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# Optical properties of organic nonlinear optical crystal—A combined experimental and theoretical study

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# ABSTRACT

The optical properties of the synthesized imidazole derivative, 1-(4-methoxyphenyl)-4,5-diphenyl-2styryl-1H-imidazole, has been studied both experimentally and theoretically. Fluorescence enhancement have been found in the presence of transition metal ions and this may result from the suppression of radiationless transitions from the n- $\pi^*$  state in the chemosensors. Quantum chemical calculations of heat of formation, optimized geometry, NLO, HOMO–LUMO, MEP and NBO analysis of 1-(4-methoxyphenyl)-4,5-diphenyl-2-styryl-1H-imidazole (mpdsi) have been carried out by using density functional theory (DFT/B3LYP) method with 6-31G(d,p) as basis set. This chromophore possess more appropriate ratio of off-diagonal versus diagonal  $\beta$  tensorial component ( $r = \beta_{xyy}/\beta_{xxx} = -0.002$ ) which reflects the inplane non-linearity anisotropy. Since they have largest  $\mu\beta_0$  value, the reported imidazole can be used as potential NLO material. The solvent effect on the absorption and fluorescence has been analyzed simultaneously.

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# 1. Introduction

Research on heterocyclic imidazole derivatives is wide because of their optical properties [1]. These compounds play an important role in chemistry as mediators for synthetic reactions, primarily for preparing functionalized materials [2]. Imidazole nucleus present in the human organisms namely the amino acid histidine, Vitamin-B12, a component of DNA base structure, purines, histamine and biotin and present in many natural and synthetic drug molecules, i.e., azomycin, cimetidine and metronidazole. They have significant analytical applications due to their fluorescence and chemiluminescence properties [3].

Searching organic materials with non-linear optical (NLO) properties are usually concentrated on molecules with donor–acceptor  $\pi$ -conjugation (D- $\pi$ -A) and deals with the substituent effects on the degree of  $\pi$ -conjugation, steric hindrance and the hyperpolarizability of the substances [4]. Currently there is an insufficient understanding for designing optimal NLO materials, even certain classes of D- $\pi$ -A compounds have been theoretically studied [5]. Not only the push–pull effect in D- $\pi$ -A compounds quantified, but also a linear dependence of the push–pull quotient ( $\pi^*/\pi$ ) on molar hyperpolarizability were detected [6]. Thus,  $\pi^*/\pi$  is a sensitive parameter of the donor–acceptor quality of compounds

for potential NLO applications. In this paper we have focused the synthesized imidazole derivative has non-linear optical (NLO) behaviour. This chromophore possesses more appropriate ratio of off-diagonal versus diagonal  $\beta$  tensorial component ( $r = \beta_{xyy}/\beta_{xxx}$ ) which reflects the inplane non-linearity anisotropy since they have largest  $\mu\beta_0$  value, the reported imidazole can be used as potential NLO material and their photophysical properties have been investigated in a wide variety of solvents.

# 2. Experimental

# 2.1. Optical measurements and composition analysis

NMR spectra were recorded on a Bruker 400 MHz NMR instrument. The ultraviolet-visible (UV-vis) spectra were measured on a UV-vis spectrophotometer (Perkin Elmer, Lambda 35) and corrected for background due to solvent absorption. Photoluminescence (PL) spectra were recorded on a (Perkin Elmer LS55) fluorescence spectrometer.

## 2.2. Non-linear optical measurements

The second harmonic generation efficiency was assessed by Kurtz powder technique [7] at IISc., Bangalore, India. It is a well established tool to evaluate the conversion efficiency of non-linear optical materials. A Q-switched Nd: YAG laser operating at the fundamental wavelength of 1064 nm, generating about 4.1 mJ and

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pulse width of 8 ns was used for the present experimental study. The input laser beam was passed through an IR reflector and then incident on the powder form of the specimen, which was packed in a glass capillary tube. The output energy was detected by a photodiode detector integrated with oscilloscope assembly.

# 2.3. Computational details

Quantum mechanical calculations have been carried out using Gaussian-03 program [8]. As the first step of our DFT calculation, the geometry taken from the starting structure was optimized.

