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Characterization, physiochemical and computational studies of the newly synthesized novel imidazole derivative

Jayaraman Jayabharathi*, Venugopal Thanikachalam, Ramalingam Sathishkumar

Department of Chemistry, Annamalai University, Annamalainagar 608002, Tamilnadu, India

HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Catalan–Taft parameter shows acidity of the solvent, C_β or C_{SB} has a negative value.
- The steric interaction must be reduced in order to obtain larger β_0 values.
- NBO analysis: elucidates the intramolecular, hybridization and delocalization within the molecule.
- Electronic properties: probable charge transfer (CD) taking place inside the chromophore.
- ► The charge distribution was calculated by the NBO and Mulliken methods.

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The photophysical properties of imidazole derivative were studied in several solvents. The observed fluorescence quantum yield is attributed to a loss of planarity in the excited state provided by the non coplanarity of the aryl rings attached to C(2) and N(1) atoms of the imidazole ring. The solvent effect on the absorption and fluorescence bands was analyzed by a multi-component linear regression in which several solvent parameters were analyzed simultaneously. DFT calculations were carried out in order to find out the NBO analysis, HOMO–LUMO energies, MEP studies and hyperpolarisability behaviour. This chromophore possess more appropriate ratio of off-diagonal versus diagonal β tensorial component ($r = \beta_{xyy} | \beta_{xxx} = 0.12$) which reflects the in plane non-linearity anisotropy. Since they have largest $\mu\beta_0$ value, the reported imidazole can be used as potential NLO material. Within this context, reasonable conclusions concerning the steric hindrance in the chromospheres, push–pull character, hyperpolarisability of the imidazole and their application as NLO materials will be drawn.

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Introduction

Research on organic luminescent materials has been keenly pursued because of their importance in technological applications related to signalling, fluorescent chemosensory materials, molecular switches and organic light emitting diodes (OLEDs) [1–3]. Organic fluorophores, especially nitrogen-containing heterocyclic compounds, have attracted attention owing to their high emission

* Corresponding author. Tel.: +91 9443940735. E-mail address: jtchalam2005@yahoo.co.in (J. Jayabharathi). efficiency [4–6]. However, as the basic structure of a fluorophore has to be modified, the investigation of substituent effects provides a route to optimizing potentially advantageous properties [7].

Imidazoles display a broad spectrum of biological activity which has made them privileged structures in combinational drug discovery libraries. The biological roles of imidazole such as antiviral, antiulcer, antihypertension and anticancer properties are well documented [8]. They have also found application as a chromophore with high extinction coefficient, readily tuneable absorption wavelength and fluorophoric properties and is desirable as a large planar synthetic building block in supramolecular chemistry [9].

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In the present paper, the photophysical properties of imidazole derivative 2-phenyl-1-p-tolyl-1H-imidazo [4,5-f][1,10]phenanthroline was investigated in a wide variety of solvents. The solvent effects on the absorption and fluorescence bands are analyzed by a multi-component linear regression in which several solvent parameters are simultaneously analyzed.

Experimental

Methods

UV-vis absorption and fluorescence spectra were recorded on Perkin Elmer spectrophotometer Lambda35 and Perkin Elmer LS55 spectrofluorimeter, respectively. Fluorescence spectra were corrected from the monochromator wavelength dependence and the photomultiplier sensibility. Fluorescence quantum yield (ϕ) was determined by means of the corrected fluorescence spectra of a dilute solution of imidazole derivative in dichloromethane, coumarin as a reference and by taking into account the solvent refractive index. The photophysical measurements of the imidazole derivative were recorded in dilute concentrations (1×10^{-5} M).

General procedure for the synthesis of the 2-phenyl-1-p-tolyl-1Himidazo[4,5-f][1,10]phenanthroline

The synthesis of 2-phenyl-1-p-tolyl-1H-imidazo[4,5-f][1,10] phenanthroline involves a four components assembling [10–15] of a mixture of 1,10-phenanthroline-5,6-dione (2.10 g, 10 mM), ammonium acetate (2.5 g, 30 mM), 4-methylaniline (1.23 g, 10 mM) and benzaldehyde (1.1 ml, 10 mM) in distilled ethanol medium (20 ml). The reaction mixture was refluxed at the boiling point of ethanol (78 °C) and the completion of the reaction was monitored by thin layer chromatography (TLC) technique using benzene: ethyl acetate (9:1) as the eluent. The reaction mixture was then extracted with dichloromethane and the resultant resinous material was purified by column chromatography.

