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# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

# Photophysical studies of fused phenanthrimidazole derivatives as versatile $\pi$ -conjugated systems for potential NLO applications

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# A R T I C L E I N F O

Article history: Received 16 November 2011 Received in revised form 22 December 2011 Accepted 16 January 2012

Keywords: ORTEP Imidazole NLO HOMO-LUMO MEP

# ABSTRACT

Two new heterocyclic imidazole derivatives consists of  $\pi$ -conjugated system attached to a phenanthrimidazole moiety have been synthesized in moderate yield by the condensation of 1,10-phenanthroline-5,6-dione with substituted aromatic aldehydes and 4-methoxyaniline in the presence of ammonium acetate in ethanol medium. The photophysical properties of these imidazole derivatives were studied in several solvents. These derivatives were evaluated concerning their solvatochromic properties and molecular optical nonlinearities. Their electric dipole moment ( $\mu$ ) and hyperpolarizability ( $\beta$ ) have been calculated theoretically and the results indicate that the extension of the  $\pi$ -framework of the ligands has an effect on the NLO properties of these imidazole derivatives. The non-zero tensor components of these imidazole derivatives reveal that they possess potent non-linear optical (NLO) behavior. The energies of the HOMO and LUMO levels and the molecular charge transfer (ICT) within the molecule.

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# 1. Introduction

New material properties can be achieved, when new conjugated systems are composed by different heterocyclic nuclei, which allow the fine tuning of important photophysical properties. As a result of the optical and conductive properties, conjugated materials containing thiophene, imidazole and phenanthroline heterocycles have found many applications [1].

Aryl-imidazo-phenanthrolines play important role in materials science and medicinal chemistry due to their optoelectronic properties [2–4]. They are used as ligands for the synthesis of metal complexes of ruthenium(II), copper(II), cobalt(II), nickel(II), manganese(II), iridium(III) and several lanthanides for nonlinear optical (NLO) applications. They are important building blocks for the synthesis of proton, anion and cation sensors. They have diverse biological applications such as probes of DNA structure and new therapeutic agents due to their capacity to bind or interact with DNA [4].

Our approach to design new  $\pi$ -conjugated systems for several potential optical applications is based on the use of six membered aromatics and imidazoles in the conjugation pathway, combined with electron deficient heterocycles such as phenanthroline. These nuclei act as an acceptor group due to the deficiency of electron

density on the ring carbon atoms. These imidazole derivatives exhibit high thermal stabilities making them interesting for several applications in materials chemistry [5,6]. Hence there is considerable interest in the synthesis of new materials with large optical nonlinearities by virtue of their potential use in device applications related to telecommunications, optical computing, optical storage, and optical information processing [7–10]. Herein we focussed the synthesis, photophysical and theoretical studies of some novel arylimidazophenanthroline derivatives (**1** and **2**) and shown as potential candidates for NLO materials by virtue of their high harmonic generation.

# 2. Experimental

# 2.1. Materials and methods

1,10-Phenanthroline-5,6-dione has been synthesized and purified according to the reported literature procedure [11]. Benzaldehyde, 4-fluorobenzaldehyde, 4-methoxyaniline and all the other reagents have been purchased from S.D. fine chemicals and used without further purification for the synthesis of these imidazole derivatives reported here (Scheme 1) [12–20].

NMR spectra have been recorded on a Bruker 400 MHz NMR instrument (Figs. 1 and 2). UV–vis absorption and fluorescence spectra have been recorded on Perkin Elmer spectrophotometer Lambda35 and Perkin Elmer LS55 spectrofluorimeter, respectively. Fluorescence spectra were corrected from the monochromator

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Scheme 1. Synthesis of imidazole derivatives (1) and (2).







Fig. 2. <sup>13</sup>C NMR spectrum of imidazole derivative (1).



Fig. 3. Absorption spectrum of imidazole derivatives (1) and (2) in various solvents.

wavelength dependence and the photomultiplier sensibility. Fluorescence quantum yields ( $\phi$ ) have been determined by means of the corrected fluorescence spectra of a dilute solution of imidazole derivatives in dichloromethane, using coumarin 47 in ethanol as a reference and by taking into account the solvent refractive index. Mass spectrum was recorded using Agilent 1100 Mass spectrometer.

#### 2.2. Computational details

Quantum mechanical calculations have been used to carry out the optimized geometry, NBO, NLO, MEP and HOMO–LUMO analysis with Guassian-03 program using the Becke3–Lee–Yang–Parr (B3LYP) functional supplemented with the standard 6-31G(d,p) basis set [21].