# 2.3.1. Hyperpolarizability calculation

The density functional theory has been used to calculate the dipole moment ( $\mu$ ), mean polarizability ( $\alpha$ ) and the total first static hyperpolarizability ( $\beta$ ) [9] for mpdsi in terms of *x*, *y*, *z* components and is given by following equations.

$$\mu = (\mu_x^2 + \mu_v^2 + \mu_z^2)^{1/2} \tag{1}$$

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{vv} + \alpha_{zz}) \tag{2}$$

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

(or)

$$\beta_{\text{tot}} = [(\beta_{xxx} + \beta_{xvv} + \beta_{xzz})^2] + (\beta_{vvv} + \beta_{vzz} + \beta_{vxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zxx})^2]^{1/2}$$
(3)

The  $\beta$  components of Gaussian output are reported in atomic units and therefore the calculated values are converted into e.s.u. units (1 a.u. = 8.3693 × 10<sup>-33</sup> e.s.u.).

# 2.3.2. Natural bond orbital (NBO) analysis

The second order Fock matrix have been carried out to evaluate the donor-acceptor interactions in the NBO analysis [10]. For each donor (*i*) and acceptor (*j*), the stabilization energy E(2) associated with the delocalization  $i \rightarrow j$  is estimated as,

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon j - \varepsilon i}$$
(4)

where  $q_i$  is the donor orbital occupancy,  $\varepsilon i$  and  $\varepsilon j$  are diagonal elements and F(ij) is the off diagonal NBO Fock matrix element. The larger the E(2) value, the more intensive is the interaction between electron donors and electron acceptors.

# 2.4. Synthesis of

# 1-(4-methoxyphenyl)-4,5-diphenyl-2-styryl-1H-imidazole (mpdsi)

The experimental procedure used is the same as described in our recent research works [11–23]. The imidazole derivative has been synthesized from an unusual four components assembling of Benzil (40 mmol), ammonium acetate (30 mmol), *p*-methoxyaniline (30 mmol) and cinnamaldehyde (30 mmol). These four components have been refluxed in ethanol for 24 h at 80 °C. The reaction mixture was extracted with dichloromethane and purified by column chromatography using hexane: ethyl acetate (9:1) as the eluent. Yield: 55%. mp = 192 °C, Anal. calcd. for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O: C, 84.08; H, 5.65; N, 6.54. Found: C, 83.00; H, 4.60; N, 7.13. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  3.85(s,3H), 6.69 (d, 1H), 7.56 (d, 1H), 6.98–7.77 (m, 19H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>):  $\delta$  55.42, 114.46, 126.32–132.58 (Aromatic carbons), 134.60, 136.82, 138.16, 146.07, 147.07, 159.29. MS: *m/e* 428.19, calcd. 429.19 [M+1].



Fig. 1. Absorption solvatochromism of mpdsi in various solvents.

# 3. Results and discussion

The absorption and emission spectra have been recorded in dichloromethane in the region of 200-500 nm. The band appeared around 276 nm ( $\lambda_{abs}$ ) and 334 nm ( $\lambda_{em}$ ) is due to the  $\pi$ - $\pi^*$  transition. Since,  $n-\pi^*$  and  $\pi-\pi^*$  transitions are in close proximity, the low intensity  $n-\pi^*$  transition is often completely overlaid by the intensive  $\pi - \pi^*$  transition [24]. The UV-visible spectrum was recorded in different solvents (Fig. 1 and Table 1). The observed solvatochromic shifts may be due to existence of non-coplanarity of the imidazole derivative [25,26]. In order to understand the coplanarity, optimization of mpdsi, DFT at B3LYP/6-31G(d,p) have been performed using Gaussian-03. Since this compound possesses poor crystalline nature, XRD data of its analogue derivative [15] have been taken for comparision. The observed dihedral angle from XRD [N3-C2-C21-C22 (-137.56°); N3-C2-C21-C26 (40.16°) and C5-N1-C11-C12 (84.05°); C5-N1-C11-C16 (-94.68°)] and DFT [N6-C3-C4-C5 (150.46°); and C1-N7-C43-C44 (98.21°); C1-N7-C43-C45 (-81.21°)] results strongly evidenced the existence of non co-planarity of imidazole nucleus (Fig. 2). The observed fluorescence spectrum (Fig. 3) is broad and more sensitive to changing the polarity of the solvents. This is in argument with the fact that greater charge transfer takes place from aromatic ring to imidazole nucleus in  $S_1$  state than  $S_0$  state which is evidenced by the decrease in the dihedral angle of N6-C3-C4-C5 and C1-N7-C43-C44 from 150.46° to 130.7° and 98.21° to 50.0°, respectively. Moreover, the reduction in the bond distances of C2-C21 from 1.45 Å to 1.32 Å on excitation from  $S_0$  to  $S_1$  state (Table 2).