Computational details

Quantum mechanical calculations were carried out with Guassian-03 program using the Becke3–Lee–Yang–Parr (B3LYP) functional supplemented with the standard 6-31G(d,p) basis set [16].



Fig. 2. The key α twist of imidazole ring at C(2).

Results and discussion

UV-vis absorption and fluorescence spectra of the imidazole derivative are shown in Fig. 1. In apolar solvents, the main absorption band is appeared around 320 nm, whereas the fluorescence spectrum appeared around 400 nm. The fluorescence spectrum of the imidazole derivative is shifted to higher energies with respect to parent compound [17,18] in common solvents. These spectral shifts are attributed to the higher electron-releasing character of the methyl group located at C(45) carbon atom. In the case of alcoholic solvents, bathochromic shifts was observed for both absorption and emission providing large Stokes shift. These results suggest an important geometrical rearrangement in the S₁ excited state and these observations are in good agreement with the literature report [19].



Fig. 1. Absorption (a) and fluorescence (b) spectra of the imidazole derivative in various solvents.

 Table 1

 Selected bond lengths, bond angles and torsional angles for the imidazole derivative.

Bond connectivity	Bond length (Å)	Bond connectivity	Bond angle (°)	Bond connectivity	Torsional angle (°)
C9-N22	1.4660	C9-N22-	105.3334	C9-N22-	166.0636
C5-N21	1.4633	C6- N21-	101.4371	C6-N21- C33-C34	-162.2460
N21-C33	1.4825	N22- C9-C6	109.2752	C6-N21- C33-N22	17.3368
N22-C33	1.3530	N21-C33- N22	111.8793	C21-N33- N22-C9	-13.5193
C9–C8	1.3974	N21-C33- C34	124.0687	N21-C33- C34-C35	179.7634
C6-C3	1.3974	N22-C33- C34	124.0505	N21-C33- C34-C36	-0.2324
N21-C23	1.4700	C33-C34- C35	120.0013	C3-C6- N21-C33	165.7824
C33-C34	1.5400	C33-C34- C36	119.9988	C8-C9- N22-C33	-170.9811
C6-C9	1.3774	C6- N21- C23	113.4015	N22-C9- C8-C7	170.9658
C30-C45	1.5400	C6- C9-C8	122.8647	N21-C6- C3-C4	176.0212
N19-C7	1.3395	C9- C6-C3	122.8797	C1-C5- N20-C4	0.0544
N19-C13	1.3442	C28– C30– C45	119.9994	C7-N19- C13-C12	0.0332
N20-C4	1.3396	C26–C30– C45	119.9989	N19-C7- C4-N20	1.5567
N20-C5	1.3444	C7-N19- C13	120.6109	C8-C7-C4- N20	-178.2292
		C4-N20-C5	120.6070	C25-C28- C30-C45	179.3393
		N19-C7-C4	121.0603	C24-C26- C30-C45	180.0000



Fig. 3. Resonance structures (a and b) of the imidazole chromophore.

The key twist (α) is used to indicate the twist of imidazole ring from the aryl ring at N(21) (Fig. 2). It reveals that α twist is correlated with fluorescent property, the larger α twist, the more is the drop the fluorescence quantum yield (0.30). Due to the delocalized conjugation the bond between the imidazole nitrogen and the aniline attached carbon atom (N21-C23) is no longer a pure single bond, as evident from the X-ray data of the parent compound. When the two rings are deviated from each other, the p-orbital overlapping will be reduced. The partial conjugation will lead to less rigid structure; therefore, radiationless twist motion will deactivate the emitting state, leading to the low quantum yields. Thus the fluorophores with the substitution at C(34) with a minimum loss of fluorescence property. All these results are in good agreement with the theoretical values (Table 1). However, from the theoretical values it can be found that most of the optimized 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 were aimed at the isolated molecule in the gaseous phase whereas the XRD results were aimed at the molecule in the solid state.

