

## **Estimation Of The Ground State And First Excited State Dipole Moment Of Styryl Dyes Based On 7-[(E)-2-(Phenyl)Vinyl]-2-(4-Methoxy) Phenylimidazo [1,2-A] Pyridine Nucleus By The Solvatochromic Method**

**Siddheshwar D. Jadhav\*, Nandkumar A. Borade**

Department of Chemistry,

Kirti M. Doongursee College, Dadar (W), Mumbai (MH) India-40001

**Abstract:** *The ground state ( $\mu_g$ ) and the excited state ( $\mu_e$ ) dipole moments of two styryl dyes were studied at room temperature in various organic solvents. The dipole moments ( $\mu_g$  and  $\mu_e$ ) were estimated from solvatochromic shifts of absorption and emission spectra as function of the refractive index ( $n$ ) and dielectric constant ( $\epsilon$ ) using Bilot-Kawski, Bakshiev, Lippert Mataga, Kawaski-Chamma-Viallet and Reichardt Methods. Then in order to estimate a theoretical investigation, the dipole moments were calculated in the respective organic solvents with computational method (TDDFT/B3LYP). Intramolecular charge-transfer (ICT) and twisted intramolecular charge transfer (TICT) have been observed due to higher values of excited state dipole moment than ground state dipole moment. The results show that excited state dipole moments of dyes are higher than ground state dipole moments of styryl dyes. The small change in the dipole moments was found after the introduction of sulphur and methoxy group in the styryl dyes are observed. It is observed that dipole moment value of excited state ( $\mu_e$ ) is higher than that of the ground state in both the styryl dyes indicating that these dyes are more polar in nature in the excited state than in the ground state.*

**Keywords :** *Ground and excited state dipole moments, photophysical, styryls, imidazo[1,2-a]pyridine, Solvatochromic shift*

### **1. Introduction:**

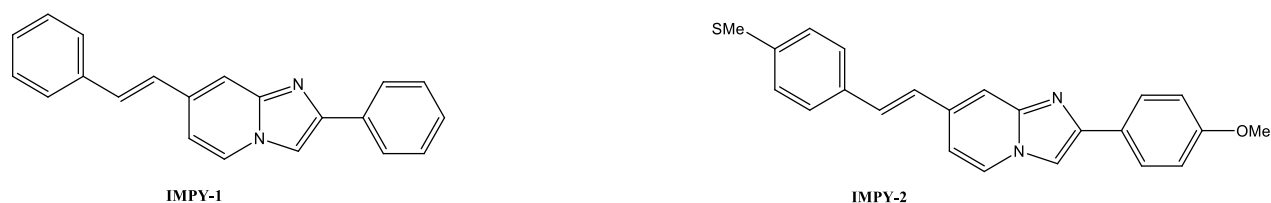
Electronic density in the ground state and the excited state is an important factor to reveal information about the overall electronic and geometrical structure of the molecule [1]. Dipole moment describes quantitative electronic distribution throughout the structure of the organic molecule. Prior knowledge of dipole moments in both states is useful to design non-linear optical (NLO) materials and estimation of the nature of the excited state as well as allows one to judge the site of nucleophilic and electrophilic attacks in some photochemical transformation[2]. A change in the solvent mean the change in polarity, dielectric constant or change in polarisability of the surrounding medium and hence the ground and excited states of the molecule[3]. A modification in donor-acceptor groups separated by a conjugated bridge (D- $\pi$ -A) with the push-pull type of arrangement effects on dipole moments of the molecule and they are useful to design general

guidelines for molecules of good nonlinear optical material (NLO) [4–8]. The required high first-order molecular hyperpolarizability for the second-order process is dependent on a proper push-pull effect operating in the molecule. Those push-pull organic  $\pi$ -systems intrinsically is related to intramolecular charge transfer in excited states [9–14] and such organic material is of great interested in NLO research [15–19]. Therefore, developing quantitative dipole moment measurement and solvation interactions has been of the highest interests[20,21].

Push-pull type of styryl dyes with such a system is one of the most significant classes of colorants in term of their high technological applications. Structural diversified fluorescent cationic and neutral styryl dyes typically employed in advanced material such as laser dyes[20], optical or electro-optical devices or sensor materials [22,23], solar cell sensitizer [24], DNA probes and voltage-sensitive dyes in cardiac tissue[25–28]. Recently derivatives of imidazo[1,2-a]pyridine used as a biomarker of hypoxic tumor cells, multiple fluorescent chemosensors, in an electron transport layer of an organic light emission device, as a fluorescent high-affinity ligand in dopamine D3 receptor[29] due to their promising nonlinear optical properties[30].

Several methods are used to determine the dipole moment of the singlet excited state based on the spectral shift caused either externally by electrochromism or internally by solvatochromism[31]. The electrochromism method such as electric-dichroism[32], electronic polarization of fluorescence[33], microwave conductivity [34] and Stark splitting[35] are considered to be very accurate. But their use is limited due to equipment sensitive and they restricted to relatively very simple molecules[3]. In the thermochromic method, the same expressions as in solvatochromic method is used instead of many solvents, only one selected solvent of moderate polarity as a function of temperature is selected[36–41]. Solvatochromism is the simplified, informative and widely accepted method to determine the excited state dipole moments without the use of any external field[42,43]. It is based on a linear correlation between the wave number of the absorption and emission maxima with solvent polarity functions  $f(\epsilon, n)$  which involves relative permittivity ( $\epsilon$ ) and refractive index ( $n$ ) of the medium.

In this context, we have studied the singlet ground state and excited state dipole moments of Methylsulfanylphenyl and methoxyphenyl substituted two imidazo[1,2-a]pyridine styryl dyes in different solvent polarity media. These values and solvatochromic behaviors support to understand the properties of environment's polarity on the structural configuration of them in the ground and excited states and dipole moment. However, ground state and excited state dipole moment study is urgent need of of imidazo[1,2-a]pyridine class derivatives. The ground state and excited state dipole moments are determined by using well-known Bilot–Kawski, Lippert–Mataga, Bakhshiev, Kawski–Chamma–Viallet, Reichardt solvatochromic shift methods as well as by computational method.