Table 1Absorption and emission datas of mpdsi.

Solvents	mpdsi			
	$\lambda_{abs} (nm)$	$\lambda_{emi} (nm)$	Stokes shift (cm <sup>-1</sup> )	
Hexane	278	334	6006	
1,4-dioxan	297	363	6186	
Benzene	291	368	7257	
Toluene	288	371	7775	
Chloroform	281	374	8844	
Ethyl acetate	282	389	9736	
Diethyl ether	284	389	9472	
Dichloromethane	276	334	6345	
DMSO	269	390	11,615	
Butanol	263	396	12,796	
Ethanol	261	373	11,534	
Methanol	271	418	13,051	
Acetonitrile	272	378	10,392	
Ethyl methyl ketone	281	406	10,912	



Fig. 2. Optimized structure of mpdsi.





Fig. 3. Emission solvatochromism of mpdsi in various solvents.

# 3.1. Quantum yield and radiation kinetics

The fluorescence quantum yield (0.52) for mpdsi have been measured in acetonitrile, using coumarin 47 in ethanol as a standard according to the equation,

$$\Phi_{\text{unk}} = \Phi_{\text{std}} \left( \frac{I_{\text{unk}}}{I_{\text{std}}} \right) \left( \frac{A_{\text{std}}}{A_{\text{unk}}} \right) \left( \frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2 \tag{5}$$

where  $\Phi_{unk}$ ,  $\Phi_{std}$ ,  $I_{unk}$ ,  $I_{std}$ ,  $A_{unk}$ ,  $\Phi_{unk}$  and  $\Phi_{std}$  are the fluorescence quantum yields, the integration of the emission intensities,