# 3. Results and discussion

# 3.1. Photophysical studies of the imidazole derivatives 1 and 2

UV-vis absorption and fluorescence spectra (Table 1) of these imidazole derivatives **1** and **2** are shown in Figs. 3 and 4,

respectively. In apolar solvents, the main absorption band is centered around 270 nm with a high molar absorption coefficient, whereas the fluorescence spectrum is centered around 370 nm with a fluorescence quantum yield around 0.38.

The observed red shift absorption maxima ( $\lambda_{max}$ ) suggest an increase of molecular hyperpolarizability, according to the theoretical NLO studies. The absorption maxima ( $\lambda_{max}$ ) have been compared with the  $\pi^*$  values for each solvent, determined by Kamlet and Taft [22]. The observed results show that these imidazole derivatives exhibited positive solvatochromism with respect to their charge transfer (CT) absorption band. The position of the absorption maximum shifted to longer wavelengths as the polarity of the solvent increased due to a greater stabilization of the excited state relative to the ground state with an increase of solvent polarity.

#### 3.2. Twisting structure and XRD analysis

The fluorescence spectrum of the imidazole derivative 2 is shifted to higher energies with respect to compound 1 in common solvents. These spectral shifts were attributed to the higher



Fig. 4. Emission spectrum of imidazole derivatives (1) and (2) in various solvents.

# Table 1

Photophysical data of the imidazole derivatives **1** and **2** in different solvents.

Solvent	Imidazole derivative	e (1)		Imidazole derivative ( <b>2</b> )			
	$\lambda_{ab} (\pm 0.1 \text{ nm})$	$\lambda_{fl}$ (±0.4 nm)	$\Delta \upsilon_{ m ss}( m cm^{-1})$	$\lambda_{ab}$ (±0.1 nm)	$\lambda_{fl}$ (±0.4 nm)	$\Delta \upsilon_{ m ss}~( m cm^{-1})$	
Hexane	272	378	10,310	273	377	10,105	
1,4-Dioxane	276	396	10,979	270	389	11,330	
Benzene	274	386	10,590	281	388	9814	
Chloroform	276	390	10,591	277	390	10,460	
Ethyl acetate	271	389	11,193	275	387	10,524	
Dichloromethane	274	390	10,855	275	388	10,590	
Butanol	269	394	11,794	275	386	10,457	
Ethanol	274	398	11,371	274	398	11,371	
Methanol	275	404	11,611	275	375	9697	
Acetonitrile	273	409	12,180	273	393	11,185	
DMSO	269	410	12,784	276	377	9707	
1-Propanol	273	396	11,378	274	384	10,455	

#### Table 2

Selected bond lengths, bond angles and torsional angles for the imidazole derivative (2).

Bond connectivity	Bond length (Å) <sup>a</sup>	Bond connectivity	Bond angle (°)	Bond connectivity	Torsional angle (°)
C3—C6	1.4409 (1.4321)	С3—С6—С9	121.8614 (123.04)	C3—C6—C9—C8	-1.8322 (-3.5)
C6—C9	1.3663 (1.3770)	C3-C6-N15	132.7598 (131.74)	C2-C3-C6-N15	1.2692 (0.8)
C6-N15	1.3968 (1.3840)	C8-C9-N16	127.0967(127.30)	C3-C6-N15-C23	-178.4425(-175.82)
C9—N16	1.3740 (1.3789)	C9-N16-C23	106.7446 (104.52)	C3-C6-N15-C17	-1.4544(-2.3)
N15-C23	1.3855(1.3752)	N15-C23-N16	110.9912(112.63)	N15-C6-C9-N16	-0.5353(-0.78)
N16-C23	1.3053 (1.3168)	C6-N15-C17	126.8748 (128.80)	C6-N15-C23-N16	-0.1705 (-0.73)
N15-C17	1.4284 (1.4402)	N16-C23-C24	122.3559 (124.59)	C6-N15-C17-C18	81.2192 (82.65)
C22-031	1.3661 (-)	N15-C17-C18	120.0807 (119.73)	C6-N15-C23-C24	-177.7521 (-179.76)
031–C32	1.4315 (-)	C20-C22-O31	115.7374 (-)	N15-C23-C24-C25	37.0943 (56.56)
C23-C24	1.4730 (1.4782)	C22-031-C32	121.9927 (-)	N16-C23-C24-C25	-145.2018(-122.35)
C29—F30	1.3733 (-)	C23-C24-C25	123.8171 (121.16)	N16-C23-C24-C26	32.2310 (55.54)
		C28-C29-F30	118.7298 (-)	C25-C27-C29-F30	179.7448 (-)
				C6-N15-C17-C18	81.2192 (82.65)
				N15-C17-C19-C21	179.9334 (177.39)
				C20-C22-O31-C32	179.4798 (-)
				C9-C6-N15-C17	177.4109 (174.37)

 $R[F^2 > 2\sigma(F^2)] = 0.042$ ; wR( $F^2$ ) = 0.117; R indices (all data) = 0.0458.

