



Estimation of ground and excited-state dipole moments of 1, 2-diazines by solvatochromic method and quantum-chemical calculation

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ABSTRACT

Using the theory of solvatochromism, the difference in the excited-state (μ_e) and ground-state (μ_g) dipole moments was determined from Lippert–Mataga, Bakhshiev, Kawski–Chamma–Viallet, and McRae equations for three 1,2-diazines (pyrrolo-pyridazine derivatives). All of these equations are based on the variation of Stokes shift with solvent's relative permittivity and refractive index. Further, the change in dipole moment value ($\Delta\mu$) was also calculated using the variation of Stokes shift with the molecular-microscopic empirical solvent polarity parameter. Theoretical μ_g values were evaluated by quantum chemical calculations using the DFT method by adopting B3LYP/6-31G* level of theory (Gaussian 03) and using the AM1 method (Chem3D Ultra 8.0). It was observed that, dipole moments of diazines in the excited-state (μ_e) were greater than the corresponding ground-state values (μ_g), indicating a substantial redistribution of the π -electron densities in a more polar excited-state. Also, with the increase in the polarity of the solvent, the fluorescence emission peak undergoes a red-shift, confirming a $\pi \rightarrow \pi^*$ transition.

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1. Introduction

Recently, the 1,2-diazine derivatives have proved to be invaluable materials in the field of medicine, optoelectronics and agriculture, with applications in the areas of biomedical, material sciences and electronics [1]. 1,2-diazines were found to play an important role due to their pharmaceutical applications which include a wide range of biological activities, such as antiviral, anticarcinogenic, antituberculosis, antimicrobials, antifungal, anti-inflammatory, antihypertensive, antithrombics, anticoagulants, antidepressant, anxiolytics, anticonvulsant, analgesic, anti-multiple sclerosis, antidiabetes, antiulcer, antisecretory, and antiasthma. 1,2-diazine derivatives find their applications in the field of optoelectronics mainly as highly fluorescent derivatives [in displays, components of organic light emitting devices (OLED), field effect transistors (FET), in sensors, in biosensors, in lasers, in semiconductor and nonlinear optical materials (NLO), and in photovoltaic cells]. Also, these derivatives exhibit liquid crystal properties. In the field of agriculture, diazines are useful as herbicides and also serve as grow up factors for plants.

A dipole moment represents a direct measure of the electron distribution in a molecule. Excitation of a molecule by a photon causes a redistribution of charges leading to conformational changes in the excited-state. This can result in an increase or decrease of the dipole moment of an excited-state as compared to the ground-state. The

excited-state dipole moment of a molecule is an important parameter, which reveals information on the electronic and geometrical structures of the molecule in the short-lived excited-state. The knowledge of dipole moments of first electronically excited-singlet state (S_1) of the molecules is quite useful in designing materials with nonlinear optical properties [2], and elucidating the nature of the excited states. It also reflects the charge distribution in the molecule and facilitates to predict the site of attack by electrophilic and nucleophilic reagents in some photochemical reactions. Further, the experimental data on dipole moments are useful in parameterization in quantum chemical methods [3]. The excited-state dipole moments of fluorescent molecules reported in this article also determine the tunability range of the emission energy as a function of the polarity of the medium.

The dipole moment is a physical constant, which can be obtained by experimental and theoretical methods. A number of excellent textbooks, monographs, and reviews devoted to dipole moments are available and provide detailed information on the theory of dipole moments [4–9]. Although most of these references are not recent, they have served as excellent sources of information.

Experimental methods for the determination of singlet excited-state dipole moments are based on experimental ground-state dipole moments and a change of the position of a spectral band (in an electronic spectrum) caused by an electric field, which can be either external (electrochromism) or internal (solvatochromism). The electro-optic methods (electrochromism) such as electronic polarization of fluorescence [10], electric-dichroism [9], microwave conductivity [11] and

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Stark splitting [12] are generally considered to be very accurate, but their use is limited because they are considered as equipment sensitive and the studies have been restricted to relatively very simple molecules. The solvatochromic method is experimentally much simpler and widely accepted, as it does not use any external field [13,14]. This method is based on a linear correlation between the wave numbers of the ultraviolet–visible absorption and fluorescence maxima, and a solvent polarity function which involves both relative permittivity, ϵ_r , and refractive index, n , of the medium [15–21]. Koutek [21] has shown that under suitable conditions, the solvatochromic method yields fairly satisfactory results. Recently, several authors have published experimental and theoretical studies on ground-state and excited-state dipole moments of a variety of fluorescent molecules using the solvatochromic method [22–27].

