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"Estimation of Ground and Excited State Dipole Moments of aryl Boronic acid Derivative by Solvatochromic Shift Method"

G. V. Muddapur · N. R. Patil · S. S. Patil · R. M. Melavanki · R. A. Kusanur

Abstract In the present work, the absorption and fluorescence spectra of newly synthesized aryl boronic acid derivative namely 2-Methylphenyl boronic acid (2MPBA) have been recorded in various solvents of different polarities. The ground state dipole moment of 2MPBA was obtained from quantum chemical calculations. Solvatochromic correlations were used to estimate the ground state (μ_g) and excited state (μ_e) dipole moments. The excited state dipole moments are observed to be greater than the ground state dipole moment and ground and excited state dipole moments are not parallel but subtend by an angle of 88^0. Further, the changes in dipole moment ($\Delta\mu$) were calculated both from solvatochromic shift method and microscopic solvent polarity parameter (E_T^N), and the value are compared. The spectral variations were analyzed by Kamlet-Taft parameters.

Keywords Solvent polarity · DFT · Boronic acid · Kamlet-Taft · Angle between dipole moments

G. V. Muddapur · N. R. Patil (✉)
Department of Physics, B V B College of Engineering and Technology, Hubli 580031, Karnataka, India
e-mail: patilnr23@gmail.com

S. S. Patil
Department of Physics, Government R G S P U College, Kittur 591115, Karnataka, India

R. M. Melavanki (✉)
Department of Physics, M S Ramaiah Institute of Technology, Bangalore 560054, Karnataka, India
e-mail: melavanki74@rediffmail.com

R. A. Kusanur
Department of Chemistry, R V College of Engineering, Bangalore 560059, Karnataka, India

Introduction

Boronic acids and their derivatives establish a family of dyes which are applicable indifferent fields of science and technology. Boronic acids have potential applications and they are very important in synthetic organic, materials, bioorganic, and medicinal chemistry as well as chemical biology. In organic chemistry, boronic acids are very important in Suzuki-Miyaura coupling, aromatic functionalization (such as amination) with a heteroatom containing functional group and protection of diols. In materials chemistry, boronic acids are important in crystal engineering, construction of polymers with reversible properties, building unique molecular architects, functionalization of nanostructures, separation and purification of glycosylated products and feed-back controlled drug delivery (glucose). In bioorganic chemistry, boronic acid is a commonly used recognition moiety for the design and synthesis of sensors for carbohydrates, amino acids, in medicinal chemistry, boronic acids are important for the preparation of inhibitors of hydrolytic enzymes in boron neutron capture therapy (BNCT), quorum sensing inhibition, antifungal agent development, and the inhibition of other enzymes. Among all the biologically active boronic acids, bortezomib is an FDA-approved anticancer agent. In chemical biology, boronic acids are used in the detection and sensing of peroxides, recognition and sensing of the tetraserine motif in protein, development of new MRI contrast agents [1]. Further, Boronic acids exhibit strong fluorescence in the UV and VISIBLE region which makes them suitable for used as colorants, dye laser media and as nonlinear optical chromspheres [2]. Solvent effect on the absorption and fluorescence characteristics of organic compounds has been a subject of interesting investigation [3, 4]. Knowledge of ground and electronically excited state dipole moments of a molecule are important properties that provide valuable information about the electronic and geometrical structure of the molecule in short lived state.

Among the different methods of determining excited state dipole moment (μ_e) solvatochromic method [5–8] is the most widely used one. This method has been based on a linear correlation between the wave numbers of the absorption and fluorescence maxima and a solvent polarity function. Such correlations have been derived from quantum mechanical second order perturbation and Onsager's reaction field theories for development of solvent polarity functions. The most employed solvent polarity functions are those obtained by Lippert–Mataga [9], Bakhshiev [10], Kawski–Chamma–Viallet [11–13], which use both dielectric constant (ε) and refractive index (n) of the medium as empirical parameters. Several workers have made extensive experimental and theoretical studies on ground state (μ_g) and excited state (μ_e) dipole moments using different techniques in variety of organic fluorescent compounds like coumarins [14–20], Carboxamides [21], thiophenes [22], ketocyanine dyes [23], and in some laser dyes [24–31] etc. Because of the tremendous importance of boronic acids, there is interest in finding ways to increase their structural diversity. Hence, in the present work we report the effects of solvent on absorption and emission spectra, and estimation of ground and excited state dipole moments of title compound namely 2-Methylphenyl boronic acid (2MPBA) by solvatochromic shift method and also theoretical computed results from ab initio calculations using DFT. However, there are no reports available in literature on the estimation of ground and excited state dipole moments for aryl boronic acids. This has prompted us to carryout the present work.

