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Tuning the push–pull configuration for efficient second-order nonlinear optical properties in some chalcone derivatives

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ABSTRACT

Using the density functional theory methods, we effectively tune the second-order nonlinear optical (NLO) properties in some chalcone derivatives. Various unique push–pull configurations are used to efficiently enhance the intramolecular charge transfer process over the designed derivatives, which result in significantly larger amplitudes of the first hyperpolarizability as compared to their parent molecule. The ground state molecular geometries have been optimized using B3LYP/6-311G** level of theory. A variety of methods including B3LYP, CAM-B3LYP, PBE0, M06, BHandHLYP and MP2 are tested with 6-311G** basis set to calculate the first hyperpolarizability of parent system **1**. The results of M06 are found closer to highly correlated MP2 method, which has been selected to calculate static and frequency dependent first hyperpolarizability amplitudes of all selected systems. At M06/6-311G** level of theory, the permanent electronic dipole moment (μ_{tot}), polarizability (α_0) and static first hyperpolarizability (β_{tot}) amplitudes for parent system **1** are found to be 5.139 Debye, 274 a. u. and 24.22×10^{-30} esu, respectively. These amplitudes have been significantly enhanced in designed derivatives **2** and **3**. More importantly, the (β_{tot}) amplitudes of systems **2** and **3** mount to 75.78×10^{-30} and 128.51×10^{-30} esu, respectively, which are about 3 times and 5 times larger than that of their parent system **1**. Additionally, we have extended the structure-NLO property relationship to several newly synthesized chalcone derivatives. Interestingly, the amplitudes of dynamic frequency dependent hyperpolarizability $\mu\beta_\omega$ (SHG) are also significantly larger having values of 366.72×10^{-48}, 856.32×10^{-48} and 1913.46×10^{-48} esu for systems **1**–**3**, respectively, at 1400 nm of incident laser wavelength. The dispersion behavior over a wide range of change in wavelength has also been studied adopting a range of wavelength from 1907 to 544 nm. Thus, the present work realizes the potential of designed derivatives as efficient NLO-phores for modern NLO applications.

1. Introduction

The nonlinear optical (NLO) material is among the most interesting and starling materials of present era. NLO material has the ability to change the wavelength of incident laser light resulting into second harmonic generation (SHG) and third harmonic generation (THG) effects. Soon after the discovery of first functional laser, the NLO material has been in limelight of scientific interest and a huge pile of materials have been reported till now. Nevertheless, NLO material-designing field has got a recent momentum since the replacement of electron by photon as carrier of information. The applications of NLO materials are ranging from efficient data storage to holographic imaging, frequency doubling and mixing, and telecommunication etc. [1,2]. Over the past few years, our group has proposed several designs to efficiently design the NLO materials with significantly larger first hyperpolarizabilities. These include different types of materials including organic [3–6], inorganic [7,8], organic-inorganic hybrid [9,10] materials, which are explored as efficient NLO materials. Every class of material inherits its own advantages and disadvantages. For example, inorganic materials are relatively stable but usually accompanied with poor amplitudes of first hyperpolarizability. On the other hand, organic materials are not only possess larger amplitudes of hyperpolarizability but also provide a divers variety of structures as well as ease of fabrication and

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low economic costs. Recently, a number of push–pull π-conjugated organic chromophores are investigated by studying their experimental and theoretical first hyperpolarizabilities to check their possible applications as efficient NLO materials [11–16]. Furthermore, including bithienylpyrrole NLO-phores where enhancement of the SHG is achieved through the introduction of a second thiophene [17], two series of novel push–pull chromophores with pyrrole as an electron donor group [18], push–pull bithiophene azo-chromophores bearing thiazole and benzothiazole acceptor moieties[19] are important to mentioned here. Similarly, semiempirical analysis of azo chromophores, [20] thermally stable thiazole and benzothiazole push–pull chromophores [21], Push–pull chromophores incorporated in 1,3-dithiol-2-ylidene moiety as new electro-optics materials[22] were proposed. Along the above reported literature of organic classes, chalcones have been frequently trialed for their potential use in NLO applications [23]. For instance, Prasad et al., have reported the synthesis and characterization of 1,5-di-*p*-tolylpenta-1,4-dien-3-one (DTDO) along with their computationally calculated static first hyperpolarizabity [24]. Menezes et al., have grown pyridine based chalcone single crystals and checked the role of pyridine ring to modulate NLO properties of these molecules [25]. Sajan et al., have grown the single crystal of 3,4-dimethoxy chalcone and studied their electro-optical properties by computational techniques [26]. Among other recent noticeable chalcone syntheses and characterizations are 3-(3-fluorophenyl)-1-[4-(methylsulfanyl) phenyl] prop-2-en-1-one [27], (2*E*)-3-(2-methylphenyl)-1-(4-nitrophenyl) prop-2-en-1-one [28], 1-(3-Nitrophenyl)-5-phenylpenta-2,4-dien-1-one [29], 2-cyano-*N*-(1-phenylethyl) acetamide [30] and 1-(4-Bromophenyl)-3-(napthalen-2- yl)prop-2-en-1-one (C19H13BrO) etc. Based on techniques used in those studies, the above reported chalcone derivatives have been characterized as good NLO molecules. Nevertheless, a common feature of all the above reported chalcone derivatives is the lack of a prominent push–pull configuration which is a rudimentary principle to design efficient NLO-phores. The motivation of present study is to use modern quantum chemical methods to limelight chalcone based push–pull configurations that can lead to proficient NLO properties. For this purpose, we have selected a realistic approach by selecting one know parent chalcone molecule with average NLO properties [31]. Subsequently derivatives have been made from the parent molecule to tune the NLO properties through push–pull configurations.