<sup>a</sup> Values given in the brackets are corresponding to XRD values of **3**.

inductive electron-acceptor character of the fluorine atom located at C(29) carbon atom. These results suggest an important geometrical rearrangement in the S<sub>1</sub> excited state and this finding is in good agreement with the literature report [23]. To understand the geometry of the molecule both in ground and excited states, X-ray data of its analog compound **3** (Fig. 5) reported by Jayabharathi et al. [24] is taken for discussion. The crystal study of compounds 1 and 2 is currently under progress. X-ray data of 3 (Table 2) reveal that the fused ring system is essentially planar. The obtained dihedral angles of 77.41° and 56.26° with the phenyl ring attached to N(1)nitrogen and phenyl ring attached to C(2) carbon the imidazole ring respectively. The dihedral angle between the two phenyl rings is 65.50°. The molecular modeling of **1** and **2** has been examined by density functional theory calculation [25]. Though XRD data is in good agreement with the theoretical results (Table 2), the theoretical bond lengths, bond angles and dihedral angles differs slightly from the XRD values. Since 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 key twist ( $\alpha$ ) is used to indicate the twist of imidazole ring from the aldehydic phenyl ring at C(2) (Fig. 6). The observed emission wavelength reveals that existence of  $\alpha$  twist drops the fluorescence quantum yield. Such a clear correlation indicates the importance of non-coplanarity between the imidazole and the phenyl ring at C(2). 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. As the result, the bond is no longer a pure single bond, as evident from the X-ray data of **3**. When the two rings are deviated from each other, the *p*-orbital overlapping will be reduced. The partial conjugation will lead to less



Fig. 5. ORTEP diagram of 1,2-Diphenyl-1H-imidazo[4,5-f][1,10]phenanthroline (1).



**Fig. 6.** The key  $\alpha$  twist of imidazole ring at C(2).

rigid structure. Therefore, radiationless twist motion will deactivate the emitting state, leading to the low quantum yields. Thus, it is suggested that fluorophores with the substitution at C(2) with a minimum loss of fluorescence property.

The distortion of the geometry in the excited state implies a decrease in the resonance energy so that 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.

#### 3.3. Taft and Catalan solvatochromism

A multi-parameter correlation analysis is employed in which a physicochemical property is linearly correlated with several solvent parameters by means of Eq. (1):

$$(XYZ) = (XYZ)_0 + C_aA + C_bB + C_cC + \cdots$$
(1)

where (XYZ)<sub>0</sub> 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. [22] propose the  $\pi^*$ ,  $\alpha$  and  $\beta$  scales, whereas more recently Catalan et al. [26] suggest the SPP<sup>N</sup>, SA and SB scales to describe the polarity/polarizability, the acidity and basicity of the solvents as shown in the Eqs. (2) and (3).

$$y = y_0 + a_\alpha \alpha + b_\beta \beta + c_{\pi^*} \cdot \pi^* \quad (\text{Kamlet-Taft})$$
(2)

$$y = y_0 + a_{SA}SA + b_{SB}SB + c_{SPP}SPP \quad (Catalan) \tag{3}$$

The correlation (Fig. 7a and b) of the absorption as well as fluorescence wavenumbers obtained by the multi-component linear regression employing the Taft and Catalan solvent parameters with the experimental values given in Table 3. The polarity/polarizability of the solvent coefficient  $[c_{\pi^*} \text{ or } c_{\text{SPP}}^N]$  value correlating the solvatochromic shifts with the solvent polarity. The coefficient controlling the H-donor capacity or acidity of the solvent  $[c_{\alpha}$ or  $c_{\text{SA}}]$ , is the lowest coefficient, therefore, the solvent acidity does not play an important role in absorption and fluorescence displacements. The coefficient representing the electron releasing ability or basicity of the solvent  $[c_{\beta} \text{ or } c_{\text{SB}}]$  has a negative value, suggesting that the absorption and fluorescence bands shift to lower energies with the increasing electron-donating ability of the



**Fig. 7.** (a) Correlation between the experimental absorption wavenumber with the predicted values obtained by a multicomponent linear regression using the  $\pi^*$ ,  $\alpha$  and  $\beta$ -scale (Taft) solvent parameters for (1) and (2). (b) Correlation between the experimental fluorescence wavenumber with the predicted values obtained by a multicomponent linear regression using the  $\pi^*$ ,  $\alpha$  and  $\beta$ -scale (Taft) solvent parameters for (1) and (2).