The spectral shifts were observed in the fluorescence band of the imidazole derivative with respect to the parent, can be interpreted by the Brunings–Corwin effect [20]. Because the distortion of the geometry in the excited state implies a decrease in the resonance energy, the fluorescence band is bathochromically shifted to a higher extent than the absorption band. Moreover, the loss of planarity in the excited state of the imidazole derivative could explain the lower fluorescence quantum yield in apolar solvents owing to an increase in the non-radiative processes.

However, the shape of the absorption band is independent of the imidazole concentration suggesting the poor aggregation and it is a suitable behaviour in the performance of active media of lasers. Indeed, high concentration is necessary to bring about laser action, and the presence of aggregates could drastically reduce the fluorescence quantum yield owing to the efficient quenching of the monomer fluorescence by the aggregates. However, experimental data indicate that the fluorescence band is shifted to lower energies by increasing the concentration. This bathochromic shift is attributed to reabsorption and reemission phenomena [21] and this result corroborates the importance of registering photophysical properties in dilute solutions.

The 3D plots of the frontier orbitals HOMO and LUMO is shown in Fig. S1. 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. The HOMO is located on the imidazole ring, phenanthroline ring, partly on the aldehydic ring attached to the C(34) whereas LUMO is located on the phenanthroline ring, imidazole ring and aldehydic ring attached to the C(34). The HOMO \rightarrow LUMO transition implies that intramolecular charge transfer takes place within the molecule. The energy gap (E_g) has been calculated from the HOMO and LUMO levels. The decrease in the HOMO and LUMO energy gap explains the probable charge transfer (CD) inside the chromophore.

The electron density at position C(34) and the aryl ring attached to the C(34) carbon is augmented in the HOMO with respect to that in the LUMO state. Taking into account the resonance structures of the imidazole chromophore (Fig. 3), we observed that the resonance structure "b" has the largest charge separation along the short molecule axis. Consequently, its contribution would be more important in the S₀ ground states than in the S₁ excited states. Thus, the polar solvents would stabilize the S₀ state more extensively than the S₁ state, thereby increasing the energy gap between both states and explaining the solvatochromic shifts [22].

To analyze the solvatochromic effects, we checked several methods [23,24]. Neither the absorption nor the fluorescence wavenumbers linearly correlate with the Lippert parameter $\Delta f(\varepsilon,n^2)$ [25], which considers the solvent polarity/polarizability or with the Reichardt parameter E_T^N (30) [26] which takes into account several solvent properties (polarity and H-bond donor capacity) in a common parameter. For these reasons, a multi parameter correlation analysis is employed in which a physicochemical property is linearly correlated with several solvent parameters by means of Eq. (1):

$$(XYZ) = (XYZ)_0 + C_a A + C_b B + C_c C + \cdots$$
(1)

where $(XYZ)_0$ is the physicochemical property in an inert solvent and C_a , C_b , C_c and so forth are the adjusted coefficients that reflect the dependence of the physicochemical property (XYZ) on several solvent properties. Solvent properties that mainly affect the photophysical properties of aromatic compounds are polarity, H-bond donor capacity and electron donor ability. Different scales for such parameters can be found in the literature, Taft et al. [27] propose



Fig. 4. Correlation between the experimental absorption and fluorescence wavenumber with the predicted values obtained by a multicomponent linear regression using the π_* , α and β -scale (Taft) solvent parameters for the imidazole derivative.

Table 2

Adjusted coefficients ($(v_{x})_0, c_a, c_b$ and c_c) and correlation coefficients (r) for the multilinear regression analysis of the absorption v_{ab} and fluorescence v_{fl} wavenumbers and Stokes shift (Δv_{ss}) of the imidazole derivative with the solvent polarity/polarizability, and the acid and base capacity using the taft (π *, α and β) and the Catalan (SPP^N, SA and SB) scales.