Theory

Theoretical Calculations of Ground State Dipole moments

The ground state dipole moments of the 2MPBA were calculated using quantum chemical calculations. All the computations were carried out using Gaussian 09 program on a Pentium- 4 PC and the basis set level used is B3LYP/6–31 g*.

Experimental Calculation of Ground and Excited State Dipole Moments

The three independent equations used for the estimation of excited state dipole moment of boronic acid derivatives are as follows.

Lippert's equation [9],

$$\left(\overline{v}_a - \overline{v}_f\right) = m_1 F_1(\varepsilon, n) + \text{Constant} \tag{1}$$

Bakhshiev's equation [10],

$$\left(\overline{v}_a - \overline{v}_f\right) = m_2 F_2(\varepsilon, n) + \text{Constant} \tag{2}$$

Kawski-Chamma-Viallet's equation [11–13].

$$\frac{\left(\overline{v}_a + \overline{v}_f\right)}{2} = m_3 F_3(\varepsilon, n) + \text{Constant} \tag{3}$$

where $\overline{v}_a$ and $\overline{v}_f$ are absorption and emisssion maxima wavenumbers in cm^{-1}, $\left(\overline{v}_a - \overline{v}_f\right)$ is Stokes shift, $\frac{\left(\overline{v}_a + \overline{v}_f\right)}{2}$ is arithmetic mean of absorption and emission wave number, ε and n are dielectric constant and refractive index of solvents respectively. The expressions for [Lippert's polarity equation] $F_1(\varepsilon, n)$, [Bakhshiev's polarity equation] $F_2(\varepsilon, n)$, and [Kawski-Chamma-Viallet's polarity equation] $F_3(\varepsilon, n)$ are given as

$$F_1(\varepsilon, n) = \left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right] \tag{4}$$

$$F_2(\varepsilon, n) = \left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right]\frac{(2n^2+1)}{(n^2+2)} \tag{5}$$

$$F_3(\varepsilon, n) = \frac{2n^2+1}{2(n^2+2)}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] + \frac{3(n^4-1)}{2(n^2+2)^2} \tag{6}$$

From Eqs. (4)-(6) it follows that $(\overline{v}_a - \overline{v}_f)$ versus $F_1(\varepsilon, n)$, $(\overline{v}_a - \overline{v}_f)$ versus $F_2(\varepsilon, n)$ and $1/2(\overline{v}_a + \overline{v}_f)$ versus $F_3(\varepsilon, n)$ should give linear graphs with slopes m_1, m_2 and m_3 respectively and are given as

$$m_1 = \frac{2\left(\mu_e - \mu_g\right)^2}{hca^3}$$

$$m_2 = \frac{2\left(\mu_e - \mu_g\right)^2}{hca^3}$$

$$m_3 = \frac{2\left(\mu^2_e - \mu^2_g\right)}{hca^3}$$

Where μ_g and μ_e are the ground and excited state dipole moments of the solute molecules. h is Planck's constant and c

is velocity of light, 'a' is the radius of the solute molecule and the value was calculated from the molecular volume of molecule (http://www.molinspiration.com/cgi-bin/properties). If the ground state and excited states are parallel, the following expressions are obtained on the basis of Eqs. (8) and (9) [32, 33].

$$\mu_g = \frac{m_3 - m_2}{2} \left[\frac{hca^3}{2m_2} \right]^{1/2} \tag{7}$$

$$\mu_e = \frac{m_3 + m_2}{2} \left[\frac{hca^3}{2m_2} \right]^{1/2} \tag{8}$$

and

$$\mu_e = \left[\frac{m_2 + m_3}{m_3 - m_2} \right] \mu_g \quad \text{for } m_3 > m_2 \tag{9}$$

If dipole moments μ_e and μ_g are not parallel to each other and form an angle ϕ, then ϕ can be calculated using Eq. (10).

$$\cos\phi = \frac{1}{2\mu_g\mu_e} \left[\left(\mu_g^2 + \mu_e^2 \right) - \frac{m_3}{m_2} \left(\mu_e^2 - \mu_g^2 \right) \right] \tag{10}$$

Molecular-Microscopic Solvent Polarity Parameter (E_T^N)