Fig. 8. Resonance structures (I and II) of the imidazole chromophore.

solvent. This effect can be interpreted in terms of the stabilization of the resonance structures of the chromophore (Fig. 8). Resonance structure "II" 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  $S_1$  state and the stabilization of the  $S_1$  state with the solvent basicity would be more important than that of the  $S_0$  state. Consequently, the energy gap between the  $S_1$  and  $S_0$  states decreases and the absorption and fluorescence wavelengths shift to longer wavelength with increasing solvent basicity.

#### 3.4. Second harmonic generation (SHG) studies

Second harmonic signal of 40 mV and 42 mV were obtained for the imidazole derivatives **1** and **2** 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 [27,28]. 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.

#### Table 4

Electric dipole moment (*D*), polarizability ( $\alpha$ ) and hyperpolarizability ( $\beta_{total}$ ) of **1** and **2**.

Parameter	1	2
Dipole moment (D)		
$\mu_{\mathrm{x}}$	-7.4089	-2.8610
$\mu_y$	-0.4545	1.4449
$\mu_z$	-0.9658	-1.2847
$\mu_{ ext{total}}$	7.4854	3.4530
Polarizability (α)		
$\alpha_{\rm xx}$	-173.4208	-190.6077
$\alpha_{\rm xy}$	17.2806	-13.8204
$\alpha_{yy}$	-162.7023	-156.8421
$\alpha_{\rm xz}$	8.9074	4.9408
$\alpha_{yz}$	8.5832	-10.6596
$\alpha_{zz}$	-175.1103	-186.5096
$\alpha  imes 10^{-24}$ (esu)	-25.2549	-26.3776
Hyperpolarizability		
$\beta_{\rm xxx}$	-145.3533	-115.0533
$\beta_{\rm xxy}$	71.8808	-12.2879
$\beta_{\rm xyy}$	-56.6777	17.0836
$\beta_{ m yyy}$	-42.9243	37.2364
$\beta_{\rm xxz}$	-54.4800	-9.4232
$\beta_{\rm xyz}$	-26.6085	8.0924
$\beta_{yyz}$	11.1701	-5.3027
$\beta_{\rm xzz}$	-39.8778	-7.0947
$\beta_{yzz}$	-8.5337	-11.5510
$\beta_{zzz}$	6.3180	6.5528
$\beta  imes 10^{-31}$ (esu)	21.2155	91.7753
$\mu eta_{ m o}  imes 10^{-31}$ (esu)	158.8065	316.9001

### 3.5. Comparison of $\mu \beta_0$

Theoretical investigation plays an important role in understanding the structure-property relationship, which is able to assist in designing novel NLO chromophores. The electrostatic first hyperpolarizability ( $\beta$ ) and dipole moment ( $\mu$ ) of the imidazole chromophores have been calculated by using Gaussian 03 package [21]. From Table 4, 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  $\lambda_{max}$  is red-shifted when compared with unsubstituted

#### Table 3

Adjusted coefficients ( $(\upsilon_x)_0$ ,  $C_a$ ,  $C_b$  and  $C_c$ ) and correlation coefficients (r) for the multilinear regression analysis of the absorption  $\upsilon_{ab}$  and fluorescence  $\upsilon_{fl}$  wavenumbers and Stokes shift ( $\Delta \upsilon_{ss}$ ) of the imidazole derivative 1 and 2 with the solvent polarity/polarizability, and the acid and base capacity using the Taft ( $\pi^*$ ,  $\alpha$  and  $\beta$ ) and the Catalan (SPP<sup>N</sup>, SA and SB) scales.