Mangalagiu et al. [28] and Zbancioc et al. [29] have reported the synthesis, and studies on the absorption and fluorescence spectra of three 1,2-diazines (Fig. 1) in different organic solvents. In the present work, we report the estimation of ground- and excited-state dipole moments for these diazines. To the best of our knowledge, there are almost no reports on the determination of μ_g and μ_e values for these

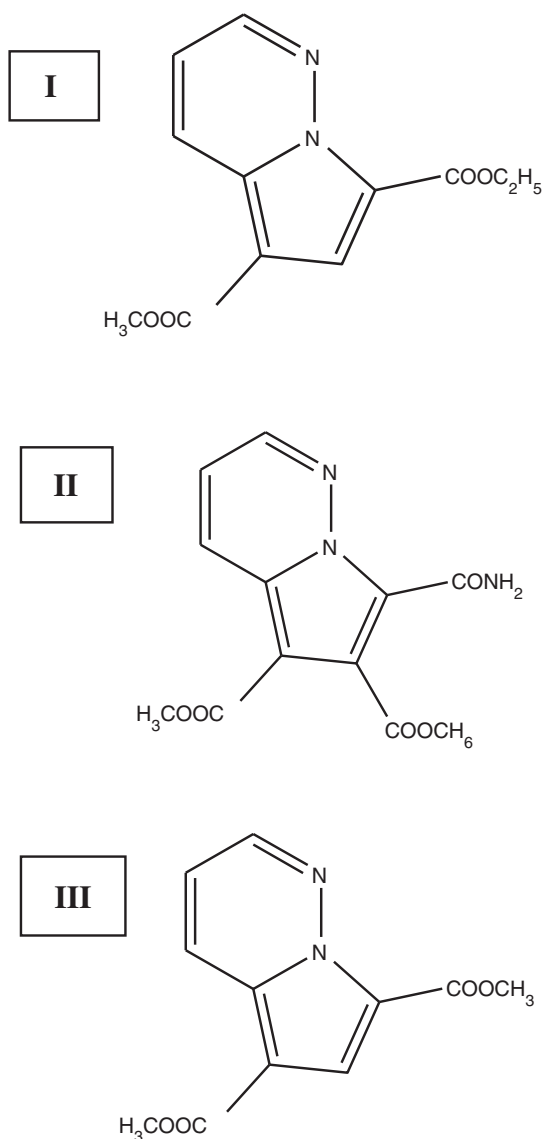


Fig. 1. Molecular structures of 1,2-diazines (I, II, and III).

1,2-diazines, and hence there is a dearth of information on their dipole moments. This prompted us to carry out the present investigation. In this article, we have also compared the experimental μ_g values with theoretical μ_g values obtained by quantum chemical calculations, e.g. Gaussian 03 [30].

2. Mathematical equations for the evaluation of dipole moments

2.1. Solvatochromic method

The displacement of electronic absorption and fluorescence spectra of a solute is related to its interaction with the solvent. These interactions can be non-specific, when they depend only on multiple and polarizability properties of solute and solvent molecules. When the liquid solvent surrounds a solute molecule, then the solvent can affect the solute molecule by its polarity. The number of electronic states which can be defined for a molecule are determined through Schrödinger wave equation, $E\psi = H\psi$, where E , H and ψ being the total energy, Hamiltonian and wave function of a state, respectively. The wave function, ψ , gives information about the nature of the state.

By employing the simplest quantum-mechanical second-order perturbation theory of a spherical solute and taking into account Onsager's model of reaction field for a polarizable dipole moment, the following two equations for the difference and sum of wave numbers corresponding to absorption, $\bar{\nu}_a$, and fluorescence maxima, $\bar{\nu}_f$, were obtained [10,19,31]:

$$\bar{\nu}_a - \bar{\nu}_f = \frac{(\vec{\mu}_e - \vec{\mu}_g)^2}{hc} (1 - \alpha f')^{-1} [f(1 - \alpha f')^{-1} - f'(1 - \alpha f')^{-1}] + \text{constant} \quad (1)$$

$$\bar{\nu}_a + \bar{\nu}_f = -\frac{(\vec{\mu}_e^2 - \vec{\mu}_g^2)}{hc} \left\{ (1 - \alpha f')^{-1} [f(1 - \alpha f')^{-1} - f'(1 - \alpha f')^{-1}] + f'(2 - \alpha f')(1 - \alpha f')^{-1} \right\} + \text{constant} \quad (2)$$

where $\bar{\nu}_a$ and $\bar{\nu}_f$ are absorption and fluorescence maxima wave numbers in cm^{-1} . α is the mean static isotropic polarizability of the solute. f and f' are reaction field factors which depend on the shape and the Onsager cavity radius, a , of the solute and also on the relative permittivity, ϵ_r , and the refractive index, n , of the solvent.

Eqs. (1) and (2) can be written in the simple form as [31],

$$\bar{\nu}_a - \bar{\nu}_f = m_1 f(\epsilon_r, n) + \text{constant} \quad (3)$$

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -m_2 \varphi(\epsilon_r, n) + \text{constant} \quad (4)$$

where

$$\varphi(\epsilon_r, n) = \frac{f(\epsilon_r, n)}{2} + g(n) \quad (5)$$

$$m_1 = \frac{2(\vec{\mu}_e - \vec{\mu}_g)^2}{hca^3} = \frac{2(\mu_e^2 + \mu_g^2 - 2\mu_e\mu_g \cos \varphi)}{hca^3} \quad (6)$$

and

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3}. \quad (7)$$

In Eqs. (6) and (7), μ_e and μ_g are the excited- and ground-state dipole moments of the solute molecule, respectively. The symbols h and c are Planck's constant and velocity of light in vacuum, respectively. ' a ' is the Onsager cavity radius of the solute molecule and its value can be evaluated by atomic increment method [32]. Generally, when dipole

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