**Fig. 1** Structures of 7-[(E)-2-(phenyl)vinyl]-2-phenylimidazo[1,2-a]pyridine derivatives.

## 2. Material and Theoretical Methods:

The experimental data for calculating dipole moment in various solvents were used from previous published work[44,45]. These calculations were performed for five solvents that were used in the experiment: acetonitrile, tetrahydrofuran, toluene, dichloromethane and dimethylsulphoxide. Stroke shift calculation highest intensity absorption ( $\lambda_{\max}$ ) is considered and it increases as the polarity of solvent increases for all dyes. Methods of calculating dipole moment are as follows.

**2.1. Method I:** Bakshiev[39] and Bilot-Kawski co-workers[38,46] obtained a simple quantum mechanical second-order perturbation theory which involves dielectric function ( $\epsilon$ ) and the refractive index ( $n$ ) of the medium in a linear correlation between stroke shift and solvent polarity function. The method uses two functions for the solvent's polarizability, for simplicity they will be referred to as  $f_1(\epsilon, n)$  and  $f_2(\epsilon, n)$  governed by the following equations:

$$(\bar{\nu}_{abs} - \bar{\nu}_{emn}) = \left[ \frac{2(\mu_e - \mu_g)^2}{hc a^3} \right] f_1(\epsilon, n) + \text{Constant} \quad (1)$$

$$(\bar{\nu}_{abs} + \bar{\nu}_{emn}) = \left[ \frac{-2(\mu_e^2 - \mu_g^2)}{hc a^3} \right] f_2(\epsilon, n) + \text{Constant} \quad (2)$$

Where  $\bar{\nu}_{abs}$  is the energy of the absorbance maximum in wavenumbers and  $\bar{\nu}_{emn}$  is the energy of the emission maximum in wavenumber,  $h$  is Planck's constant,  $c$  is velocity of light, and  $a$  is Onsager's cavity radius,  $\mu_e$  is ground state dipole moment and  $\mu_g$  is excited state dipole moment of the molecule.  $f_1(\epsilon, n)$  and  $f_2(\epsilon, n)$  solvent polarity functions and given by

$$f_1(\epsilon, n) = \left[ \frac{2n^2 + 1}{n^2 + 2} \right] \cdot \left[ \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (3)$$

$$f_2(\epsilon, n) = f_1(\epsilon, n) + 3 \left[ \frac{n^4 - 1}{(n^2 + 2)^2} \right] \quad (4)$$

Using the Bilot-Kawski theory, the ground state ( $\mu_g$ ) and excited-state ( $\mu_e$ ) dipole moment can be measured by plotting  $f_1(\epsilon, n)$  against the Stokes shift  $(\bar{\nu}_{abs} - \bar{\nu}_{emn})$ , as well as  $f_2(\epsilon, n)$  against  $(\bar{\nu}_{abs} + \bar{\nu}_{emn})$  for different solvents. Treating this Eq. 1 and Eq. 2 as a equation of straight line,  $y = mx + c$

Where the slopes  $m_1$  and  $m_2$  are given by

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hc a^3} \quad (5)$$

$$m_2 = \frac{-2(\mu_e^2 - \mu_g^2)}{hc a^3} \quad (6)$$

The slopes of these plots ( $m_1$  and  $m_2$ ), are used in the following equations to determine the dipole moments for ground states and excited states

$$\mu_g = \frac{(m_2 - m_1)}{2} \left[ \frac{hc a^3}{2m_1} \right]^{1/2} \quad (7)$$

$$\mu_e = \frac{(m_2 + m_1)}{2} \left[ \frac{hc a^3}{2m_1} \right]^{1/2} \quad (8)$$

$$\mu_e = \left[ \frac{(m_2 + m_1)}{(m_2 - m_1)} \right] \mu_g \quad \text{for } m_2 > m_1 \quad (9)$$

Generally, the dipole moments in the ground state ( $\mu_g$ ) and excited state ( $\mu_e$ ) 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 other independent equations used for the estimation of ground- and excited-state dipole moments are as follows. In above theory deviations from the dielectric solvatochromism plot  $f_1(\epsilon, n)$  and  $f_2(\epsilon, n)$  are observed due to non consideration of short range specific interactions between the solvent and solute molecules. Interactions contributed in solute and solvent such as hydrogen bonding and electron-pair donor/electron pair acceptor interactions. Hence other optimal methods are available Lippert–Mataga, Bakhshiev and Kawski–Chamma–Viallet methods.

In these methods, absorption and emission wave number values are expressed with polarity functions by following independent equations proposed by Lippert–Mataga (Eq.11) [41][40] Bakhshiev (Eq. 13) [39] and Kawski–Chamma–Viallet[47][48] (Eq. 15).

## 2.2. Method II: Lippert-Mataga Equation

$$\bar{\nu}_{abs} - \bar{\nu}_{emn} = \frac{2(\mu_e - \mu_g)^2}{hc a^3} f_{LM}(\epsilon, n) + Constant \quad (11)$$

$$\text{Where } f_{LM}(\epsilon, n) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (12)$$

$$\text{slope is } m_{LM} = \frac{2(\mu_e - \mu_g)^2}{hc a^3} \text{ after rearranging } \mu_e = \sqrt{\frac{m_{LM} hc a^3}{2}} + \mu_g \quad (13)$$

## 2.3. Method III: Bakhshiev Equation

$$\bar{\nu}_{abs} - \bar{\nu}_{emn} = \frac{2(\mu_e - \mu_g)^2}{hc a^3} f_{BK}(\epsilon, n) + Constant \quad (14)$$

$$\text{Where } f_{BK}(\epsilon, n) = \left[ \frac{2n^2 + 1}{n^2 + 2} \right] \cdot \left[ \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (15)$$

$$\text{slope is } m_{BK} = \frac{2(\mu_e - \mu_g)^2}{hc a^3} \text{ after rearranging } \mu_e = \sqrt{\frac{m_{BK} hc a^3}{2}} + \mu_g \quad (16)$$