Imidazole derivative (1)				
$(\upsilon_x)$	$(v_x)_0 (cm^{-1})$	$(\pi^*)$	Cα	$c_{eta}$
$\begin{array}{l} \lambda_{ab} \\ \lambda_{fl} \\ \Delta \upsilon_{ss} = \upsilon_{ab} - \upsilon_{fl} \\ Imidazole \ derivative (1) \end{array}$	$\begin{array}{c} (3.64\pm0.012)\times10^4\\ (2.59\pm0.025)\times10^4\\ (1.05\pm0.025)\times10^4 \end{array}$	$\begin{array}{c} (0.63 \pm 2.546) \times 10^3 \\ - (3.59 \pm 5.035) \times 10^3 \\ (4.23 \pm 5.089) \times 10^3 \end{array}$	$\begin{array}{l} -(1.24\pm 8.509)\times 10^3\\ (6.24\pm 16.828)\times 10^3\\ -(7.49\pm 17.010)\times 10^3\end{array}$	$\begin{array}{c} (0.76\pm5.300)\times10^3\\ -(4.08\pm13.518)\times10^3\\ (4.84\pm13.663)\times10^3\end{array}$
$(\upsilon_x)$	$(v_x)_0 (cm^{-1})$	$c_{\rm SPP}^{\rm N}$	C <sub>SA</sub>	C <sub>SB</sub>
$\begin{array}{l} \lambda_{ab}\lambda_{fl} \\ \Delta \upsilon_{ss} = \upsilon_{ab} - \upsilon_{fl} \end{array}$	$\begin{array}{c} (3.65\pm0.012)\times10^{4}\\ (2.58\pm0.021)\times10^{4}\\ (1.07\pm0.024)\times10^{4} \end{array}$	$-(2.20\pm5.451) imes10^3 -(12.62\pm9.595) imes10^3 (10.413\pm10.780) imes10^3$	$\begin{array}{c} (9.58\pm22.602)\times10^3\\ (46.34\pm39.787)\times10^3\\ -(36.76\pm44.701)\times10^3\end{array}$	$\begin{array}{l} -(9.70\pm23.211)\times10^3\\ -(46.58\pm40.858)\times10^3\\ (36.88\pm45.905)\times10^3\end{array}$
Imidazole derivative (2)	· · · ·			
$(\upsilon_x)$	$(v_x)_0 (cm^{-1})$	$(\pi^*)$	Cα	$c_{eta}$
$\begin{array}{l} \lambda_{ab} \\ \lambda_{fl} \\ \Delta \upsilon_{ss} = \upsilon_{ab} - \upsilon_{fl} \\ \text{Imidazole derivative} \left( 2 \right) \end{array}$	$\begin{array}{c} (3.62\pm0.051)\times10^{4}\\ (2.59\pm0.068)\times10^{4}\\ (1.14\pm0.107)\times10^{4} \end{array}$	$\begin{array}{c} (17.67\pm10.336)\times10^3\\ -(7.00\pm13.84)\times10^3\\ (18.41\pm21.596)\times10^3\end{array}$	$\begin{array}{l} -(49.58\pm 34.544)\times 10^3 \\ (34.73\pm 46.261)\times 10^3 \\ -(73.14\pm 72.177)\times 10^3 \end{array}$	$\begin{array}{l} (34.69\pm27.748)\times10^3\\ -(32.245\pm37.160)\times10^3\\ (60.627\pm57.977)\times10^3\end{array}$
$(\upsilon_x)$	$(v_x)_0 (cm^{-1})$	C <sup>N</sup> <sub>SPP</sub>	C <sub>SA</sub>	C <sub>SB</sub>
$\lambda_{ab} \\ \lambda_{fl} \\ \Delta \upsilon_{ss} = \upsilon_{ab} - \upsilon_{fl}$	$\begin{array}{c} (3.71\pm0.057)\times10^4\\ (2.67\pm0.065)\times10^4\\ (1.12\pm0.109)\times10^4 \end{array}$	$\begin{array}{l} -(18.20\pm 55.893)\times 10^3\\ -(28.94\pm 29.371)\times 10^3\\ -(12.73\pm 49.131)\times 10^3\end{array}$	$\begin{array}{c} (69.37\pm107.306)\times10^3\\ (101.49\pm121.787)\times10^3\\ (55.367\pm203.720)\times10^3 \end{array}$	$\begin{array}{c} -(67.80\pm110.257)\times10^3\\ -(89.16\pm125.067)\times10^3\\ -(62.884\pm209.206)\times10^3\end{array}$

Table	e 5
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Significant donor-acceptor interactions of dfppip and their second-order perturbation energies (kcal/mol). Donor type ( $\pi$ ); acceptor type ( $\pi^*$ ).