Bond lengths (Å)	Experimental XRD (Å)	Bond angles (°)	Experimental XRD (°)	Torsional angles (° )	Experimental XRD (°)	
C1-C2	1.4208	C2-C1-C20	105.9867 N7-C1-C2-N6		-0.0235	
C1-N7	1.4063	C7-C1-C20	124.1956 N7-C1-C2-C14		179.0615	
C1-C20	1.4528	C1-C2-C14	127.6070 C20-C1-C2-N6		179.2649	
C2-N6	1.3966	C6-C2-C14	122.6351	C2-C1-N7-C3	0.047	
C2-C14	1.4541	C4-C3-N6	123.6221	C2-C1-N7-C43	-177.8346-179.2921	
C3-C4	1.4575	C3-C4-C5	124.8386	C20-C1-C7-C3	-55.1174	
C3-C6	1.3601	C4-C5-C8	124.0757	C2-C1-C20-C21	124.5622	
C4-C5	1.3413	C2-N6-C3	106.7168	C2-C1-C20-C22	124.0555	
C5-C8	1.4542	C1-N7-C3	107.0277	N7-C1-C20-C21	-0.0105	
C7-C43	1.4152	C1-N7-C43	125.5590	C1-C2-N6-C3	-179.1497	
C8-C9	1.4047	C1-N7-C43	127.3749	C14-C2-N6-C3	-179.1497	
C8-C10	1.4023	C5-C8-C9	127.3749	C1-C2-C14-C15	-35.7003 145.3052	
C9-C11	1.3922	C5-C8-C10	121.9673	C1-C2-C14-C15	143.2771	
C10-C12	1.3937	C9-C8-C10	118.9761	C1-C2-C14-C16	150.4634	
C11-C13	1.3954	C8-C9-C11	120.4327	N6-C2-C14-C15	-29.7142	
C12-C13	1.3942	C8-C10-C12	120.3785	N6-C3-C4-C5	-179.8983	
C14-C16	1.4030	C9-C11-C13	120.1796	N7-C3-C4-C5	-2.067	
C15-C17	1.3931	C10-C12-C13	120.2483	C4-C3-N7-C1	-0.0562	
C16-C18	1.3937	C11-C13-C12	119.7823	C4-C3-N7-C43	-178.9323-156.7997	
C17-C19	1.3947	C2-C14-C15	120.4044	N6-C3-N7-C1	23.8653	
C18-C19	1.3945	C2-C14-C16	120.2684	C3-C4-C5-C8	98.2171	
C20-C21	1.4026	C14-C15-C17	120.2481	C4-C5-C8-C9	-81.2064	
C20-C22	1.4018	C14-C16-C18	120.1014	C4-C5-C8-C10	-79.2338	
C21-C23	1.3934	C15-C17-C19	120.2113	C1-N7-C43-C44	-179.9501	
C22-C24	1.3936	C16-C18-C19	120.3171	C1-N7-C43-C45	-0.0595	
C23-C25	1.3950	C17-C19-C18	119.8005	C3-N7-C43-C44	179.7550	
C24-C25	1.3946	C1-C20-C21	119.8355	C5-C8-C9-C11	0.4195	
C44-C46	1.3866	C21-C20-C22	119.4862	C10-C8-C9-C11	0.3665 0.0450	
C45-C48	1.3923	C20-C22-C24	120.1426	C9-C8-C10-C12	-0.4759	
C46-C50	1.4080	C21-C23-C25	120.2490	C9-C11-C13-C12	0.4893	
C48-C50	1.3993	C23-C25-C24	119.8957	C2-C14-C15-C17	0.1866	
C50-O53	1.3790	N7-C43-C44	120.3291	C2-C14-C16-C18	-0.2143	
053–C54	1.4239	N7-C43-C45	120.4391	C2-C14-C15-C17	0.0935	
		C44-C43-C45	119.2294	C15-C14-C16-C18	-0.0795	
		C43-C45-C48	120.4751	C14-C15-C17-C19	0.3490	
		C44-C46-C50	119.6789	N7-C43-C44-C46	-179.8831	
		C45-C48-C50	119.6814	N7-C43-C44-C46	0.0975	
		C46-C50-O53	114.8751	N7-C43-C44-C48	-0.0126	
		C48-C50-O53	124.6157	C47-C44-C46-C50	-178.4401	
		C50-O53-C54	116.2880	C44-C46-C50-O53		



Fig. 4. Emission spectra of mpdsi for various metal ions.

the absorbance's at the excitation wavelength and the refractive indexes of the mpdsi and the standard, respectively. The radiative  $(k_r)$  and non-radiative  $(k_{nr})$  rate constants have been calculated from the following equations by using life time  $(\tau)$ :

$$k_r = \frac{\Phi_p}{\tau} \tag{6}$$

$$k_{\rm nr} = \frac{1}{\tau} - \frac{\Phi_{\rm p}}{\tau} \tag{7}$$

$$\tau = (k_{\rm r} + k_{\rm nr})^{-1} \tag{8}$$

The calculated radiative, non-radiative and life time of  $S_1$  excited state are 0.22, 0.21 and 2.3 ns, respectively.

### 3.2. mpdsi as a fluorescent chemosensor

Imidazole derivatives have been used to construct highly sensitive fluorescent chemosensors for sensing and imaging of metal ions and its chelates in particular those with Ir<sup>3+</sup> are major components for organic light emitting diodes and are promising candidates for fluorescent chemosensors for metal ions, if their radiationless channel could be blocked by metal binding. In the presence of metal ions such as Mn<sup>2+</sup>, Pb<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup> and Cu<sup>2+</sup>. The observed enhancement of fluorescence was observed to a different extent which shows that the metal ions binding blocks the radiationless decay channel in mpdsi (Fig. 4). The radiative  $(k_r)$  and non-radiative  $(k_{nr})$  rate constants have been calculated for mpdsi in  $Cu^{2+}$  in acetonitrile. The observed non-radiative emission  $(k_{nr})$ in mpdsi may be due to  $n-\pi^*$  transition [27]. It was found that the substantial increase in the quantum yield in presence of Cu<sup>2+</sup> is due to dramatic decrease in non-radiative transition whereas the radiation constant remains unchanged within the experimental error i.e., the radiationless decay due to  $n-\pi^*$  transitive in mpdsi is blocked upon metal binding and the emission of chelate [Cu<sup>2+</sup>-mpdsi] originates only from  $\pi - \pi^*$  transition.