**2.4. Method IV:** Kawaski-Chamma-Viallet Equation

$$\frac{\bar{\nu}_{abs} - \bar{\nu}_{emn}}{2} = \frac{-2(\mu_e^2 - \mu_g^2)}{hca^3} f_{KCV}(\epsilon, n) + Constant \quad (17)$$

$$\text{Where } f_{KCV}(\epsilon, n) = \left[ \frac{2n^2 + 1}{2(n^2 + 2)} \right] \left( \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + \frac{3}{2} \left[ \frac{n^4 - 1}{(n^2 + 2)^2} \right] \quad (18)$$

$$\text{slope is } m_{KCV} = \frac{-2(\mu_e^2 - \mu_g^2)}{hca^3} \text{ after rearranging } \mu_e = \sqrt{\frac{(-m_{KCV})hca^3}{2} + \mu_g^2} \quad (19)$$

**2.5. Method V:** Reichardt solvent polarity function In bulk solvent polarity function, polarisability, hydrogen bonding effect, electron pair effect, complex formation and molecular aspects of solvation are ignored[31]. The other method employing molecular-microscopic solvent polarity parameter  $E_T^N$  scale proposed by Reichardt[42] correlates the spectral shift better than the traditionally used bulk solvent polarity function.

$$\bar{\nu}_{abs} - \bar{\nu}_{emn} = (m_{E_T^N}) E_T^N + Constant \quad (20)$$

$$\text{Where slope } m_{E_T^N} = 11307.6 \left[ \left( \frac{\Delta\mu}{\Delta\mu_B} \right)^2 \left( \frac{a_B}{a_0} \right)^3 \right] \quad (21)$$

Dipole moment calculated by the equation

$$\mu_e - \mu_g = \sqrt{\frac{m_{E_T^N} 81}{11307.6 \left( \frac{6.2}{a_0} \right)^3}}$$

$$\mu_e = \sqrt{\frac{m_{E_T^N} 81}{11307.6 \left( \frac{6.2}{a_0} \right)^3}} + \mu_g \quad (22)$$

$m_{E_T^N}$  is slope obtained from the linear plot of Stokes shift versus microscopic solvent polarity  $E_T^N$  by using equation.

**2.6. Method VI:** Dipole moment obtained from Density Functional Theory (DFT) by Gaussian program. The geometric conformation of styryl dye was optimized using the 6-31G(d) basis sets in the B3LYP level of theory, and the keyword "Volume" was used in order to calculate the Onsager radius of the molecule. The Onsager radius of dyes were calculated to be 5.42-5.58 and 5.76-5.96 in various solvents for IMPY-1 and IMPY-2 respectively, which were later used to calculate the experimental dipole moments. All the computations of styryl dyes in solvents were carried out using the Polarizable Continuum Model (PCM) [49]. Gaussian 09 program [50] was used for all the DFT and TDDFT computations and the results were visualized with GaussView 5.0 [51]. TD-DFT calculations were run to determine molecular orbital (MO) transitions for various excited states and to determine the most likely transitions. These calculations were performed using SCRF PCM models for five solvents that were used in the experiment: acetonitrile, tetrahydrofuran, toluene, dichloromethane and

dimethylsulphoxide. Onsager cavity radii ( $a$ ) for investigated samples were determined theoretically according to their optimized geometry.

### 3. Results and discussion:

#### Estimation of Dipole moments:

Solvent polarity function values  $f_2(\epsilon, n)$ ,  $f_{LM}(\epsilon, n)$ ,  $f_{BK}(\epsilon, n)$ ,  $f_{KCV}(\epsilon, n)$  and molecular microscopic solvent function  $E_T^N$  for the various solvents and solvent mixtures used in this article are summarized in **Table 1**. The bulk solvent polarity functions were calculated using the values of relative permittivity and refractive index for mixtures obtained by Eqs. (3), (4), (12), (15), (16) and (18).

**Table 1**

Solvent polarity parameters of the solvents.

Solvents <sup>a</sup>	$\epsilon^b$	$n^c$	$f_1(\epsilon, n)$	$f_2(\epsilon, n)$	$f_{LM}(\epsilon, n)^d$	$f_{BK}(\epsilon, n)^e$	$f_{KCV}(\epsilon, n)^f$	$E_T^N^g$
Toluene	2.38	1.4969	0.1147	0.7854	0.0132	0.0291	0.3499	0.0990
THF	7.58	1.4072	0.6097	1.1629	0.2096	0.5491	0.5511	0.2070
DCM	8.93	1.4242	0.6555	1.2312	0.2171	0.5903	0.5830	0.3090
ACN	37.5	1.3441	0.9080	1.3767	0.3054	0.8631	0.6659	0.4600
DMSO	46.7	1.4793	0.9205	1.5685	0.2631	0.8400	0.7442	0.4440

<sup>a</sup> Abbreviations for the solvent mixtures are: THF=Tetrahydrofuran, DCM=Dichloromethane, ACN=Acetonitrile, DMSO=Dimethylsulphoxide.

<sup>b</sup> Dielectric constant.

<sup>c</sup> Refractive Index.

<sup>d</sup> Lippart-Mataga solvent polarity function.

<sup>e</sup> Bakhshiev solvent polarity function.

<sup>f</sup> Kawski-Chamma-Viallet solvent polarity function.

<sup>g</sup> Reichardt microscopic solvent polarity function.

The absorption and emission maxima wavenumbers, Stokes shift, and the arithmetic mean of Stokes shift values (in  $\text{cm}^{-1}$ ) determined for all three molecules IMPY-1 and IMPY-2 in different solvents are given in Tables 2.

**Table 2** Solvatochromic data of three dyes in different solvents.

Solvents	IMPY-1					IMPY-2				
	$\lambda_a$	$\lambda_f$	$\Delta\gamma$	X	y	$\lambda_a$	$\lambda_f$	$\Delta\gamma$	x	y
Toluene	380	397	1127	25752	51505	375	411	2336	25499	50998
THF	377	416	2487	25282	50564	372	432	3734	25015	50030
DCM	376	416	2557	25317	50634	372	433	3787	24988	49976
ACN	372	418	2958	25403	50805	369	433	4006	25097	50195
DMSO	379	425	2856	24957	49915	375	441	3991	24671	49342

$\lambda_a$  = Absorption wavelength in nm,  $\lambda_b$  = Emission wavelength in nm,  $\Delta Y$  = Stroke shift in ( $\text{cm}^{-1}$ ),  $x = \left(\frac{\bar{\nu}_{abs} + \bar{\nu}_{emn}}{2}\right)$  in ( $\text{cm}^{-1}$ ),  $y = \bar{\nu}_{abs} + \bar{\nu}_{emn}$  in ( $\text{cm}^{-1}$ ).