Imidazole derivative (1)					Imidazole d	erivative (2	2)						
Donor (i)	ED/e	Acceptor (j)	ED/e	<i>E</i> (2) a.u.	E(j) - E(i)	F(i, j)	Donor (i)	ED/e	Acceptor (j)	ED/e	<i>E</i> (2) a.u.	E(j) - E(i)	F(i, j)
C1-C2	1.9603	C5-N14	0.0101	45.28	0.49	0.134	C1-C2	1.9789	C5-N14	0.0115	46.62	0.50	0.137
C3-C4	1.9709	C1-C2	0.0142	38.23	0.48	0.125	C3-C4	1.9698	C1-C2	0.0151	39.57	0.49	0.128
C5-N14	1.9878	C3-C4	0.0314	40.14	0.53	0.136	C5-N14	1.9869	C3-C4	0.0326	43.59	0.54	0.142
C10-C11	1.9810	C12-N13	0.0100	46.40	0.49	0.134	С7—С8	1.9705	C10-C11	0.0145	36.53	0.50	0.125
C17-C19	1.9740	C18-C20	0.0119	43.44	0.50	0.132	C10-C11	1.9797	C12-N13	0.0112	47.35	0.50	0.137
C18-C20	1.9768	C21-C22	0.0258	46.16	0.47	0.133	C12-N13	1.9869	С7—С8	0.0323	41.03	0.55	0.139
C21-C22	1.9794	C17-C19	0.0252	53.32	0.47	0.143	N16-C23	1.9820	C6—C9	0.0263	36.05	0.59	0.138
C24-C26	1.9719	C25-C27	0.0143	41.13	0.49	0.127	C17-C19	1.9737	C18-C20	0.0134	44.63	0.51	0.135
C24-C26	1.9719	C28-C29	0.0159	39.71	0.48	0.124	C18-C20	1.9745	C17-C19	0.0252	34.86	0.49	0.118
C25-C27	1.9796	C24-C26	0.0235	41.61	0.47	0.126	C18-C20	1.9745	C21-C22	0.0265	44.83	0.49	0.134
C25-C27	1.9796	C28-C29	0.0159	44.76	0.48	0.131	C21-C22	1.9789	C17—C19	0.0252	51.58	0.49	0.143
C28-C29	1.9803	C24-C26	0.0235	45.59	0.47	0.132	C24-C25	1.9737	C26-C28	0.0143	45.08	0.49	0.134
C28-C29	1.9803	C25-C27	0.0143	39.30	0.48	0.124	C26-C28	1.9742	C24-C25	0.0230	36.71	0.48	0.120
LpN15	1.6572	C6—C9	0.0260	52.70	0.53	0.150	C26-C28	1.9742	C27—C29	0.0238	50.96	0.48	0.140
LpN15	1.6572	N16-C23	0.0129	72.18	0.51	0.171	C27—C29	1.9810	C24-C25	0.0230	46.49	0.50	0.137
LpO30	1.9738	C21-C22	0.0258	36.83	0.64	0.147	LpN15	1.9991	C6—C9	0.0263	51.21	0.55	0.150
C3—C4	1.9709	C1-C2	0.0142	293.38	0.02	0.115	LpN15	1.9991	N16-C23	0.0119	78.52	0.53	0.182
C3—C4	1.9709	С7—С8	0.0306	441.17	0.01	0.107	LpF30	1.9999	C27—C29	0.0238	20.86	0.78	0.124
C5—N14	1.9878	C1-C2	0.0142	384.84	0.01	0.120	LpO31	1.9997	C21-C22	0.0265	38.43	0.64	0.150
C6—N9	1.9706	С7—С8	0.0306	371.65	0.02	0.109	C3—C4	1.9698	C1-C2	0.0151	426.59	0.01	0.118
C7—C8	1.9722	C10-C11	0.0134	290.89	0.02	0.116	C3—C4	1.9698	C6—C9	0.0263	377.20	0.01	0.108
C12—N13	1.9877	C10-C11	0.0134	240.25	0.02	0.119	C3—C4	1.9698	C7—C8	0.0323	311.25	0.02	0.109
N16-C23	1.9829	C6—C9	0.0260	163.28	0.02	0.087	C12—N13	1.9869	C10-C11	0.0145	316.55	0.02	0.123
N16-C23	1.9829	C24-C26	0.0235	77.41	0.03	0.075	N16-C23	1.9820	C6—C9	0.0263	129.38	0.03	0.091
C17—C19	1.9740	C18-C20	0.0119	220.58	0.03	0.121	C17—C19	1.9737	C18-C20	0.0134	624.64	0.01	0.124
C21-C22	1.9794	C18—C20	0.0119	302.90	0.02	0.121	C27—C29	1.9810	C26—C28	0.0143	510.98	0.01	0.126

imidazole. Therefore, it is clear that the hyperpolarizability is a strong function of the absorption maximum. The  $\beta$  values (Table 4) computed here might be correlated with UV–vis spectroscopic data in view of a future optimization of the microscopic NLO properties. The band centered around 320 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 [29–32].

#### 3.6. Octupolar and dipolar components

These imidazole derivatives possess a more appropriate ratio of off-diagonal versus diagonal  $\beta$  tensorial component ( $r = \beta_{xyy}/\beta_{xxx}$ ) [r = 0.39 (1) and -0.15 (2)] 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. Hence, the steric interaction must be reduced in order to obtain larger  $\beta_0$  values.