## 3.3. Potential energy surface (PES) scan studies of mpdsi (1)

The potential energy surface scan about C46–C50–O53–C54 is performed by using B3LYP/6-31G (d,p) level. During the calculation all the geometrical parameters have been simultaneously relaxed while the C46–C50–O53–C54 torsional angles have been varied in steps of 0°, 10°, 20°, 30°...360°. The potential energy surface diagram (Fig. 5) clearly reveals that the minimum energy conformation



Fig. 5. Potential energy surface diagram of mpdsi.

corresponds to the one in which *p*-methoxyphenyl ring attached to the nitrogen atom (N7) is tilted to an angle of 150.46° (about [N6-C3-C4-C5) and the styryl ring attached to the carbon atom (C3) is in the angle of 98.21° (about C1-N7-C43-C44) which are in good agreement with the XRD results.

# 3.4. Steric hindrance in imidazoles: X-ray analysis

DFT calculation reveal that the imidazole ring is essentially planar and makes dihedral angle of 150.46° and 98.21° with the p-methoxyphenyl and styryl rings, respectively. The key twist, designated as  $\alpha$  have been examined and it is used to indicate the twist of imidazole ring from the styryl ring at C(3). The  $\alpha$  twist originates from the interaction of substituent at N(7) of the imidazole with the substituent at C(3). The present structural information allows us to further explore the correlation between structural features and fluorescent property. It reveals that  $\alpha$  twist is correlated with fluorescent property, the larger the  $\alpha$  twist, the more drops in the fluorescence quantum yield. Such a clear correlation indicates the importance of coplanarity between imidazole and the styryl ring at C(3) and this correlation can be ascribed to the conjugation rigidity. When the two adjacent aromatic species are in a coplanar geometry, the *p*-orbitals from the C–C bond connecting the two species will have maximal overlapping and the two rings will have a rigid and partial delocalized conjugation, as the result, the bond is no longer a pure single bond, as evident from the X-ray data. The present bond distance of C3–C4 is 1.45 Å (Table 2) is shorter than the regular single bond distance between two sp2 carbons (1.48 Å), because of delocalization. When the two rings are deviated from each other, the *p*-orbital overlapping will be reduced. However, from the theoretical values it was found that most of the optimized



Fig. 6. Orientation of dipole moments.

bond lengths, bond angles and dihedral angles are slightly higher than that of XRD values. These deviations can be attributed to the fact that the theoretical calculations have been aimed at the isolated molecule in the gaseous phase whereas the XRD results were aimed at the molecule in the solid state.

# 3.5. Second harmonic generation (SHG) studies of mpdsi

Second harmonic signal of 40 mV was obtained for mpdsi by an input energy of 4.1 mJ/pulse. But the standard KDP crystal gave a SHG signal of 110 mV/pulse for the same input energy. The second order non-linear efficiency will vary with the particle size of the powder sample [28]. Higher efficiencies can be achieved by optimizing the phase matching [29]. On a molecular scale, the extent of charge transfer (CT) across the NLO chromophore determines the level of SHG output, the greater the CT and the larger the SHG output.

# 3.6. Comparison of $\mu\beta_0$

The overall polarity of the synthesized imidazole derivative was small when their dipole moment aligned in a parallel fashion (Fig. 6). When the electric field is removed, the parallel alignment of the molecular dipole moments begins to deteriorate and eventually the imidazole derivative loses its NLO activity. The ultimate goal in the design of polar materials is to prepare compounds which have their molecular dipole moments aligned in the same direction [30].

Theoretical investigation plays an important role in understanding the structure-property relationship, which is able to assist in designing novel NLO chormophores. The electrostatic first hyperpolarizability ( $\beta$ ) and dipole moment ( $\mu$ ) of the imidazole chromophore have been calculated by using Gaussian-03 package [8]. From Table 3, it is found that the imidazole chromophore show larger  $\mu\beta_0$  values, which is attributed to the positive contribution of their conjugation. This chromophore exhibits larger non-linearity and its  $\lambda_{abs}$  is red-shifted when compared with unsubstituted imidazole. Therefore, it is clear that the hyperpolarizability is a strong function of the absorption maximum. Since even a small absorption at the operating wavelength of optic devices can be detrimental, it is important to make NLO chromophores as transparent as possible without compromising the molecule's non-linearity.