In order to determine the dipole moment, graphs are plotted  $(\bar{\nu}_{abs} - \bar{\nu}_{emn})$  versus  $f_1(\epsilon, n)$ ,  $(\bar{\nu}_{abs} + \bar{\nu}_{emn})$  versus  $f_2(\epsilon, n)$  for Bilot kawaski function,  $(\bar{\nu}_{abs} - \bar{\nu}_{emn})$  versus  $f_{LM}(\epsilon, n)$  for Lippert-Mataga function,  $(\bar{\nu}_{abs} - \bar{\nu}_{emn})$  versus  $f_{BK}(\epsilon, n)$  for Bakhshiev function,  $\left(\frac{\bar{\nu}_{abs} + \bar{\nu}_{emn}}{2}\right)$  versus  $f_{KCV}(\epsilon, n)$  for Kawaski-Chamma-Viallet function and  $(\bar{\nu}_{abs} - \bar{\nu}_{emn})$  versus  $E_T^N$  for solvent polarity function, which are given in **Fig 2** and **Fig 3**. Slope, intercepts and correlation coefficients are given in **Table 3**.

**Table 3** Slopes and Regression Coefficient of other dyes for all different functions.

		$f_1(\epsilon, n)$	$f_2(\epsilon, n)$	$f_{LM}(\epsilon, n)$	$f_{BK}(\epsilon, n)$	$f_{KCV}(\epsilon, n)$	$E_T^N$
IMPY-1	Slope	2212.59	-769.07	6534.18	2160.35	-1710.95	4237.82
	R.C.	0.9635	0.7217	0.9892	0.9713	0.7948	0.7886
IMPY-2	Slope	2061.7	-1883.4	61223.6	2012.41	-1822.43	3827.44
	R.C.	0.9254	0.8515	0.9610	0.9323	0.8304	0.7115

R.C.= Regression Coefficient

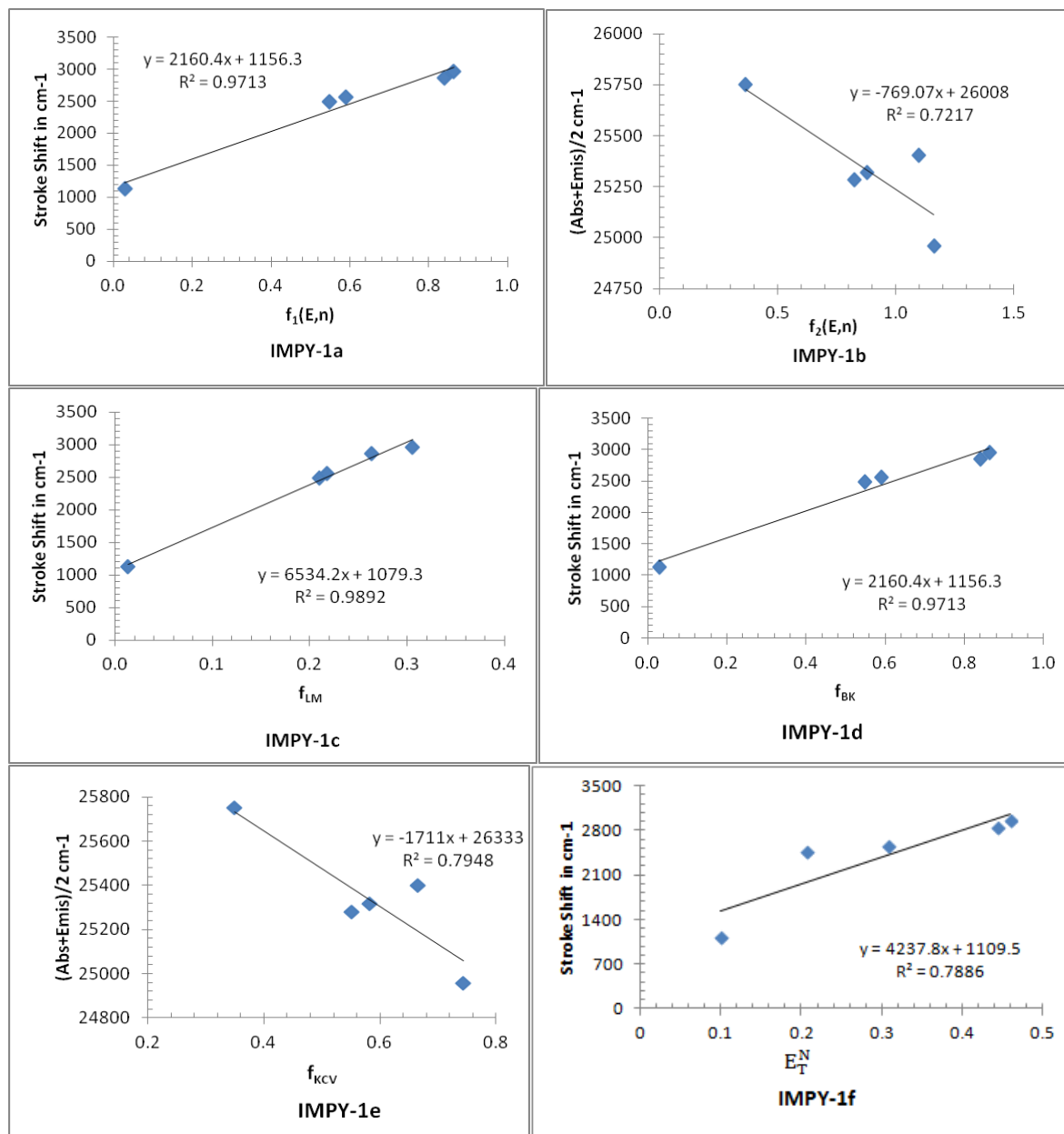
As can be seen from Table 3, correlation coefficients are found in the range of 0.7115 to 0.9892 depending on the solvent polarity, which is indicative of good linearity for these correlations.