The  $\beta$ -tensor [33] can be decomposed in 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  $(1 - \sqrt{3})/\sqrt{3}(\sqrt{3} + 1) = -0.16$  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:

$$\left| \substack{2\mathsf{D}\\J=1}\beta \right| = \left(\frac{3}{4}\right) \left[ \left(\beta_{\mathsf{XXX}} + \beta_{\mathsf{XYY}}\right)^2 + \left[ \left(\beta_{\mathsf{YYY}} + \beta_{\mathsf{YXX}}\right)^2 \right]$$
(4)

Table 6

Percentage of s and p-character on each natural atomic hybrid of the Natural Bond Orbital for the imidazole derivatives 1 and 2.

Imidazole derivative (1)					Imidazole deriv	vative ( <b>2</b> )							
Bond (A—B)	E <sub>D</sub> /energy (a.u.)	ED <sub>A</sub> %	ED <sub>B</sub> %	s%	p%	Bond (A—B)	E <sub>D</sub> /energy (a.u.)	ED <sub>A</sub> %	ED <sub>B</sub> %	s%	p%		
С6—С9	0.7146	51.06	48.94	33.44	66.56	C6—C9	0.7125	50.77	49.23	34.92	65.08		
	0.6996	-	-	32.84	67.16		0.7016	-	-	34.68	65.32		
C6-N15	0.6073	36.88	63.12	27.62	72.38	C6-N15	0.6082	36.99	63.01	27.14	72.86		
	0.7945	-	-	32.70	67.30		0.7938	-	-	32.56	67.44		
C9-N16	0.6476	41.94	58.06	29.34	70.66	C9-N16	0.6465	41.80	58.20	28.74	71.26		
	0.7619	-	-	32.74	67.26		0.7629	-	-	33.60	66.40		
N15-C17	0.7945	63.13	36.87	35.70	64.30	N15-C17	0.7948	63.17	36.83	34.56	65.44		
	0.6072	-	-	27.44	72.56		0.6069	-	-	26.75	73.25		
N15-C23	0.8017	64.27	35.73	31.55	68.45	N15-C23	0.7987	63.80	36.20	32.86	67.14		
	0.5977	-	-	28.33	71.67		0.6017	-	-	29.46	70.54		
N16-C23	0.7626	58.15	41.85	34.40	65.50	N16-C23	0.7649	58.51	41.49	37.35	62.65		
	0.6469	-	-	32.63	67.37		0.6442	-	-	32.74	67.26		
C23-C24	0.7062	49.87	50.13	39.01	60.99	C23-C24	0.7064	49.90	50.10	37.77	62.23		
	0.7080	-	-	30.60	69.40		0.7078	-	-	31.01	68.99		
C22-030	0.5732	32.85	67.15	24.93	75.07	C29—F30	0.5169	26.72	73.28	21.62	78.38		
	0.8194	-	-	32.01	67.99		0.8560	-	-	29.37	70.63		
030-C31	0.8310	69.06	30.94	29.25	70.75	C22-031	0.5714	32.65	67.35	24.93	75.07		
	0.5563	-	-	20.37	79.63		0.8207	-	-	34.38	65.62		
						031-C32	0.8331	69.40	30.60	30.11	69.89		
							0.5532	-	-	19.99	80.01		



Fig. 9. Bar diagram representing the charge distribution of imidazole derivatives (1) and (2) using NLO and NBO methods.

$$\left\|_{J=3}^{2D}\beta\right\| = \left(\frac{1}{4}\right) \left[\left(\beta_{xxx} - {}_{3}\beta_{xyy}\right)^{2} + \left[\left(\beta_{yyy} - \beta_{yxx}\right)^{2}\right]$$
(5)

The parameter  $\rho^{2D} [\rho^{2D} = ||_{J=3}^{2D}\beta||/||_{J=1}^{2D}\beta||]$  is convenient to compare the relative magnitudes of the octupolar and dipolar components of  $\beta$ . The observed positive small  $\rho^{2D}$  value for compound **1** (5.938) and compound **2** (1.540) reveals that the  $\beta_{iii}$  component cannot be zero and these are dipolar components. Since most of the practical applications for second order NLO chromophores are based on their dipolar components and this strategy is more appropriate for designing highly efficient NLO chromophores.