2. Computational details

All the optimized and stable geometries for chalcone derivatives have been obtained using B3LYP with 6-311G** basis set, which is considered a gateway approach in contemporary computational chemistry. The stability of all optimized geometries has been further confirmed by calculating their analytical frequencies. There are several studies where B3LYP has successfully reproduced the experimental structures [9,32]. It is not necessarily true that any method good for studying geometric structure should also be good for calculation of hyperpolarizability. To select a best DFT functional for first hyperpolarizability calculations, we have calculated the polarizability and first hyperpolarizability for system **1** with six different methods including B3LYP [33], CAM-B3LYP [34], PBE0 [35], BHandHLYP [36], M06 [37] and MP2 [38] method at 6-311G** basis set. A comparison of calculated static first hyperpolarizabilities has been made in Table S1. It can be seen that the M06 results are in good agreement with highly correlated and a standard reference MP2 method (see Table S1 of Supporting information) [39]. The M06/6-311G** level of theory is selected for calculation of dipole moment, polarizability and first hyperpolarizability of all systems. The static first hyperpolarizability (β_{tot}) and its components for all systems were calculated using finite field (FF) approach at M06/6-311G** level of theory. The FF method, which is originally developed by Kurtz et al. [40] has been widely used to calculate the first hyperpolarizability of several molecules and it has provided very consistent results with experimental relationship [5,41–43]. and other theoretical approaches like Time-dependent-sum over states (TD-SOS) methods and response theory [44]. In FF approach, usually a static electric field (F) is applied and the energy (E) of the molecule is stated in terms of following Eq. (1)

$$E = E^{(0)} - \mu_1 F_1 - \frac{1}{2}\alpha_{ij}F_iF_j - \frac{1}{6}\beta_{ijk}F_iF_jF_k - \frac{1}{24}\gamma_{ijkl}F_iF_jF_kF_l - \dots \quad (1)$$

Here $E^{(0)}$ represents the total energy of molecule in the absence of an electronic field, μ is the vector component of the dipole moment, α is the linear polarizability, β and γ are the second and third-order polarizabilities, respectively, while x, y and z label the i, j and k components, respectively. It can be seen from Eq. (1) that differentiating E with respect to F obtains the μ, α, β, and γ values.

In our present investigation, we have calculated the electronic dipole moment, molecular polarizability, polarizability anisotropy and molecular first hyperpolarizability. For a molecule, its dipole moment (μ) is defined as follows:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right) \quad (2)$$

The average polarizability (α_0) can be calculated by following equations:

$$\alpha_0 = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \quad (3)$$

For anisotropy of polarizability ($\Delta\alpha$)

$$\Delta\alpha = \frac{1}{\sqrt{2}}\sqrt{\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2\right]} \quad (4)$$

Similarly, the magnitude of the total first static hyperpolarizability (β_{tot}) can also be calculated using following eq.

$$\beta_{tot} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{\frac{1}{2}} \quad (5)$$

where

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \quad (6)$$

$$\beta_x = \beta_{yyy} + \beta_{xxy} + \beta_{yzz} \quad (7)$$

$$\beta_x = \beta_{zzz} + \beta_{xxz} + \beta_{yyz} \quad (8)$$

The second-order polarizability (β) that is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. According to Kleinman symmetry ($\beta_{xyy} = \beta_{yxy} = \beta_{yyx}$, $\beta_{yyz} = \beta_{yzy} = \beta_{zyy}$,... likewise other permutations also take same value), the 27 components of the 3D matrix can be reduced to 10 components. These components have been calculated using GAUSSIAN 09 [45].

For dynamic (frequency dependent) electric field induced SHG (EFISHG) first hyperpolarizabilities ($\mu\beta$), the measurement provide information on the projection of the vector part of β on the dipole moment vectors as given by following Eq.

$$\beta_\omega(-2\omega;\omega,\omega) = \beta_\omega = \frac{3}{5}\sum_{\zeta}^{x,y,z} = \frac{\mu_\zeta\beta_\zeta}{||\mu||} \quad (9)$$

where μ is the norm of dipole moment vector and μ_ζ and β_ζ are the components of μ and β vectors. The EFISHG first hyperpolarizability ($\mu\beta$) values can be finally calculated using following relationship:

$$\mu\beta_\omega = \frac{5}{3}\mu.\beta_\omega \quad (10)$$