To determine the transference region and hence to know the suitability for microscopic non-linear optical applications, the UV–visible spectra have been recorded by using the spectrometer in the range of 200–780 nm. The absorption spectrum was shown in the UV region between 260 and 296 nm. The increased transparency in the visible region might enable the microscopic NLO behaviour with non-zero values [31–33]. All the absorption bands are due to  $\pi \rightarrow \pi^*$  transitions. The computed  $\beta$  values (Table 3) have been correlated with UV–visible spectroscopic data in order to understand the molecular-structure and NLO relationship in view

### Table 3

Electric dipole moment (*D*), polarizability ( $\alpha$ ) and hyperpolarizability ( $\beta_{total}$ ) of mpdsi.

Parameter	mpdsi (1)
Dipole moment (D)	
$\mu_{x}$	0.2044
$\mu_y$	-0.4776
$\mu_z$	-2.0152
$\mu_{ m tot}$	-2.2884
Polarizability ( $\alpha$ )	
axx	508.6269
$\alpha_{xy}$	-14.4608
$\alpha_{vv}$	195.7711
axz	-40.6890
$\alpha_{yz}$	-15.3935
$\alpha_{zz}$	396.8649
$\alpha_{tot} \times 10^{-23} \text{ esu}$	5.4402
Hyperpolarizability ( $\beta$ )	
β <sub>xxx</sub>	3559.6137
$\beta_{xxy}$	-258.4129
$\beta_{xyy}$	-6.0330
$\beta_{yyy}$	-9.2657
$\beta_{xxz}$	19.5005
$\beta_{xyz}$	-19.7016
$\beta_{yyz}$	-52.0586
$\beta_{xzz}$	-770.6952
$\beta_{yzz}$	5.6209
$\beta_{zzz}$	135.0122
$\beta_{ m tot}  imes 10^{-31}   m esu$	241.6480
$\mu eta_0  imes 10^{-31}  \mathrm{esu}$	552.9873

of a future optimization of the microscopic NLO properties. The band at around 290 nm exhibits a solvatochromic shift, characteristic of a large dipole moment and frequently suggestive of a large hyperpolarizability. This compound show red shift in absorption with increasing solvent polarity, accompanied with the upward shifts non-zero values in the  $\beta$ -components.

### 3.7. Octupolar and dipolar components of mpdsi

The imidazole possesses more appropriate ratio of off-diagonal versus diagonal  $\beta$  tensorial component ( $r = \beta_{xyy}/\beta_{xxx}$ ) which reflects the inplane non-linearity anisotropy and the largest  $\mu\beta_0$  values. The difference of the  $\beta_{xyy}/\beta_{xxx}$  ratios can be well understood by analyzing their relative molecular orbital properties. Theoretically investigated electrostatic first hyperpolarizabilities ( $\beta_0$ ) and dipole moment ( $\mu$ ) of the chromophores explained by the reduced planarity in such chromophores caused by the steric interaction between the two styryl and *p*-methoxyphenyl rings at C(3) and N(7) atoms. Hence, the steric interaction must be reduced in order to obtain larger  $\beta_0$  values.

The  $\beta$  tensor [34] can be decomposed in a sum of dipolar  $(J = 1^{2D}\beta)$  and octupolar  $(J = 3^{2D}\beta)$  tensorial components, and the ratio of these two components strongly depends on their 'r' ratios. The zone for  $r > r_2$  and  $r < r_1$  corresponds to a molecule of octupolar and dipolar, respectively. The critical values for  $r_1$  and  $r_2 \operatorname{are}(1 - \sqrt{3})/\sqrt{3}\sqrt{3} + 1) = -0.16 \operatorname{and}(\sqrt{3} + 1)/\sqrt{3}\sqrt{3} - 1) = -2.15$ , respectively. Complying with the pythagorean theory and the projection closure condition, the octupolar and dipolar components of the  $\beta$  tensor can be described as:

$$\left\| J^{2D} = 1\beta \right\| = \left(\frac{3}{4}\right) \left[ \left(\beta_{XXX} + \beta_{XVV}\right)^2 \right] + \left[ \left(\beta_{VVV} + \beta_{VXX}\right)^2 \right]$$
(9)

$$\left\| J \stackrel{2D}{=} 3\beta \right\| = \left(\frac{1}{4}\right) \left[ (\beta_{xxx-3} + \beta_{xvv})^2 \right] + \left[ (\beta_{vvv} - \beta_{vxx})^2 \right]$$
(10)

Second order	perturbation	theory	analysis	of Fock	matrix i	n NBO	for mp	odsi.

