Optical properties of 1,2-diaryl benzimidazole derivatives – A combined experimental and theoretical studies

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HIGHLIGHTS

- DFT calculation is in good agreement with single crystal XRD data.
- Steric interaction must be reduced in order to obtain larger β_0 values.
- NBO analysis elucidates the delocalization within the molecule.
- Benzimidazoles can be used as potential NLO materials.
- Charge distribution was calculated by NBO and Mulliken methods.

GRAPHICAL ABSTRACT
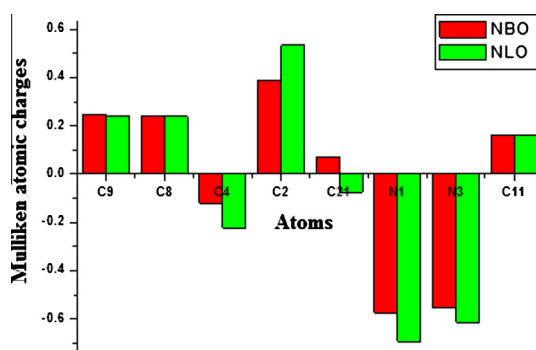
ABSTRACT

Some novel 1,2-diaryl benzimidazole derivatives have been designed, synthesized and characterized by mass, ^{1}H, ^{13}C-NMR spectral studies and single crystal XRD. The charge distribution has been calculated from the atomic charges by non-linear optical (NLO) and natural bond orbital (NBO) analyses have been calculated by abinitio method. Synthesized 1,2-diaryl benzimidazole derivatives have the largest $\mu_g\beta_0$ value and can be used as potential NLO materials. Analysis of the molecular electrostatic potential (MEP) energy surface exploited the region for non-covalent interactions in the molecule. Calculated bond lengths, bond angles and dihedral angles are found to be slightly higher than that of X-ray diffraction values of its experimental datas.

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Introduction

Benzimidazole based chromophores have received increasing attention due to their distinctive linear, non-linear optical properties and also due to their excellent thermal stability in guest–host systems [1]. The imidazole ring can be easily tailored to accommodate functional groups, which allows the covalent incorporation of the NLO chromophores into polyamides leading to NLO side chain polymers [2]. Most π-conjugated systems play a major role in determining second-order NLO response [3]. Searching organic materials with non-linear optical (NLO) properties is usually concentrated on molecules with donor–acceptor π-conjugation (D-π-A) and deals with the substituent effects on the degree of π-conjugation, steric hindrance and the hyperpolarisability of the substances [4]. Nowadays there is an insufficient understanding for designing optimal NLO materials, even certain classes of D-π-A compounds were theoretically studied [5]. Searching for organic materials with nonlinear optical (NLO) properties is usually concentrated on molecules with donor–acceptor π-conjugation (D-π-A) and deals with the systematic investigation of substituent effects on the degree of π-conjugation, steric hindrance and the hyperpolarisability of the substances. Besides, geometrical arrangement of the molecules in the solid state, their interaction

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and other physicochemical properties (e.g. strong intramolecular charge-transfer absorptions) and engineering possibilities are also important [4]. At present, there is an insufficient understanding of all influences for designing optimal NLO materials, even if the influencing factors in certain classes of D-π-A compounds were theoretically studied [5]. To quantify the push–pull effect in D-π-A compounds, bond length alternation (BLA) and out-of-plane distortions of the polarized C=C double bonds, available from X-ray studies, have been employed for a long time [6]. Alternatively, dipole moment measurements [7], bond lengths [8], barriers to rotation about the partial C=C double bonds [9] (from dynamic NMR studies), and the occupation quotients (π/π^*) [10] of the bonding (to quantify the acceptor activity) and anti-bonding orbital (to quantify the donor activities) of these C=C double bonds were adopted. Not only the push–pull effect in D-π-A compounds could be quantified, but also a linear dependence of the push–pull quotient (π^*/π) on molar hyperpolarisability of these compounds were detected. Thus, π^*/π proves to be an easily accessible, general and sensitive parameter of the donor–acceptor quality of compounds for potential NLO applications. Furthermore, we have reported the Quantum chemical analysis ((DFT/B3LYP) method with 6-311G++(d,p) as basis set) of benzimidazole derivatives **1–6** (heat of formation, geometrical structure, vibration wave numbers, NLO and NBO analysis) and the optimized geometrical parameters obtained by DFT calculation is in good agreement with single crystal XRD data. The Mulliken and NBO charge analysis were also calculated and discussed about the more basic nature of the nitrogen atom of the imidazole derivatives. The electric dipole moment (μ) and the first-hyperpolarisability (β) value of the investigated molecules have been studied by both experimentally and theoretically which reveal that they have non-linear optical (NLO) behavior with non-zero values. These chromophores possess a more appropriate ratio of off – diagonal versus diagonal β tensorial component ($r = \beta$ xyy/β xxx) which reflects the inplane nonlinearity anisotropy since they have largest $\mu\beta_0$ values, the reported benzimidazoles can be used as potential NLO materials.