(v_x)	$(v_x)_0 {\rm cm}^{-1}$	(π^*)	Cα	c_{eta}	r
λ_{ab} λ_{fl} $\Delta v_{ss} = v_{ab} - v_{fl}$	$\begin{array}{l}(3.158\pm 0.056)\times 10^{4}\\(2.606\pm 0.032)\times 10^{4}\\(0.558\pm 0.059)\times 10^{4}\end{array}$	$\begin{array}{l}(9.083\pm11.465)\times10^{3}\\-(3.345\pm6.530)\times10^{3}\\(12.429\pm11.840)\times10^{3}\end{array}$	$\begin{array}{c} (18.210\pm 38.319)\times 10^3 \\ (1.041\pm 21.826)\times 10^3 \\ (19.251\pm 39.572)\times 10^3 \end{array}$	$\begin{array}{l} -(6.682\pm 30.780)\times 10^3\\ -(3.384\pm 17.532)\times 10^3\\ -(3.298\pm 31.786)\times 10^3\end{array}$	0.72 0.89 0.58
(v_x)	$(v_x)_0 {\rm cm}^{-1}$	C ^N _{SPP}	C _{SA}	$c_{\rm SB}$	r
λ_{ab} λ_{fl} $\Delta v_{ss} = v_{ab} - v_{fl}$	$\begin{array}{c} (3.270\pm0.046)\times10^{4} \\ (2.589\pm0.027)\times10^{4} \\ (0.689\pm0.066)\times10^{4} \end{array}$	$\begin{array}{c} -(33.841\pm16.882)\times10^3\\ -(15.104\pm9.931)\times10^3\\ -(18.737\pm24.318)\times10^3\end{array}$	$\begin{array}{c} (110.16\pm70.04)\times10^3\\ (73.014\pm41.202)\times10^3\\ (37.147\pm100.894)\times10^3\end{array}$	$\begin{array}{l} -(96.50\pm73.03)\times10^3\\ -(85.56\pm42.96)\times10^3\\ -(10.943\pm105.19)\times10^3\end{array}$	0.52 0.56 0.88

Table 3

Electric dipole moment (*D*), polarizability (α) and hyperpolarisability (β_{total}) of dfpmpip.

Parameter	(1)
Dipole moment (D)	
$\mu_{\mathbf{x}}$	7.0477
$\mu_{\mathbf{v}}$	1.6071
μ _z	0.2928
$\mu_{ m total}$	7.2345
Polarizability (α)	
α_{xx}	-169.6561
α_{xy}	14.8095
α_{yy}	-153.3569
α _{xz}	-0.1322
α_{yz}	-3.5970
α _{zz}	-165.9687
$\alpha \times 10^{-24}$ (esu)	-2.4155
Hyperpolarisability	
β_{XXX}	144.3615
β_{xxy}	-61.4484
β_{xyy}	17.8130
β_{yyy}	39.2124
β_{xxz}	-6.3283
β_{xyz}	-5.4965
β_{yyz}	18.6430
β_{xzz}	26.3167
β_{yzz}	8.3599
β _{zzz}	1.5491
$\beta \times 10^{-32}$ (esu)	163.7230
$\mu\beta imes 10^{-32}$ (esu)	1184.4540

the π^* , α and β scales, whereas more recently Catalan et al. [28] suggest the SPP^N, SA and SB scales to describe the polarity/polarizability, the acidity and basicity of the solvents respectively.