The dipole moment with the first excited singlet state of dyes is calculated by using the slope of Bilot-Kwaski graph and putting in Eq. (7) and (8) represented in **Table 3**. The value of Onsagar cavity radius for all dyes taken with respect to solvents from optimized B3LYP/6-31G(d) Level of DFT Gaussian Program as represented in Table 4, 5 and 6. The different graphs are plotted for different function and represented as **Fig. 2** and **Fig. 3** and their slopes and regression coefficients are shown in **Table 3**. The Excited state dipole moment calculated by considering ground state dipole moment from Bilot-Kawaski Eq. (8). Further excited state dipole moments are calculated by using Lippert–Mataga (Eq. (13)), Bakhshiev (Eq. (16)), Kawaski-Chamma-Viallet (Eq. (19)) and Reichardt (Eq. (22)) relations respectively. The theoretically calculated ground state dipole moments ( $\mu_g$ ) are in between 3.04 and 0.87 D. Computational higher dipole moment is due to exaggerated uneven electronic distribution in a model system compared to that of the real molecule and some computational artefacts. Experimental and Computational study shows higher dipole moment in an excited state and also increasing as the polarity of solvent increases.

**Table 4** Ground-state and singlet excited-state dipole moments (in Debye, D).

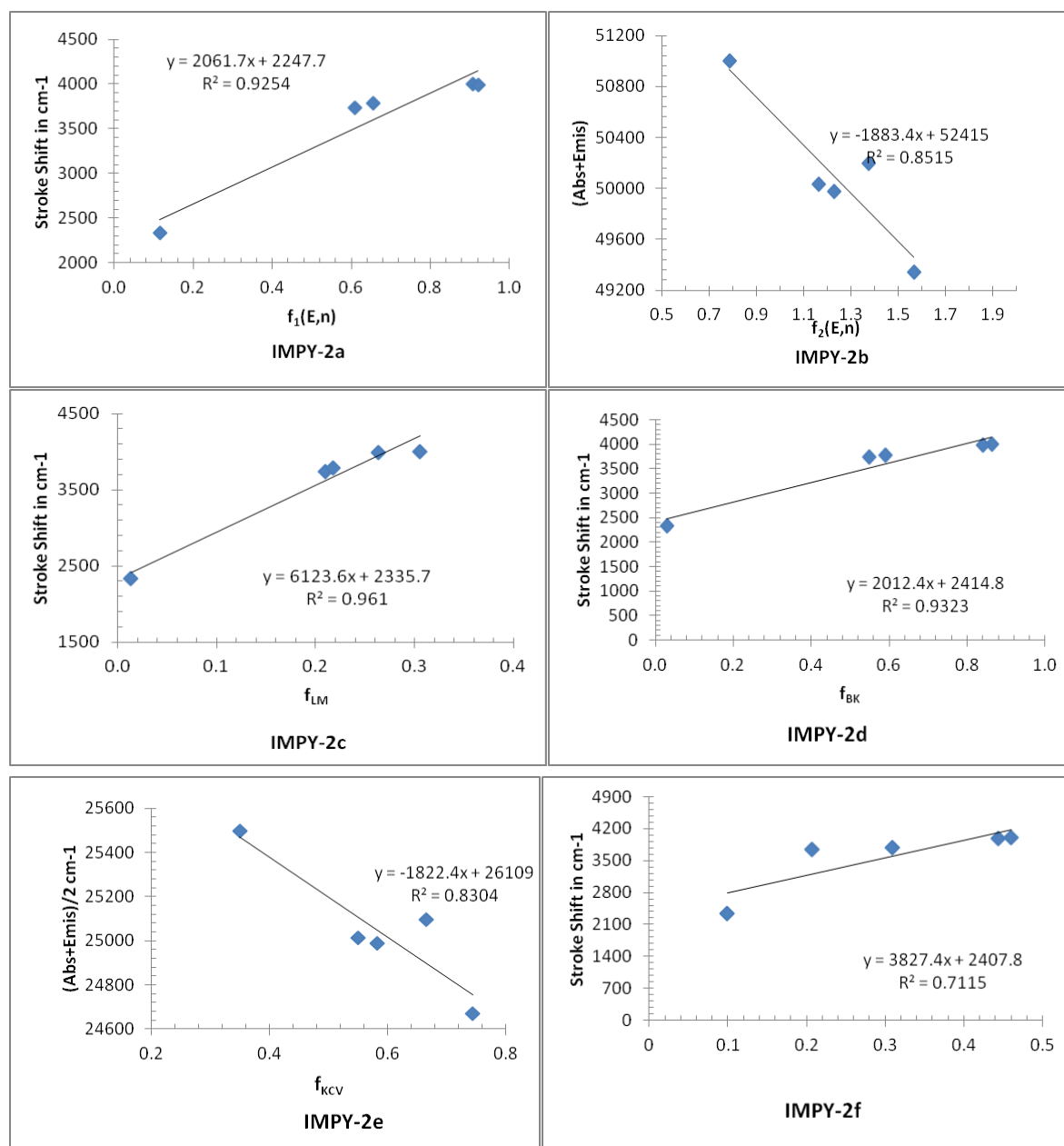
Dyes	$a^a$	GS DM <sup>b</sup>		Excited State dipole moment					
		B-K <sup>c</sup>	DFT <sup>d</sup>	TD-DFT <sup>d</sup>	B-K <sup>c</sup>	LM <sup>e</sup>	BK <sup>f</sup>	KCV <sup>g</sup>	Reich <sup>h</sup>
IMPY-1	5.45	0.59	3.04	3.13	5.38	10.85	6.49	5.28	7.28
IMPY-2	5.66	0.26	0.87	1.17	5.83	10.77	6.29	5.74	6.27