The empirical polarity parameter E_T^N proposed by Reichardt [34] gave towering results with solvatochromic shift of dipolar molecule. The results correlate better with microscopic solvent polarity E_T^N rather than the traditionally used bulk solvent polarity functions involving dielectric constant (ε) and refractive index (n) as in the later error estimation of Onsager cavity radius 'a' has been minimized. This method is based on empirical solvent polarity parameter E_T^N to estimate excited state dipole moment. It also correlates the spectral shift better than the traditionally used bulk solvent polarity function. In this method the problem associated with the estimation of Onsager cavity radius has been minimized and also this polarity scale includes intermolecular solute/solvent hydrogen bond donor/acceptor interactions along with solvent polarity. The theoretical basis for the correlation of the spectral band shift with E_T^N was proposed by Reichardt and developed by Ravi et al. [35] is according to Eq. (11):

$$\overline{v}_a - \overline{v}_f = 11307.6 \left[\left(\frac{\Delta\mu}{\Delta\mu_b} \right)^2 \left(\frac{a_B}{a} \right)^3 \right] E_T^N + constant \tag{11}$$

Where $\Delta\mu_b = 9D$ and $a_B = 6.2 \, A^0$ are the change in dipole moment on excitation and Onsager cavity radius of molecule respectively and $\Delta\mu$ and 'a' v are the corresponding quantities for the solute molecule of interest. A dimensionless normalized scale E_T^N was introduced in order to avoid the use of non SI unit kal/mol in E_T (30) solvent polarity scale and is defined by Eq. (12), using water ($E_T^N = 1$) and tetramethylsilane (TMS= $E_T^N = 0$) as extreme reference solvents [35].

$$E_T^N = \frac{E_T(Solvent) - E_T(TMS)}{E_T(Water) - E_T(TMS)} = \frac{E_T(Solvent) - 30.7}{32.4} \tag{12}$$

The change in dipole moment ($\Delta\mu$) can be evaluated from the slope of the stokes shift versus E_T^N plot and is given by Eq. (13).

$$\Delta\mu = \left(\mu_e - \mu_g \right) = \sqrt{\frac{mX\,81}{\left(6.2/a \right)^3 11307.6}} \tag{13}$$

where 'm' is the slope obtained from the plot of Stokes shift $\left(\overline{v}_a - \overline{v}_f \right)$ versus microscopic solvent polarity (E_T^N) using Eq. (11). The microscopic solvent polarity parameter (E_N^T) values of solvents were taken from literature [34].

Kamlet-Taft Solvatochromic Parameters

The multiple linear regression method proposed by Kamlet and co-workers [36] has also been used to correlate absorption transition energy ($\overline{v}_a$), fluorescence transition energy ($\overline{v}_f$) and stoke's shift ($\overline{v}_a - \overline{v}_f$) with an index of the solvents dipolarity / polarizability which is a measure of the solvent's ability to stabilize a charge or dipole through non specific dielectric interactions (π^*), and indices of the solvent's hydrogen-bond donor (HBD) strength (α) and hydrogen-bond acceptor (HBA) strength (β), according to the Eq. (14);

$$y = y_0 + a\alpha + b\beta + c\pi^* \tag{14}$$

where, y is the spectroscopic property under consideration, y_0 is respective spectroscopic property in gas phase, a, b, and c are respectively measures of solvents HBD, HBA and dipolarity / polarisability.

Solvatochromic effect has been used to determine the magnitude of the solute-solvent interactions such as the polarizability/dipolarity parameter, π^*, of the solvent, as well as giving information about hydrogen bond donor (HBD), α and/or acceptor (HBA), β ability of the solvent which can be evaluated by multi linear regression analysis. The Kamlet–Taft approaches [35] have been applied to separate the influence of non-specific interactions, from specific interactions.
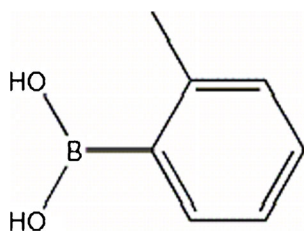
Fig. 1 Molecular structure of 2MPBA

The nonspecific interactions are expressed by Catalan's SP parameter (solvent polarizability) as well as by the π^* or SPP parameter (both of which represent a combination of the solvent dipolarity and polarizability). The signs of $a\alpha$ and $b\beta$ coefficients vary from one compound to another, and, in most cases they present weaker values than c coefficients, which indicate that the ability of the solvent to donate or accept hydrogen bonds is weaker than the solute-solvent dipole-dipole interactions. The disadvantage of the Kamlet-About-Taft (KAT) approach is:

a. The dipolarity and polarizability of the solvent are included in only one parameter - π^*. The use of a polarizability correction term $d\delta$ is not suitable for solving the problem, because it does not allow differentiation of the polarizability effects between two related solvents (δ has only three values: 1.0 for aromatic, 0.5 for poly halogenated and 0.0 for aliphatic solvents).

b. Determination of the Kamlet–Taft parameters (α, β and π^*) is not based on a well defined reference process, rather they are derived from an average of measurements using numerous samples.