#### 3.7. Natural Bond Orbital (NBO) analysis

NBO analysis [34] have been performed for these imidazole derivatives **1** and **2** at the DFT/B3LYP/6-31++G (d,p) level in order to elucidate the intramolecular, charge transfer within the molecule and the results have been tabulated in Tables 5 and 6. Several donor–acceptor interactions have been observed in the imidazole derivatives (**1** and **2**) 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, fluorine and nitrogen atoms. The  $\sigma$  system shows some contribution to the delocalization, and the important contributions to the delocalization corresponds to



Fig. 10. (a) MEP surface diagram of imidazole derivatives (1) and (2). (b) HOMO-LUMO molecular orbitals of imidazole derivatives (1) and (2).

the donor-acceptor interactions for the imidazole derivatives **1** and **2** are LpN15  $\rightarrow$  N16-C23, C3-C4  $\rightarrow$  C1-C2, C3-C4  $\rightarrow$  C7-C8, C5-N14  $\rightarrow$  C1-C2, C6-C9  $\rightarrow$  C7-C8, C7-C8  $\rightarrow$  C10-C11, C12-N13  $\rightarrow$  C10-C11, N16-C23  $\rightarrow$  C6-C9, C17-C19  $\rightarrow$  C18-C20, C21-C22  $\rightarrow$  C18-C20 (for compound **1**) and C3-C4  $\rightarrow$  C1-C2, C3-C4  $\rightarrow$  C6-C9, C3-C4  $\rightarrow$  C7-C8, C12-N13  $\rightarrow$  C10-C11, N16-C23  $\rightarrow$  C6-C9, C17-C19  $\rightarrow$  C18-C20, C27-C29  $\rightarrow$  C26-C28 (for compound **2**).

The charge distribution of the imidazole derivatives **1** and **2** has been calculated from the atomic charges by NBO and NLO analyses (Fig. 9). These methods reveal that among the nitrogen atoms N15 and N16, oxygen and fluorine atom, N15 is considered as more basic site [31]. When compared to nitrogen atoms (N13, N14, N15 and N16), fluorine and oxygen atoms are less electronegative [35]. The charge distribution shows that the more negative charge is concentrated on N15 atom in both derivatives whereas the partial positive charge resides at hydrogen atoms. The percentage of s and p-character [36] in each NBO natural atomic hybrid orbital are displayed in Table 6 for both the imidazole derivatives **1** and **2**. For all the carbon, nitrogen fluorine and oxygen atoms, around 37% s-character and 63% of p-character have been observed.

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

Molecular electrostatic potential (MEP) maps (Fig. 10a) show the distribution of charges across the surface of a molecule. This diagram is used to understand the reactive behavior 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 the imidazole derivatives **1** and **2** shows that the nitrogen, fluorine and oxygen atoms represent the most negative potential region. The hydrogen atoms bear the positive charge and the predominance of green region in the MEP surfaces corresponds to a potential halfway between the two extremes red and dark blue color.

The HOMO orbital acts as an electron donor and the LUMO orbital that acts as the electron acceptor. The 3D plots of the frontier orbitals HOMO and LUMO is shown in Fig. 10b. In compound **1**, the HOMO is located on the aldehydic phenyl ring, imidazole ring and phenanthroline ring, and the LUMO is located on the phenanthroline ring, the imidazole ring and partly on the aldehydic phenyl ring. In case of compound **2**, the HOMO is located on the aldehydic phenyl ring, imidazole ring and partly on the phenanthroline ring and the LUMO is located on the aldehydic phenyl ring, imidazole ring and partly on the phenanthroline ring and the LUMO is located partly on the phenanthroline ring and on the carbon atoms (C2 and C5) of the imidazole ring. The HOMO  $\rightarrow$  LUMO transition implies that intramolecular charge transfer takes place [37] within the molecule. The energy gap (Eg) of these imidazole derivatives has been calculated from the HOMO and LUMO levels. The energy gap explains the probable charge transfer (CD) inside the chromophore.

# 4. Conclusions

The observed emission wavelength reveals that the existence of  $\alpha$  twist drops the fluorescence quantum yield. Such a clear correlation indicates the importance of non-coplanarity between the imidazole and the aryl ring at C(2). The electron releasing ability or basicity of the solvent [ $c_{\beta}$  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. The band centered around 320 nm exhibits a solvatochromic shift, characteristic of a large dipole moment and frequently suggestive of a large hyperpolarizability. The calculated dipolar and octupolar components supported that these imidazole derivatives are efficient NLO chromophores. The observed positive small  $\rho^{2D}$  value for compound **1** (5.938) and compound **2** (1.540) show that the  $\beta_{iii}$  component cannot be zero and these are dipolar components.

#### Acknowledgments

One of the authors Dr. J. Jayabharathi, Associate Professor, Department of Chemistry, Annamalai University is thankful to Department of Science and Technology [No. SR/S1/IC-07/2007] and University Grants commission (F. No. 36-21/2008 (SR)) for providing funds to this research study.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2012.01.066.

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