Donor (i)	Туре	ED/e	Acceptor (j)	Туре	ED/e	E(2)	E(j) - E(i)	F(ij)
C1-C2(2)	π	1.9726	C3-N6(2)	$\pi^*$	0.3585	28.05	0.48	0.108
C3-N6(2)	π	1.9832	C1-C2(2)	$\pi^*$	0.3063	39.00	0.57	0.139
C8-C9(2)	π	1.9753	C10-C12(2)	$\pi^*$	0.3167	39.06	0.48	0.124
C8-C9(2)	π	1.6366	C11-C13(2)	$\pi^*$	0.3348	43.60	0.48	0.130
C10-C12(2)	π	1.9810	C8-C9(2)	$\pi^*$	0.3651	41.91	0.49	0.129
C10-C12(2)	π	1.6691	C11-C13(2)	$\pi^*$	0.3348	41.53	0.49	0.127
C11-C13(2)	π	1.9814	C8-C9(2)	$\pi^*$	0.3651	41.79	0.49	0.128
C11-C13(2)	π	1.6595	C10-C12(2)	$\pi^*$	0.0130	41.65	0.49	0.128
C14-C15(2)	π	1.9732	C16-C18(2)	$\pi^*$	0.3204	40.22	0.48	0.126
C14-C15(2)	π	1.6410	C17-C19(2)	$\pi^*$	0.0143	43.90	0.48	0.130
C16-C18(2)	π	1.9810	C14-C15(2)	$\pi^*$	0.0208	41.41	0.49	0.128
C16-C18(2)	π	1.6651	C17-C19(2)	$\pi^*$	0.3418	42.61	0.48	0.128
C17-C19(2)	π	1.9813	C14-C15(2)	$\pi^*$	0.3586	41.61	0.49	0.129
C17-C19(2)	π	1.6651	C16-C18(2)	$\pi^*$	0.0126	41.13	0.49	0.128
C20-C22(2)	π	1.9730	C21-C23(2)	$\pi^*$	0.0133	40.36	0.49	0.126
C20-C22(2)	π	1.6548	C24-C25(2)	$\pi^*$	0.0142	41.85	0.48	0.127
C21-C23(2)	π	1.9808	C20-C22(2)	$\pi^*$	0.0241	41.60	0.49	0.128
C21-C 23(2)	π	1.6609	C24-C25(2)	$\pi^*$	0.3328	42.92	0.49	0.129
C24-C25(2)	π	1.9814	C20-C22(2)	$\pi^*$	0.3616	43.04	0.49	0.130
C24-C25(2)	π	1.6614	C21-C23(2)	$\pi^*$	0.3162	40.61	0.49	0.127
C43-C45(2)	π	1.9756	C44-C46(2)	$\pi^*$	0.0108	44.19	0.50	0.133
C 43-C45(2)	π	1.6960	C48-C50(2)	$\pi^*$	0.0243	31.53	0.49	0.113
C44-C46(2)	π	1.9779	C43-C45(2)	$\pi^*$	0.0240	33.68	0.49	0.116
C44-C46(2)	π	1.6988	C48-C50(2)	$\pi^*$	0.3517	44.74	0.49	0.134
C48-C50(2)	π	1.9805	C43-C45(2)	$\pi^*$	0.3536	52.29	0.49	0.143
C48-C50(2)	π	1.6618	C44-C46(2)	$\pi^*$	0.3005	30.96	0.51	0.113
LP N7(1)	$\pi$	1.6332	C1-C2(2)	$\pi^*$	0.3063	51.67	0.54	0.152
LP N7(1)	π	1.6332	C3-N6(2)	$\pi^*$	0.3585	75.64	0.50	0.175

The parameter  $\rho^{2D}[\rho^{2D} = \left\| J = 3\beta/J = 1\beta \right\|$ ] is convenient to com-

pare the relative magnitudes of the octupolar and dipolar components of  $\beta$ . The observed positive small  $\rho^{2D}$  value (0.096) reveals that the  $\beta_{iii}$  component cannot be zero and these are dipolar component. Since most of the practical applications for second order NLO chromophores are based on their dipolar components, this strategy is more appropriate for designing highly efficient NLO chromophores.