The effect of solvent polarizabity (π^*), hydrogen bond donor (α) and acceptor abilities (β) of solvents on the
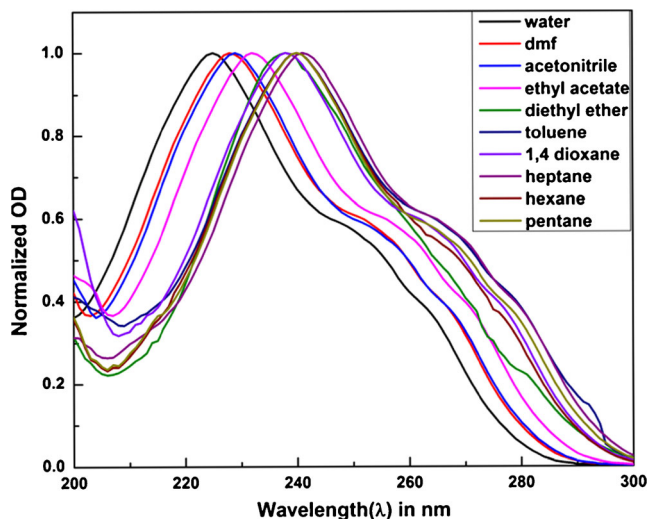

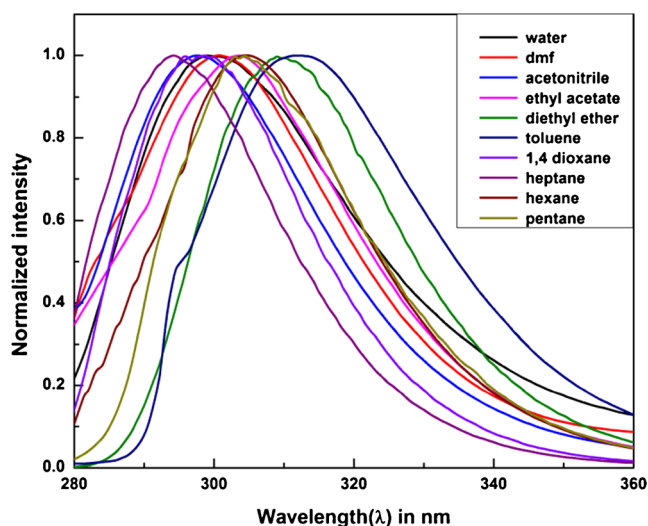Fig. 2 Normalized absorption spectra of in 2MPBA in different solvents

Fig. 3 Normalized emission spectra 2MPBA in different solvents

photophysics of an intramolecular charge transfer probe has been investigated. It is evident from these studies that both polarities and hydrogen bonding abilities of solvents are responsible for the solvatochromic shifts in the absorption spectrum of the probe. Quantitative analysis using Kamlet–Taft method indicates that the polarizability (π^*) and the hydrogen bond acceptor abilities (β) of the solvents are mainly responsible for the photophysics of the probe in the ground state while polarizability (π^*) and the hydrogen bond donor abilities (α) of the solvents play the major role in determining its excited state properties.

Materials and Methods

Materials

The 2-Methylphenyl boronic acid (2MPBA) was synthesized in our laboratory using standard methods [37]. The molecular structure of molecule is given in Fig. 1. The solvents used in the present study namely water, dimethyl formamide (dmf), acetonitrile, ethyl acetate, diethyl ether (dee), toluene, 1–4 dioxane, heptane, hexane and pentane were obtained from S-D-Fine Chemicals Ltd., India and they were of spectroscopic grade.

Measurement of Absorption and Fluorescence Spectra

The absorption spectra of the 2MPBA were recorded using Lab India UV/VIS 3000 spectrophotometer over a wavelength range 200–700 nm and the fluorescence spectra were recorded using Hitachi F-2700 FL Spectrophotometer with standard Quartz cuvette. All these measurements were carried out at room temperature. The uncertainty in the measured

Table 1 Solvatochromic data of 2MPBA along with the calculated values of polarity functions