Fig. 4 shows the obtained correlation between the absorption and fluorescence wavenumbers calculated by the multi-component linear regression employing the Taft-proposed solvent parameters and the experimental values listed in Table 2. It lists the obtained adjustment and correlation coefficients by the Taft and Catalan parameters. The dominant coefficient affecting the absorption and fluorescence bands of imidazole derivative is that describing the polarity/polarizability of the solvent, C_{π^*} or $C_{\text{SPP}}^{\text{N}}$ having a positive value, corroborating the above-mentioned solvatochromic shifts with the solvent polarity. The coefficient controlling the Hdonor capacity or acidity of the solvent, C_{α} or C_{SA} , is the lowest coefficient; therefore, the solvent acidity does not play an important role in absorption and fluorescence displacements. The adjusted coefficient representing the electron releasing ability or basicity of the solvent, C_{β} or C_{SB} has a negative value, suggesting that the absorption and fluorescence bands shift to lower energies with the increasing electron-donating ability of the solvent. This effect can be interpreted in terms of the stabilization of the resonance structures of the chromophore (Fig. 3). Resonance structure "b" has the positive charge located at the nitrogen atom and it will be stabilized in basic solvents because this resonance structure is predominant in the S₁ state, as discussed above and the stabilization of the S₁ state with the solvent basicity would be more important than that of the S₀ state. Consequently, the energy gap between the S₁ and S₀ states decreases and the absorption and fluorescence wavelengths shift to longer wavelengths with increasing solvent basicity.

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. S2). 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 [29].

Table 4

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Donor (i)	Туре	ED/e	Acceptor (j)	Туре	ED/e	E(2)	E(j) - E(i)	F(I, j)
C1-C2	π	1.9807	C5-N20	π^*	1.9870	23.23	0.28	0.072
C3-C4	π	1.9705	C1-C2	π^*	1.9807	19.42	0.28	0.068
C3-C4	π	1.5684	C6-C9	π^*	1.9690	19.02	0.27	0.064
C5-N20	π	1.9870	C3-C4	π^*	1.9705	20.62	0.32	0.076
C7–C8	π	1.9723	C6-C9	π^*	1.6639	18.91	0.26	0.063
C7–C8	π	1.5747	C10-C12	π^*	1.9814	18.31	0.28	0.067
C10-C12	π	1.9841	C13-N19	π^*	1.9869	23.90	0.28	0.073
C13-N19	π	1.9869	C7-C8	π^*	1.9723	19.99	0.32	0.075
N22-C33	π	1.9806	C6-C9	π^*	1.9790	20.39	0.32	0.077
C23-C24	π	1.9735	C25-C28	π^*	1.9768	19.90	0.29	0.067
C23-C24	π	1.6727	C26-C30	π^*	1.9767	17.84	0.30	0.065
C25-C28	π	1.9768	C23-C24	π^*	1.9735	18.58	0.28	0.065
C25-C28	π	1.6713	C26-C30	π^*	1.6337	21.35	0.29	0.071
C26-C30	π	1.9767	C23-C24	π^*	1.6727	23.89	0.27	0.072
C26-C30	π	1.6337	C25-C28	π^*	1.6713	19.54	0.28	0.066
C34-C36	π	1.9713	C35-C37	π^*	1.9797	19.58	0.28	0.067
C34-C36	π	1.6481	C39-C41	π^*	1.9807	19.81	0.28	0.067
C35-C37	π	1.9797	C34-C36	π^*	1.9713	20.07	0.28	0.068
C35-C37	π	1.6594	C39-C41	π^*	1.6558	20.91	0.28	0.068
C39-C41	π	1.9807	C34-C36	π^*	1.6484	20.74	0.28	0.069
C39-C41	π	1.6558	C35-C37	π^*	1.6594	19.50	0.28	0.067
LP1-N21	π	1.5903	C6-C9	π^*	1.6639	33.62	0.29	0.088
LP1-N21	π	1.5903	N22-C33	π^*	1.9806	43.38	0.27	0.097



Fig. 5. Bar diagram representing the charge distribution of imidazole derivative using NLO and NBO methods.

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 (β) and dipole moment (μ) of the imidazole chromophore have been calculated by using Gaussian 03 package. 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 λ_{max} 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 nonlinearity.

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 200–750 nm. The increased transparency in the visible region might enable the microscopic NLO behaviour with non-zero values [30,31]. All the absorption bands are due to $\pi \rightarrow \pi^*$



Fig. 6. MEP surface diagram of the imidazole derivative.

transitions. The β values (Table 3) computed here might be correlated with UV–visible spectroscopic data in order to understand the molecular-structure and NLO relationship in view of a future optimization of the microscopic NLO properties. The band at around 390 nm exhibits a solvatochromic shift, characteristic of a large dipole moment and frequently suggestive of a large hyperpolarisability. This compound show red shift in absorption with increasing solvent polarity, accompanied with the upward shifts non-zero values in the β -components.