Experimental

Spectral measurements

The proton spectra at 400 MHz were obtained at room temperature using a Bruker 400 MHz NMR spectrometer. Proton decoupled ^{13}C NMR spectra were also recorded at room temperature employing a Bruker 400 MHz NMR spectrometer operating at 100 MHz. The mass spectra of the samples were obtained using a Thermo Fischer LC-Mass spectrometer in fast atom bombardment (FAB) mode. Single crystal XRD has been recorded in Agilent Xcalibur Ruby Gemini diffractometer (For 7, 8 and 12). Data collection: APEX2 (Bruker, 2008); cell refinement: APEX2 and SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009), Bruker Kappa APEXII diffractometer (for 9–11).

Non-linear optical measurements

The non-linear optical conversion efficiencies were parted using a modified set up of Kurtz and Perry. A Q-switched Nd: YAG laser beam of wavelength of 1064 nm was used with an input power of 4.1 mJ/pulse width of 10 ns, scattering geometry 90°, the repetition rate being 10 Hz, monochromater Jobin Youon Triax 550, slit width 0.5 mm, focal length of focusing lens 20 cm, PMT model number XP2262B used in Philips photonics, power supply for PMT is 1.81 KU/mA with oscilloscope Jektronix TDS 3052B.

Computational details

Quantum mechanical calculations were used to carry out the optimized geometry, NLO, NBO and HOMO–LUMO analysis with Gaussian-03 program using the Becke3-Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-31G(d,p) basis set [11]. As the first step of our DFT calculation for NLO, NBO and HOMO–LUMO analysis, the geometry taken from the starting structures were optimized and then, the electric dipole moment μ and β tensor components of the studied compounds were calculated, which has been found to be more than adequate for obtaining reliable trends in the first hyperpolarizability values.

We have reported the β_{tot} (total first hyperpolarizability) for the investigated molecules and the components of the first hyperpolarizability can be calculated using equation:

$$\beta_i = \beta_{iii} + 1/3\sum_{i\neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji}) \tag{1}$$

Using the x, y and z components, the magnitude of the first hyperpolarizability tensor can be calculated by

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

The complete equation for calculating the magnitude of first hyperpolarizability from Gaussian-03 output is given as follows:

$$\beta_{tot} = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{1/2} \tag{3}$$

All the electric dipole moment and the first hyperpolarizabilities are calculated by taking the Cartesian coordinate system (x, y, z) = (0, 0, 0) at own center of mass of the compounds.

Natural bond orbital (NBO) analysis

NBO analysis have been performed on the molecule at the DFT/B3LYP/6-31G(d,p) level in order to elucidate the intramolecular, rehybridization and delocalization of electron density within the molecule. The second order Fock matrix was carried out to evaluate the donor–acceptor interactions in the NBO analysis [12]. The interactions result is a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy $E(2)$ associated with the delocalization $i \rightarrow j$ is estimated as

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

where q_i is the donor orbital occupancy, εi and εj are diagonal elements and $F(i, j)$ is the off diagonal NBO Fock matrix element [13]. The larger the $E(2)$ value, the more intensive is the interaction between electron donors and electron acceptors, i.e., the more donating tendency from electron donors to electron acceptors and the greater the extent of charge transfer or conjugation of the whole system.

Results and discussion

Single crystal XRD analysis

Crystal structure of 1,2-diphenyl-1H-benzo[d]imidazole (**1**)

1,2-Diphenyl-1H-benzo[d]imidazole is monoclinic crystal and crystallizes in the space group $C2/c$. The cell dimensions are $a = 10.1878$ (3) Å, $b = 16.6399$ (4) Å, $c = 17.4959$ (5) Å. ORTEP diagram of **1** presented in Fig. S1a, shows that the benzimidazole unit is close to being planar (maximum deviation = 0.0102 (6) Å) and forms dihedral angles of 55.80 (2) and 40.67 (3)° with the adjacent phenyl rings; the dihedral angle between the phenyl rings is 62.37