (MEP) and solvent accessible surface (SAS) of ORO.

## Theoretical background

### Bilot–Kawski method

Kawski and co-workers [19–22] obtained a simple quantum mechanical relation for absorption ( $\tilde{\nu}_a$ ) and fluorescence ( $\tilde{\nu}_f$ ) band shifts in different solvents of varying permittivity ( $\epsilon$ ) and refractive index ( $n$ ). According to this formulism, the difference and sum of absorption,  $\tilde{\nu}_a$ , and fluorescence maxima,  $\tilde{\nu}_f$  (in  $\text{cm}^{-1}$ ) can be expressed by 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 slopes obtained from the relation (1) and (2).

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  $2\alpha/a^3 = 1$  [23] where  $\alpha$  is polarizability and  $a$  is 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  $\mu_g$  and  $\mu_e$  are the dipole moments in the ground and excited states, respectively,  $h$  Planck's constant ( $6.63 \times 10^{-34}$  J s),  $c$  the velocity of light in vacuum ( $3.0 \times 10^8$  m s $^{-1}$ ),  $a$  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 symmetry of the investigated solute molecule remains unchanged upon electronic transition and that ground and excited states dipole moments are parallel, the following expressions are obtained on the basis of Eqs. (5) and (6) [24,25].

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

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

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  $\mu_g$  and  $\mu_e$  are not parallel to each other but make an angle  $\varphi$  given by Eq. (10):

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

The short-range specific interactions between the 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 above mentioned theory.

### Lippert–Mataga, Bakhshiev and Kawski–Chamma–Viallet methods

Experimental ground and excited singlet-state dipole moments were also determined by the solvatochromic method, using the equations proposed by Lippert–Mataga (Eq. (11)) [26,27] Bakhshiev (Eq. (12)) [28] and Kawski–Chamma–Viallet (Eq. (13)) [20,29]

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

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

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

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

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

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

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

### 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 ( $\epsilon$ ) and refractive index ( $n$ ) [30]. The change in dipole moment is evaluated by using the following equation:

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