Solvents	$\bar{v}_a$ (cm$_{-1}$)	$\bar{v}_f$ (cm$_{-1}$)	$\Delta\bar{v} = \bar{v}_a - \bar{v}_f$ (cm$_{-1}$)	1/2 ($\bar{v}_a + \bar{v}_f$) (cm^{-1})	ε	n	F_1 (ε, n)	F_2 (ε, n)	F_3 (ε, n)	E_T^N
pentane	41666.667	33003.330	8663.366	37334.999	1.800	1.350	−0.006	−0.011	0.238	0.009
hexane	41666.667	32786.885	8879.781	37226.776	1.890	1.375	−0.033	−1.006E-3	0.255	0.009
heptane	41493.776	32573.290	8920.486	37033.533	1.900	1.388	−0.003	−0.006	0.267	0.012
1,4 dioxane	42016.807	33003.330	9013.506	37510.068	2.300	1.421	0.019	0.039	0.306	0.164
toluene	41666.667	32467.532	9199.134	37067.099	2.380	1.496	0.015	0.033	0.352	0.099
dee	42016.807	32362.460	9654.347	37189.634	4.260	1.352	0.167	0.377	0.429	0.210
ethyl acetate	43103.448	33222.591	9880.857	38163.020	6.080	1.372	0.174	0.493	0.499	0.228
acetonitrile	43668.122	33557.047	10111.075	38612.585	37.500	1.346	0.305	0.863	0.666	0.460
dmf	43859.649	33222.591	10637.058	38541.120	38.500	1.430	0.276	0.841	0.702	0.404
water	44444.444	33444.816	10999.628	38944.630	80.400	1.333	0.320	0.914	0.683	1.000

wavelength of absorption and fluorescence maxima is ±1 nm. The concentrations were chosen to be 1×10^{-4} M for all the organic solvents. Each time fresh homogeneous solutions were prepared to record both absorption and fluorescence spectra.

Results and Discussion

Solvent Effect on Absorption and Fluorescence Emission Spectra
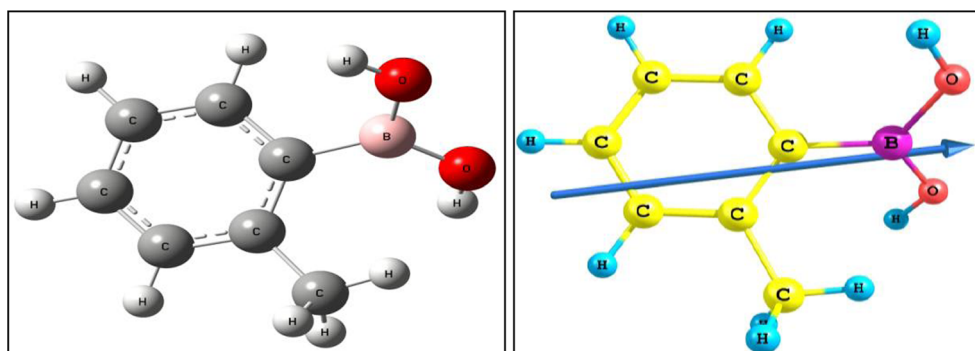
The normalized absorption and emission spectra of 2MPBA in different solvents are given in Figs. 2 & 3 respectively. The absorption spectra show a maxima around 225–241 nm with a shift of the maxima with respect to the dielectric constants of solvents used. Since only the longer wavelength is sensitive to solvent polarity, the absorption shifts with solvents has been reported. The emission spectra are recorded by exciting the sample at its longest absorption maxima. The excitation maxima coincide with the longest wavelength absorption band and this longest wavelength absorption band has been assigned as the intermolecular charge transfer transition.

The absorption and emission maxima, Stokes shift and arithmetic mean of absorption and emission peak values for the molecule in different solvents are given in Table 1. The emission spectra show a maxima around 298–309 nm. The emission spectra show a smaller shift as compared with the absorption spectra. The less pronounced emission shift with solvents implies that the ground state energy distribution is not affected to a greater extent possibly due to the less polar nature of the molecule in the ground-state rather than in the excited sate.

The magnitudes of Stokes shift vary between 8663.366 and 10999.628 cm^{-1}. The values of the Stokes shift are also indicative of the charge transfer transition. On changing solvents from a low polar one to a high polar one show a difference in Stokes shift of about 2,336 cm^{-1}, which is again an indicative of charge transfer transition. The large magnitude of Stokes shift indicates that the excited state geometry could be different from that of the ground state. The general observation is that there is an increase in the Stokes shift with increasing solvent polarity which shows that there is an increase in the dipole moment on excitation.

The solvatochromic data can be used to identify the spectra, namely $\pi \rightarrow \pi^*$ etc. It can be noticed from the Table 1 that, with an increase in the polarity of the solvent, the Stokes shift