Abbreviations <sup>a</sup>Onsagar Cavity Radius in (Å<sup>0</sup>), <sup>b</sup> Ground State Dipole Moment, <sup>c</sup>Bilot-Kawaski, <sup>d</sup>Density Finctional Theory and Time dependent density functional theory, <sup>e</sup>Lippert Mataga, <sup>f</sup>Bakshiev, <sup>KCV</sup>Kawaski-Chamma-Viallet and <sup>h</sup>Reichardt Methods



**Fig. 2** Linear plots of IMPY -1 (a)  $(\bar{\nu}_{abs} - \bar{\nu}_{emn})$  versus  $f_1(\epsilon, n)$  and (b)  $\left(\frac{\bar{\nu}_{abs} + \bar{\nu}_{emn}}{2}\right)$  versus  $f_2(\epsilon, n)$  for Bilot-Kawaski, (c)  $(\bar{\nu}_{abs} - \bar{\nu}_{emn})$  versus  $f_{LM}(\epsilon, n)$  for Lippert–Mataga, (d)  $(\bar{\nu}_{abs} - \bar{\nu}_{emn})$  versus  $f_{BK}(\epsilon, n)$  for Bakshiev, (e)  $(\bar{\nu}_{abs} - \bar{\nu}_{emn})$  versus  $f_{KCV}(\epsilon, n)$  for Kawaski–Chamma–Viallet and (f)  $(\bar{\nu}_{abs} - \bar{\nu}_{emn})$  versus  $E_T^N$  for Reichardt correlation methods of solvent polarity functions.





**Fig. 2** Linear plots of IMPY -1, Abbreviations are same in the above graphs

#### 4. Conclusions:

In conclusion, we have reported experimental and computational estimation of dipole moments of some styryls based on imidazo[1,2-a]pyridine. The dipole moment in the excited state was determined by Bilot–Kawski, Lippert–Mataga, Bakhshiev, Kawski–Chamma–Viallet, computational and Reichardt correlation methods. In all the methods the dipole moments in the excited state for styryls were found to be higher than the ground state dipole moment. This implies that styryls are more polar or stable in the excited state than in the ground state. This also indicates that the styryl dyes have a more relaxed excited state due to photon induced intramolecular charge transfer (PICT). The dipole moment is drastically increased with donor group and acceptor group

attached to imidazo[1,2-a]pyridine ring. They can become good candidates for materials in non-linear optics considering their higher first-order hyperpolarizability and structural simplicity.

## 5. Acknowledgments

Authors are gratefully acknowledged the University of Mumbai for providing financial support and Kirti College authorities for encouraging to complete project work.

## References

- [1] E. Abraham, J. Oberlé, G. Jonusauskas, R. Lapouyade, C. Rullière, Photophysics of 4-dimethylamino 4'-cyanostilbene and model compounds: dual excited states revealed by sub-picosecond transient absorption and Kerr ellipsometry, *Chem. Phys.* 214 (1997) 409–423. doi:10.1016/S0301-0104(96)00301-1.
- [2] J. ZYSS, D.S. CHEMLA, Chapter II-1 - Quadratic Nonlinear Optics and Optimization of the Second-Order Nonlinear Optical Response of Molecular Crystals BT - Nonlinear Optical Properties of Organic Molecules and Crystals, in: Academic Press, 1987: pp. 23–191. doi:http://dx.doi.org/10.1016/B978-0-12-170611-1.50006-1.
- [3] S. Joshi, S. kumari, R. Bhattacharjee, R. Sakhuja, D.D. Pant, Estimation of ground and excited-state dipole moments of synthesized coumarin derivative, (S)-(1-((7-hydroxy-2-oxo-2H-chromen-4-yl)methyl)-1H-1,2,3-triazol-4-yl)methyl 2-(((9H-fluoren-9-yl)methoxy)carbonylamino)-3-phenylpropanoate from a solvatochromic shi, *J. Mol. Liq.* 209 (2015) 219–223. doi:http://dx.doi.org/10.1016/j.molliq.2015.05.053.
- [4] W. Rettig, W. Majenz, R. Herter, J.-F. Letard, R. Lapouyade, Photophysics of stilbenoid dye systems: A comparison of experiment and theory, *Pure Appl. Chem.* 65 (1993). doi:10.1351/pac199365081699.
- [5] Z.R. Grabowski, K. Rotkiewicz, W. Rettig, Structural Changes Accompanying Intramolecular Electron Transfer: Focus on Twisted Intramolecular Charge-Transfer States and Structures, *Chem. Rev.* 103 (2003) 3899–4032. doi:10.1021/cr940745l.
- [6] D. Pines, E. Pines, W. Rettig, Dual Fluorescence and Excited-State Structural Relaxations in Donor–Acceptor Stilbenes, *J. Phys. Chem. A.* 107 (2003) 236–242. doi:10.1021/jp013171e.
- [7] A.K. Singh, M. Darshi, S. Kanvah,  $\alpha,\omega$ -Diphenylpolyenes Capable of Exhibiting Twisted Intramolecular Charge Transfer Fluorescence: A Fluorescence and Fluorescence Probe Study of Nitro- and Nitrocyano-Substituted 1,4-Diphenylbutadienes †, *J. Phys. Chem. A.* 104 (2000) 464–471. doi:10.1021/jp992275a.
- [8] B. Carlotti, R. Flamini, I. Kikaš, U. Mazzucato, A. Spalletti, Intramolecular charge transfer, solvatochromism and hyperpolarizability of compounds bearing ethenylene or ethynylene bridges, *Chem. Phys.* 407 (2012) 9–19. doi:10.1016/j.chemphys.2012.08.006.

