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SYNTHESIS AND COMPUTATIONAL STUDIES OF 1-(4-CHLOROBENZYL)-2-(4-CHLOROPHENYL)-1H-BENZIMIDAZOLE

K. Saravanan*, C. Ravichandran* & K. Jayamoorthy**

* Department of Chemistry, Eswari Engineering College, Chennai, Tamilnadu
** Department of Chemistry, St.Joseph's College of Engineering, Chennai, Tamilnadu

Abstract:

1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole has been synthesised and characterized by mass, ^{1}H, ^{13}C-NMR and elemental analysis. 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. The observed dipole moment and hyperpolarisability can be explained by the reduced planarity caused by the steric interaction in nitrogen atom attached to benzyl ring. Since the synthesized 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole has the largest $\mu_g\beta_0$ value and can be used as potential NLO materials.

Key Words: Abinitio Method DFT, NLO & NBO

Introduction:

Imidazoles display a broad spectrum of biological activities such as antiviral, antiulcer, antihypertension and anticancer properties [1]. They have also found application as a chromophore with high extinction coefficient, readily tunable absorption wavelength, and fluorophoric properties and are desirable as a large planar synthetic building block in supramolecular chemistry [2]. They are important building blocks for the synthesis of proton, anion and cation sensors. 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. 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. 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]. Not only the push–pull effect in D-π–A compounds quantified, but also a linear dependence of the push–pull quotient (π*/π) on molar hyperpolarisability were detected [6]. Thus, π*/π is a sensitive parameter of the donor–acceptor quality of compounds for potential NLO applications.

Our approach is to design newly π-conjugated benzimidazole derivative to use as materials in material chemistry [7, 8]. Hence there is considerable interest in the synthesis of new materials with optical non-linearity by virtue of their potential use in device applications related to telecommunications, optical computing, optical storage, and optical information processing [9]. Herein we report the synthesis and theoretical study of 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole.

Experimental:

Spectral Measurements: NMR spectra were recorded on Bruker 400 MHz NMR spectrometer. Mass spectrum was recorded using Agilant 1100 Mass spectrometer.

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 10ns, scattering geometry 90˚, the repetition rate being 10 Hz, monochromater Jobin Youon Triax 550, slit width 0.5 mm, focal length of focusing lens 20cm, 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 [10]. 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:

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

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

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

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

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

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 [11]. 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 → j is estimated as

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

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 [12]. 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.

General procedure for the synthesis of 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole: A mixture of corresponding 4-chloroaldehyde (2mmol), *o*-phenylenediamine (1mmol) and ammonium acetate (2.5 mmol) has been refluxed at 80

ºC in ethanol for 24 hours. The reaction was monitored by TLC and purified by column chromatography using petroleum ether: ethyl acetate (9:1) as the eluent.

Results and Discussion:

Second harmonic generation (SHG) studies 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole:

Second harmonic signals of 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole was obtained as 41 mV by an input energy of 4.1mJ/pulse. But the standard KDP crystal gave a SHG signal of 110mV/pulse for the same input energy. The second order non-linear efficiency will vary with the particle size of the powder sample [13]. Higher efficiencies are achieved by optimizing the phase matching [14]. 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.

Comparison of $\mu\beta_o$:

The overall polarity of 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole was small when their dipole moment aligned in a parallel fashion. 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 [15].

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 ($\beta_{tot}x10^{-31}$=39.2501) and dipole moment (μ_{tot}=0.9834) of the imidazole chromophore have been calculated by using Gaussian 03 package [16]. From this analysis, it is found that 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole shows larger $\mu_g\beta_o$ values, which is attributed to the positive contribution of their conjugation.

Octupolar and dipolar components of 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole:

1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole posses 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 $\mu\beta_o$ values. The difference of the β_{xyy}/β_{xxx} ratios can be well understood by analyzing their relative molecular orbital properties. The r value of 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole is -0.2975. 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 azomethine nitrogen atom. Hence, the steric interaction must be reduced in order to obtain larger β_0 values.

The β tensor [17] can be decomposed in a sum of dipolar ($\beta_{J=1}^{2D}$) and octupolar ($\beta_{J=3}^{2D}$) tensorial components, and the ratio of these two components strongly depends on their 'r' ratios. Complying with the Pythagorean theory and the projection closure condition, the octupolar and dipolar components of the β tensor can be described as:

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

$$\left\| \beta_{J=3}^{2D} \right\| = (1/4)[(\beta_{xxx} - 3\beta_{xyy})^2 + [(\beta_{yyy} - \beta_{yxx})^2 \ ] \quad (6)$$

The parameter ρ^{2D} [$\rho^{2D} = \frac{\|J^{2D}_{=3}\beta\|}{\|J^{2D}_{=1}\beta\|}$] is convenient to compare the relative magnitudes of the octupolar and dipolar components of β. The observed positive small ρ^{2D} value 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 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole 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 [18]. Several donor-acceptor interactions are observed for 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole 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 C3–C4 → C1–C2, C3–C4 → C7–N15, C7–N15 → C1–C2, C8–C10 → C9 – C11, C9 –C11 → C12 –C13, C12–C13 → C9–C11, C19–C28 → C20–C22, C20–C22 → C19–C21, LP N14 → C2 –C3 and LP N14 → C7 –N15. The charge distribution of 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole was calculated from the atomic charges by NLO and NBO analysis. These two methods predict the same trend i.e., among the nitrogen atoms N14 and N15, N14 is considered as more basic site [19]. 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 (N14 and N15), chlorine atom are less electronegative in 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole and among the nitrogen atoms N14 is considered as more basic site [20].

Molecular Electrostatic Potential Map (MEP) and Electronic Properties:

MEP surface diagram (Fig.1) is used to understand the reactive behaviour of a molecule, in that negative regions can be regarded as nucleophilic centres, whereas the positive regions are potential electrophilic sites. The MEP map of 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole clearly suggests that the nitrogen and chlorine atom 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.

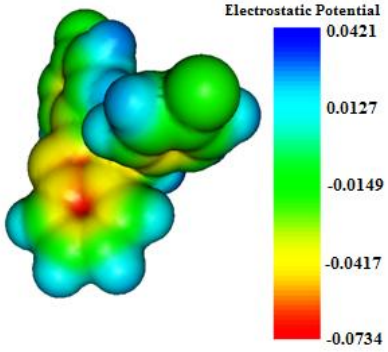

Figure 1: MEP surface diagram of 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole

Conclusions:

In this paper we have reported heterocyclic compound based chromophores as potential NLO materials. The observed dipole moment and hyperpolarisability can be explained by the reduced planarity caused by the steric interaction in nitrogen atom attached to benzyl ring. Hence, the steric interaction must be reduced in order to obtain larger β_0 values. From the DFT calculations, it was concluded that molecules of higher hyperpolarizability have larger dipole moments used as potential NLO molecules. The MEP map of 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzimidazole clearly suggests that the nitrogen and chlorine atoms represent the most negative potential region. The hydrogen atoms bear the maximum brunt of positive charge. From AIM analysis the presence of bond critical points (BCPs) of the intramolecular bonds and their energies was evaluated.

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