Fig. 4 Optimized geometry and ground state optimized molecular geometries of 2MPBA. The arrow indicates the direction of the dipole moment
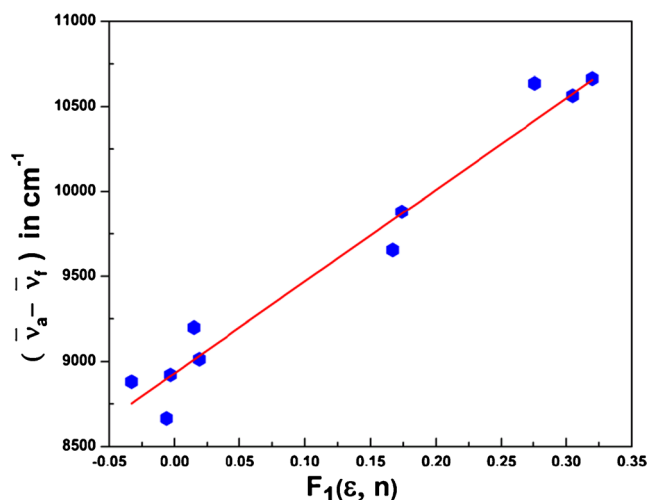
Fig. 5 The variation of Stoke's shift with F_1 (ε, n) using Lippert equation for 2MPBA

Fig. 7 The variation of arithmetic mean of absorption and emission wave number with F_3 (ε, n) using Kawski- Chamma-Viallet's equation for 2MPBA

undergoes a bathochromic shift, which confirms $\pi \rightarrow \pi^*$ transition.

Theoretical and Experimental Ground-State Dipole Moments

Theoretical calculations were performed using DFT/B3LYP level on a Pentium IV/2.8 GHz personal computer using Gaussian 09 W program package. The optimized geometry and ground state optimized molecular geometry for the title molecule are given in Fig. 4. The experimental ground state dipole moment is estimated using solvatochromic shift method. It can be seen that there is a slight variation between theoretical and experimental values of ground state dipole moments. This difference in the ground state dipole moment is due to the necessity of knowing the radius of the solute molecule in Eq. (7) as compared to experimental and
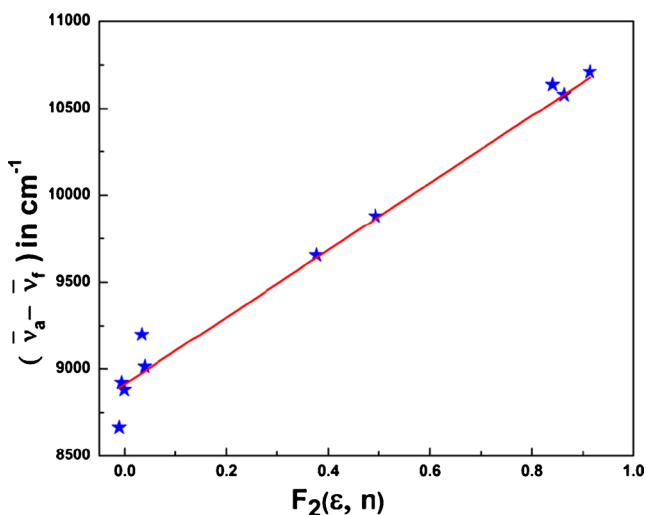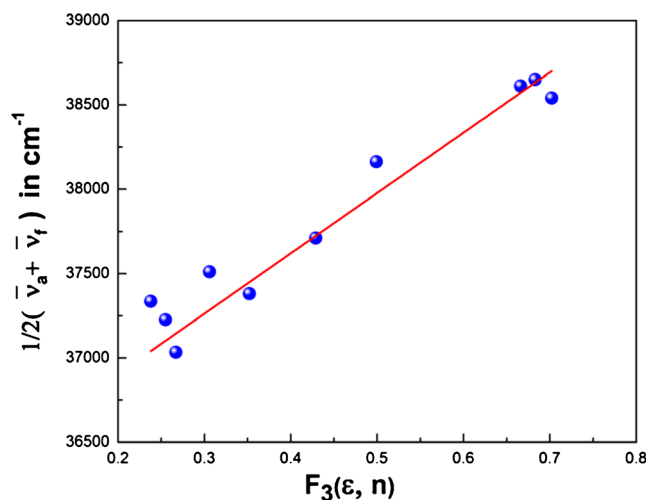
theoretical values obtained from ab initio calculations using DFT. However, the difference in the value may be due to discrepancies in the experimental and theoretical values of ground-state dipole moments. This may be due to the fact that, the experimental methods take solvent and environmental effects into account, where as ab initio calculations gives μ_g value only for molecule in a gas phase. It can be seen from Fig. 1 that the molecule looks symmetrical (in two-dimensional), but the three dimensional structure from Fig. 4 shows that they are not exactly symmetrical. However, no other experimental data on μ_g could be obtained from literature for comparison purposes.