- [9] J. Zyss, Hyperpolarizabilities of substituted conjugated molecules. III. Study of a family of donor–acceptor disubstituted phenyl-polyenes, *J. Chem. Phys.* 71 (1979) 909. doi:10.1063/1.438380.
- [10] J.L. Oudar, D.S. Chemla, Theory of second-order optical susceptibilities of benzene substitutes, *Opt. Commun.* 13 (1975) 164–168. doi:10.1016/0030-4018(75)90033-4.
- [11] D.S. Chemla, J.L. Oudar, J. Jerphagnon, Origin of the second-order optical susceptibilities of crystalline substituted benzene, *Phys. Rev. B.* 12 (1975) 4534–4546. doi:10.1103/PhysRevB.12.4534.
- [12] J.L. Oudar, D.S. Chemla, Hyperpolarizabilities of the nitroanilines and their relations to the excited state dipole moment, *J. Chem. Phys.* 66 (1977) 2664. doi:10.1063/1.434213.
- [13] J.L. Oudar, Optical nonlinearities of conjugated molecules. Stilbene derivatives and highly polar aromatic compounds, *J. Chem. Phys.* 67 (1977) 446. doi:10.1063/1.434888.
- [14] J. Zyss, Hyperpolarizabilities of substituted conjugated molecules. II. Substituent effects and respective  $\sigma$ – $\pi$  contributions, *J. Chem. Phys.* 70 (1979) 3341. doi:10.1063/1.437919.
- [15] L.R. Dalton, S.J. Benight, L.E. Johnson, D.B. Knorr, I. Kosilkin, B.E. Eichinger, B.H. Robinson, A.K.-Y. Jen, R.M. Overney, Systematic Nanoengineering of Soft Matter Organic Electro-optic Materials †, *Chem. Mater.* 23 (2011) 430–445. doi:10.1021/cm102166j.
- [16] D. Lupo, *Molecular Nonlinear Optics: Materials, Physics, and Devices*. Edited by J. Zyss, Academic Press, San Diego, CA 1994, XIII, 478 pp., hardcover, ISBN 0-12-784450-3, *Adv. Mater.* 7 (1995) 248–249. doi:10.1002/adma.19950070232.
- [17] L.R. Dalton, P.A. Sullivan, D.H. Bale, Electric Field Poled Organic Electro-optic Materials: State of the Art and Future Prospects, *Chem. Rev.* 110 (2010) 25–55. doi:10.1021/cr9000429.
- [18] X. Zheng, C. V. McLaughlin, P. Cunningham, L.M. Hayden, Organic Broadband TeraHertz Sources and Sensors, *J. Nanoelectron. Optoelectron.* 2 (2007) 58–76. doi:10.1166/jno.2007.005.
- [19] M. Lee, Broadband Modulation of Light by Using an Electro-Optic Polymer, *Science* (80-.). 298 (2002) 1401–1403. doi:10.1126/science.1077446.
- [20] J.R. Mannekutla, B.G. Mulimani, S.R. Inamdar, Solvent effect on absorption and fluorescence spectra of coumarin laser dyes: Evaluation of ground and excited state dipole moments, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 69 (2008) 419–426. doi:http://dx.doi.org/10.1016/j.saa.2007.04.016.
- [21] K. Nowak, S. Wysocki, An experimental and theoretical study of dipole moments of N-[4-(9-acridinylamino)-3-methoxyphenyl]methanesulfonamide, *Spectrochim. Acta Part A Mol.*

- Biomol. Spectrosc. 70 (2008) 805–810. doi:<http://dx.doi.org/10.1016/j.saa.2007.09.038>.
- [22] F.M. Hamer, *The cyanine dyes and related compounds*, Interscience Publishers, 1964. <https://books.google.co.in/books?id=6gkpAAAAAYAAJ>.
- [23] R. Manhardt, *Photographic systems and processes having heat alterable spectral sensitivity*, US 3630733 A, 1971. <https://www.google.com/patents/US3630733>.
- [24] S.P. Gromov, E.N. Ushakov, O.A. Fedorova, I.I. Baskin, A. V Buevich, E.N. Andryukhina, M. V Alfimov, D. Johnels, U.G. Edlund, J.K. Whitesell, M.A. Fox, Novel photoswitchable receptors: Synthesis and cation-induced self-assembly into dimeric complexes leading to stereospecific [2+2]-photocycloaddition of styryl dyes containing a 15-crown-5 ether unit, *J. Org. Chem.* 68 (2003) 6115–6125. doi:10.1021/jo034460x.
- [25] A. Matiukas, B.G. Mitrea, A.M. Pertsov, J.P. Wuskell, M.-D. Wei, J. Watras, A.C. Millard, L.M. Loew, New near-infrared optical probes of cardiac electrical activity, *Am. J. Physiol. - Hear. Circ. Physiol.* 290 (2006) H2633–H2643. doi:10.1152/ajpheart.00884.2005.
- [26] V.B. Kovalska, M.Y. Losytskyy, D. V Kryvorotenko, A.O. Balanda, V.P. Tokar, S.M. Yarmoluk, Synthesis of novel fluorescent styryl dyes based on the imidazo[1,2-a]pyridinium chromophore and their spectral-fluorescent properties in the presence of nucleic acids and proteins, *Dye. Pigment.* 68 (2006) 39–45. doi:10.1016/j.dyepig.2004.12.010.
- [27] A.I. Aranda, S. Achelle, F. Hammerer, F. Mahuteau-Betzer, M.-P. Teulade-Fichou, Vinyl-diazine triphenylamines and their N-methylated derivatives: Synthesis, photophysical properties and application for staining DNA, *Dye. Pigment.* 95 (2012) 400–407. doi:10.1016/j.dyepig.2012.04.009.
- [28] Q. Dna, X. Xie, B. Choi, E. Largy, R. Guillot, A. Granzhan, Asymmetric Distyrylpyridinium Dyes as Red-Emitting Fluorescent Probes, *Chem. - A Eur. J.* 19 (2013) 1214–1226. doi:10.1002/chem.201203710.
- [29] M. Leopoldo, E. Lacivita, E. Passafiume, M. Contino, N.A. Colabufo, F. Berardi, High-Affinity Dopamine D<sub>3</sub> Receptor Ligands as Potential Probes for Receptor Visualization, *J. Med. Chem.* 50 (2007) 5043–5047.
- [30] H. Tomoda, T. Hirano, S. Saito, T. Mutai, K. Araki, Substituent Effects on Fluorescent Properties of Imidazo(1,2-a)pyridine-Based Compounds., *Bull. Chem. Soc. Jpn.* 72 (1999) 1327–1334. doi:10.1246/bcsj.72.1327.
- [31] J. Basavaraja, H.M. Suresh Kumar, S.R. Inamdar, M.N. Wari, Estimation of ground and excited state dipole moment of laser dyes C504T and C521T using solvatochromic shifts of absorption and fluorescence spectra, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 154