Octupolar and dipolar components

The imidazole derivative possess a more appropriate ratio of off-diagonal versus diagonal β 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 β_{xyy}/β_{xxx} ratios can be well understood by analyzing their relative molecular orbital properties. The electrostatic first hyperpolarizabilities (β_0) and dipole moment (μ)

of the chromophores have been investigated theoretically. These observed results can be explained by the reduced planarity in such chromophores caused by the steric interaction between the two phenyl rings at C(23) and N(15) atoms. Hence, the steric interaction must be reduced in order to obtain larger β_0 values.

The β tensor [32] is a sum of dipolar $\binom{2D}{J=1}\beta$ and octupolar $\binom{2D}{J=3}\beta$ 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 are -0.16 and 2.15, respectively. Complying with the Pythagorean theory and the projection closure condition, the octupolar and dipolar components of the β tensor can be described as:

$$\|_{J=1}^{2D}\beta\| = (3/4)[(\beta_{xxx} + \beta_{xyy})^2 + [(\beta_{yyy} + \beta_{yxx})^2]$$
(2)

$$\|_{J=3}^{2D}\beta\| = (1/4)[(\beta_{xxx-3}\beta_{xyy})^2 + [(\beta_{yyy} - \beta_{yxx})^2]$$
(3)

The parameter ρ^{2D} is convenient to compare the relative magnitudes of the octupolar and dipolar components of β . The observed positive small ρ^{2D} value (3.07) reveals that the β_{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.

Natural bond orbital (NBO) analysis

NBO analysis have been performed for the imidazole derivative 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 [33] were tabulated in Table 4. Several donor-acceptor interactions are observed for the imidazole derivative and among the strongly occupied NBOs, the most important delocalization sites are in the π system and in the lone pairs (n) of the oxygen, fluorine and nitrogen atoms. The σ system shows some contribution to the delocalization, and the important contributions to the delocalization corresponds to the donor-acceptor interactions are $C1-C2 \rightarrow C5-N20$, C3- $C4 \rightarrow C1-C2$, $C3-C4 \rightarrow C6-C9$, $C5-N20 \rightarrow C3-C4$, $C6-C9 \rightarrow C3-C4$, $C7-C8 \rightarrow C10-C12$, $C10-C12 \rightarrow C13-N19$, $C13-N19 \rightarrow C7-C8$, N22-C33 \rightarrow C6-C9, C23-C24 \rightarrow C25-C28 and C23-C24 \rightarrow C26-C30.

The charge distribution of the imidazole derivative was calculated from the atomic charges by NLO and NBO analysis (Fig. 5). These two methods predict the same trend i.e., among the nitrogen atoms N15 and N16, N15 is considered as more basic site [34]. The charge distribution shows that the more negative charge is concentrated on N15 atom whereas the partial positive charge resides at hydrogens.

Molecular electrostatic potential map (MEP) and electronic properties

The MEP surface diagram (Fig. 6) reveals that the negative regions can be regarded as nucleophilic centres, whereas the positive regions are potential electrophilic sites. In the MEP map clearly suggests that the nitrogen atoms bear the most negative potential region. The hydrogen atoms bear the maximum brunt of positive charge. The predominance of green region corresponds to a potential halfway between the two extremes red and dark blue colour.

Conclusions

The presence of aryl ring at C(34) in the imidazole chromophore core originates a distortion from planarity in the imidazole units, mainly in the excited state, which leads to an increase in the rate constant of non-radiative deactivation and in the Stokes shift. The solvent effect on the absorption and fluorescence bands was analyzed by a multi-component linear regression in which different solvent parameters were analyzed simultaneously. DFT calculations were carried out for the NBO analysis, HOMO–LUMO energies, MEP studies and hyperpolarisability behaviour. Since they have largest $\mu\beta_0$ value, the reported imidazole can be used as potential NLO material.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.06.050.

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