Experimental Excited-State Dipole Moments

Table 1 summarizes the Stoke's shift data along with the solvent polarity function values F_1 (ε, n), F_2 (ε, n), and F_3 (ε, n) of various solvents for molecule respectively. From Eqs. (1, 2, 3) it follows that, ($\bar{v}_a - \bar{v}_f$) versus F_1 (ε, n), ($\bar{v}_a - \bar{v}_f$) versus F_2 (ε, n) and 1/2 ($\bar{v}_a + \bar{v}_f$) versus F_3 (ε, n) should be linear with slopes m_1, m_2 and m_3 respectively. 'a' is the radius of the solute molecule and the value was calculated from the molecular volume of molecule [31]. The graphs of ($\bar{v}_a - \bar{v}_f$)

Fig. 6 The variation of Stoke's shift with F_2 (ε, n) using Bakshiev's equation for 2MPBA

Table 2 Statistical treatment of the correlations of solvents spectral shifts of 2MPBA

Correlations	Slope	Correlation factor 'r'	Number of data
Lippert correlation	5397.182	0.953	10
Bakhshiev's correlation	1931.895	0.961	10
Kawski-Chamma-Viallet's correlation	3577.646	0.917	10
E_T^N correlation	2373.616	0.905	10

Table 3 Ground state and excited state dipole moments of 2MPBA

Compound	Radius 'a'(A°)	μ_g^a (D) s	μ_g^b (D)	μ_e^c (D)	μ_e^d (D)	μ_e^e (D)	μ_e^f (D)	μ_e^g (D)	$\Delta\mu^h$ (D)	$\Delta\mu^i$ (D)	$(\mu_e/\mu_g)^j$	ϕ^k
2MPBA	3.329	3.091	1.687	5.649	6.136	4.349	12.990	2.228	3.962	1.622	3.349	88^0

Debye (D)=3.33564X10^{-30} cm=10^{-18} esu cm

[a] The ground states dipole moments calculated using Gaussian software

[b] The ground states dipole moments calculated using Eq. 7

[c] The excited states dipole moments calculated using Eq. 8

[d] The experimental excited state dipole moments calculated from Lippert's equation

[e] The experimental excited state dipole moments calculated from Bakshiev equation

[f] The experimental excited state dipole moments calculated from Kawaski-Chamma-Viallet equation

[g] The excited state dipole moments calculated from E_T^N equation

[h] The change in dipole moments for μ_e and μ_g

[i] The change in dipole moments calculated from Eq. 13

[j] The ratio of excited state and ground state dipole moment

[k] The angle between ground state and excited state dipole moment

versus F_1 (ε, n), ($\overline{\nu}_a - \overline{\nu}_f$) versus F_2 (ε, n) and ½($\overline{\nu}_a + \overline{\nu}_f$) versus F_3 (ε, n) are given in Figs. 5, 6, 7. The correlation coefficients and slopes m_1 (Lippert's), m_2 (Bakshiev) and m_3 (Kawski-Chamma-Viallet's) of the fitted lines are given in Table 2. The excited-state dipole moments of the molecule are estimated using Eqs. (1, 2, 3).

For all the cases, good correlation coefficients are observed. The literature survey shows that m_3 is negative, but in our case it is positive which is in agreement with the findings of several workers [8, 16, 24, 25]. Assuming that the symmetry of the investigated molecule remains unchanged upon electronic transition, the ground and excite state dipole moments are parallel to each other. The value of μ_g obtained from theoretical, the experimental ground (μ_g) and excited-state (μ_e) dipole moments estimated using Eqs. (7 & 8), the values of $\Delta \mu$ and the ratio of μ_e and μ_g for the molecule are listed in Table 3. It is observed that the excited state dipole moments are greater than ground state dipole moments. An increase in dipole moment of a molecule on excitation and this change in dipole moment on excitation can be explained in terms of nature of emitting state or intra molecular charge transfer. It is interesting to note from the Table 3 that, small differences are observed between the estimated values of μ_e for test molecule. The μ_e value obtained by Kawski-Chamma-Viallet's method is large compared to other methods. In literature one may find that large numbers of investigators have used solvatochromic shift method (Eq. 8) to estimate excited state dipole moment.

The estimated values of μ_g and μ_e are 1.687 D and 5.649 D. The difference in values of μ_g and μ_e compared to respective values from other methods (Table 3) suggests that, μ_g and μ_e are not parallel. This has prompted us to estimate the angle between μ_g and μ_e according to Eq. (10) and the value is found to be 88^0. Hence one can conclude that μ_g and μ_e are not parallel to each other.