- (2016) 177–184. doi:<http://dx.doi.org/10.1016/j.saa.2015.10.020>.
- [32] W. LIPTAY, Dipole Moments and Polarizabilities of Molecules in Excited Electronic States, in: E.C.L.I.M.B.T.-E. States (Ed.), Elsevier, 1974: pp. 129–229. doi:<http://dx.doi.org/10.1016/B978-0-12-227201-1.50009-7>.
- [33] J. f Rabek, Progress in Photochemistry and Photophysics, in: CRC PResS, Boca Raton, 1992: pp. 1–47.
- [34] J. Czekalla, Einladung zur 60. Hauptversammlung der Deutschen Bunsen-Gesellschaft für physikalische Chemie e. V. vom 11. bis 14. May 1961 in Karlsruhe, Zeitschrift Für Elektrochemie, Berichte Der Bunsengesellschaft Für Phys. Chemie. 64 (1960) 1121. doi:[10.1002/bbpc.19600641002](https://doi.org/10.1002/bbpc.19600641002).
- [35] J.R. Lombardi, Correlation between structure and dipole moments in the excited states of substituted benzenes, J. Am. Chem. Soc. 92 (1970) 1831–1833. doi:[10.1021/ja00710a006](https://doi.org/10.1021/ja00710a006).
- [36] K. Nowak, A solvatochromic study of N-[4-(9-acridinylamino)-3-methoxyphenyl]methanesulfonamide hydrochloride: An experimental and theoretical approach, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 130 (2014) 208–213. doi:<http://dx.doi.org/10.1016/j.saa.2014.03.004>.
- [37] B. Koutek, Dipole moments in excited state. Statistical investigation of methods employing solvatochromism, Collect. Czechoslov. Chem. Commun. 43 (1978) 2368–2386. doi:[10.1135/cccc19782368](https://doi.org/10.1135/cccc19782368).
- [38] L. Bilot, A. Kawski, Zur Theorie des Einflusses von Lösungsmitteln auf die Elektronenspektren der Moleküle, Zeitschrift Fur Naturforsch. - Sect. A J. Phys. Sci. 17 (1962) 621–627. doi:[10.1515/zna-1962-0713](https://doi.org/10.1515/zna-1962-0713).
- [39] N.G. Bakhshiev, Universal intermolecular interactions and their effect on the position of the electronic spectra of molecules in 2-component solutions.7. Theory (general case for isotopic solution), Opt. Spektrosk. 16 (1964) 821–832.
- [40] E. Lippert, Dipolmoment und Elektronenstruktur von angeregten Molekülen, Zeitschrift Fur Naturforsch. - Sect. A J. Phys. Sci. 10 (1955) 541–545. doi:[10.1515/zna-1955-0707](https://doi.org/10.1515/zna-1955-0707).
- [41] N. Mataga, Y. Kaifu, M. Koizumi, Solvent Effects upon Fluorescence Spectra and the Dipolemoments of Excited Molecules, Bull. Chem. Soc. Jpn. 29 (1956) 465–470. doi:[10.1246/bcsj.29.465](https://doi.org/10.1246/bcsj.29.465).
- [42] C. Reichardt, Solvatochromic Dyes as Solvent Polarity Indicators, Chem. Rev. 94 (1994) 2319–2358. doi:[10.1021/cr00032a005](https://doi.org/10.1021/cr00032a005).
- [43] C. Párkányi, J.-J. Aaron, Dipole moments of aromatic heterocycles, in: C.P.B.T.-T. and C. Chemistry (Ed.), Theor. Org. Chem., Elsevier, 1998: pp. 233–258.

doi:[http://dx.doi.org/10.1016/S1380-7323\(98\)80011-3](http://dx.doi.org/10.1016/S1380-7323(98)80011-3).

- [44] Z. Seferoğlu, H. Ihmels, E. Şahin, Synthesis and photophysical properties of fluorescent arylstyrylimidazo[1,2-a]pyridine-based donor-acceptor chromophores, *Dye. Pigment.* 113 (2015) 465–473. doi:10.1016/j.dyepig.2014.09.016.
- [45] B. Aydiner, E. Yalçın, H. Ihmels, L. Arslan, L. Açık, Z. Seferoğlu, Arylstyrylimidazo[1,2-a]pyridine-based donor-acceptor acidochromic fluorophores: Synthesis, photophysical, thermal and biological properties, *J. Photochem. Photobiol. A Chem.* 310 (2015) 113–121. doi:10.1016/j.jphotochem.2015.05.030.
- [46] L. Bilot, A. Kawski, Notizen: Dipolmomente einiger Phthalimid-Derivate im ersten angeregten Singulettzustand, *Zeitschrift Für Naturforsch. A.* 18 (1963) 256. doi:10.1515/zna-1963-0228.
- [47] A. Kawski, Zur Lösungsmittelabhängigkeit der Wellenzahl von Elektronenbanden Lumineszierender Moleküle und über die Bestimmung der Elektrischen Dipolmomente im Anregungszustand, *Acta Phys. Pol.* 29 (1966) 507–518.
- [48] A. Chamma, P. Viallet, Determination du moment dipolaire d'une molecule dans un etat excite singulet, *C. R. Acad. Sci. Paris, Ser. C.* 270 (1970) 1901–1904.
- [49] M.W. Wong, M.J. Frisch, K.B. Wiberg, Solvent effects. 1. The mediation of electrostatic effects by solvents, *J. Am. Chem. Soc.* 113 (1991) 4776–4782. doi:10.1021/ja00013a010.
- [50] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Farkas, J.B. Foresman, J. V Ortiz, J. Cioslowski, D.J. Fox, *Gaussian 09, Revision C.01*, Gaussian 09, Revis. B.01, Gaussian, Inc., Wallingford CT. (2009).
- [51] M.J. Dennington R, Keith T, *Gaussview*, (2009).