# 3.8. Natural bond orbital (NBO) analysis

NBO analysis have been performed for mpdsi at the DFT/B3LYP/6-31++G(d,p) level in order to elucidate the intramolecular, hybridization and delocalization of electron density within the molecule. The importance of hyperconjugative interaction and electron density transfer (EDT) from lone pair electrons to the antibonding orbital has been analyzed and the results [35] were tabulated in Table 4. Several donor-acceptor interactions have been observed for the imidazole derivative and among the strongly occupied NBOs, the most important delocalization sites are in the  $\pi$  system and in the lone pairs (*n*) of the oxygen and nitrogen atoms. The  $\sigma$  system shows some contribution to the delocalization, and the important contributions to the delocalization corresponds to the donor-acceptor interactions are  $C8-C9 \rightarrow C11-C13$ ,  $C10-C12 \rightarrow C8-C9$ ,  $C10-C12 \rightarrow C11-C13$ ,  $C11-C13 \rightarrow C8-C9$ ,  $C11-C13 \rightarrow C10-C12$ ,  $C14-C15 \rightarrow C16-C18$ ,  $C14-C15 \rightarrow C17-C19$ ,  $C16-C18 \rightarrow C14-C15$ ,  $C16-C18 \rightarrow C17-C19$ ,  $C17-C19 \rightarrow C14-C15, C20-C22 \rightarrow C21-C23, C21-C23 \rightarrow C24-C25,$ C43-C45  $\rightarrow$  C48-C50, C48-C50  $\rightarrow$  C43-C45 and LPN7  $\rightarrow$  C3-N6.

The charge distribution was calculated from the atomic charges by NLO and NBO analysis (Fig. 7). These two methods predict the same trend i.e., among the nitrogen atoms N6 and N7, N6 is considered as more basic site [32]. The charge distribution shows that the more negative charge is concentrated on N15 atom whereas the partial positive charge resides at hydrogens. When compared to nitrogen atoms (N7 and N6), oxygen (O53) is more electronegative in mpdsi [36].

# 3.9. Molecular electrostatic potential map (MEP)and electronic properties

The molecular electrostatic potential surface (MEP) (Fig. 8) is a plot of electrostatic potential mapped onto the iso-electron density surface simultaneously displays molecular shape, size and electrostatic potential values of the imidazole derivative. MEP surface diagram is used to understand the reactive behaviour of a molecule, in that negative regions can be regarded as nucleophilic centers, whereas the positive regions are potential electrophilic sites. The MEP map of mpdsi clearly suggests that the nitrogen and oxygen atoms represent the most negative potential region. The hydrogen atoms bear the maximum brunt of positive charge. The predominance of green region in the MEP surfaces corresponds to a potential halfway between the two extremes red and dark blue colour.



Fig. 7. Bar diagram representing the charge distribution of mpdsi.



Fig. 8. HOMO-LUMO orbital picture of mpdsi.

The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor. HOMO is located on imidazole ring, partly styryl ring, two phenyl rings at C1 and C2 carbons and oxygen of the methoxy group whereas LUMO is located imidazole ring and styryl ring The HOMO  $\rightarrow$  LUMO transition implies that intramolecular charge transfer takes place [31] within the molecule. The energy gap  $(E_{\sigma})$  of mpdsi has been calculated from the HOMO and LUMO levels (Fig. 8). The decrease in the HOMO and LUMO energy gap explains the probable charge transfer (CD) taking place inside the chromophore.

# 4. Conclusion

The presence of  $\alpha$  twist in this imidazole drops the fluorescence quantum vield. The observed dipole moment and hyperpolarizability can be explained by the reduced planarity caused by the steric interaction between the two styryl and *p*-methoxyphenyl rings at C(3) and N(7) atoms. Hence, the steric interaction must be reduced in order to obtain larger  $\beta_0$  values. From the physicochemical studies on imidazoles it was concluded that molecules of higher hyperpolarizability have larger dipole moments used as potential NLO molecules.

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