Molecular-Microscopic Solvent Polarity Parameter (E_T^N)

Figure 8 shows that the plot of Stoke's shift as a function of E_T^N in all the solvents for 2MPBA. The linear E_T^N dependence of Stoke's shift indicates the existence of general type of solute-solvent interaction in which the Stoke's shift depends on the dielectric constant and refractive index of the solvents. The excited state dipole moment is also calculated using microscopic solvent polarity parameter (E_T^N) according to Eq. (11). The value of excited state dipole moment calculated from this method is represented as μ_e^g and is tabulated in Table 3. This value is slightly smaller than Bakshiev's equation and three times smaller than Kawaski-Chamma-Viallet equation. This could be due to the fact that the methods based on Bakshiev's and Kawaski-Chamma-Viallet equations do not consider specific solute solvent interactions such as hydrogen bonding
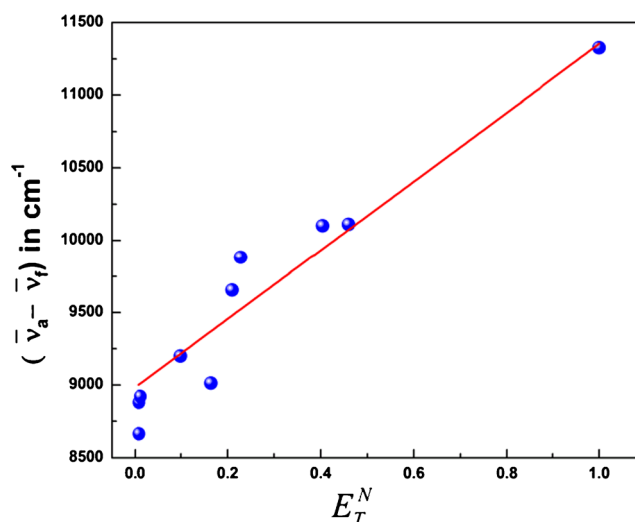

Fig. 8 The variation of Stoke's shift with E_T^N for 2MPBA

effect, complex formation and also ignore molecular aspects of salvation, whereas these aspects are incorporated in the method based on E_T^N [27]. With an increasing solvent polarity, both absorption and emission bands undergo a bathochromic shift. This indicates ICT (intermolecular charge transfer) absorption of the less dipolar ground- state molecule with dominant mesomeric structure, leading to highly dipolar-excited state and with the prominent structure of boronic acids. Hence, the excited state for the molecule is more polar than the ground state due to intermolecular charge transfer.

Kamlet-Taft Solvatochromic Parameters

In order to get information about individual contributions of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) abilities of solvents on the spectroscopic properties $\overline{\nu}_a$, $\overline{\nu}_f$ and $(\Delta \overline{\nu} = \overline{\nu}_a - \overline{\nu}_f)$ are correlated with solvatochromic parameters $^\alpha$, $^\beta$ and $^{\pi^*}$ using multiple regression. The multiple regression analysis data using Eq. (14) along with correlation coefficients in bellow equations.

$$\overline{v}_a \left(cm^{-1}\right) = 41747 + 1717\alpha + 3198\beta + 1800\pi * \ (r = 0.85)$$

$$\overline{v}_f \left(cm^{-1}\right) = 32902 + 1695\alpha + 989\beta + 1179\pi * \ (r = 0.82)$$

$$\Delta \overline{v} \left(cm^{-1}\right) = 8933 + 1233\alpha + 2627\beta + 926\pi * \ (r = 0.89)$$

From the above equations it is clear that, the non-specific dielectric interaction (π^*) has the major solvent influence for title molecule. However, the contribution of HBD and HBA parameters cannot be neglected. From the above relations it is clear that HBA (β) influence is more than HBD (α) for $\overline{\nu}_a$ and $\Delta \overline{\nu}$, whereas HBD (α) influence is more than HBA (β) is more for $\overline{\nu}_f$.

Conclusions

We have studied the spectroscopic behaviour of 2MPBA. It has been found that excited state dipole moment (μ_e) is greater than ground state dipole moment (μ_g) for the molecule. The increase in dipole moment in the excited singlet state ranges between 2.662 to 11.303 D. This demonstrates that molecule is more polar in excited state than in the ground state for all the solvents studied. The ground state dipole moment results are correlated (experimental and theoretical) in our used chemical

systems. It may be noted that there is a difference in the ground state and excited state dipole moments as estimated from Eqs. (7) and (8). It is worthwhile to stress that the discrepancies observed may be due to approximations made in both methods to estimate ground state and excited singlet state dipole moments for the title molecule. Also Eq. (13) can be used to estimate the value of excited state dipole moment by pre knowledge of the value of ground state dipole moment, without the necessity of knowing the radius of the solute. The ground and excited state dipole moments are not parallel to each other and they are subtended by an angle of 88^0. From Kamlet-Taft solvatochromic parameters, HBA (β) influence is more than HBD (α) for $\overline{\nu}$ and $\Delta \overline{\nu}$.

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