

Homo-Lumo analysis and hyperpolarizability studies of 1,3-Bis(3,4-dimethoxyphenyl)prop-2-en-1-one using quantum chemical computations

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ABSTRACT

The chalcone derivative 1,3-Bis(3,4-dimethoxyphenyl)prop-2-en-1-one (MDMDC) has been investigated by quantum chemical calculations carried out using density functional theory. The nonlinear optical properties of the molecule is studied in the gas phase. The first and the second order hyperpolarizability of the molecule is computed. The hyperpolarization along z-direction shows a substantial delocalization of charges in these directions. Highest Occupied Molecular Orbital (HOMO) energy and Lowest Unoccupied Molecular (LUMO) energy were calculated and molecular energy gap is found to be 3.6417 eV. High hyperpolarizability of molecule shows that it is good for second harmonic generation (SHG) and it has a potential candidature for organic NLO material.

Keywords: Density functional theory, Non-linear optical material, Hyperpolarizability, Homo-Lumo

1. Introduction

Non-linear optics of organic and inorganic systems has been recognized as a promising field to support new and emerging technologies of optoelectronics and photonics [1]. Organic NLO materials have high nonlinear figure-of-merit for frequency conversion, high laser damage threshold and fast optical response time as compared with inorganic NLO materials [2- 5]. In recent years much effort is being rendered to understand the origin of non-linearity and to relate the NLO responses to electronic structure and molecular geometry for designing and fabricating the NLO materials of large molecular hyperpolarizability. Knowledge of molecular geometry may help researchers to predict the physiochemical properties of the compound material in different environment. Organic NLO molecules possess particular π -conjugated systems linking a donor (D) and an acceptor (A) group show large NLO response and these groups when attached to an aromatic ring system, increase charge transfer through π -electron delocalization. Such molecules are characterized by intermolecular charge transfers that give rise to large ground and excited state dipole moments, and first-order molecular hyperpolarizability. In this present communication, 1,3-Bis(3,4-dimethoxyphenyl)prop-2-en-1-one (DMDMC) molecule is exposed to DFT analyses, first and second order hyperpolarizability studies and HOMO –LUMO analysis.

2. Theoretical Background

The non-linear optical response in organic compounds is, generally, of molecular origin and is due to (hyper) polarization of the p electrons. When the electric field E interacts with the charge distribution of the system, this interaction produces a force ($F = qE$, where q is the charge), that causes displacement of the electron density. This displacement of the centre of electron density away from the nuclear framework results in a separation of positive and negative charge and consequently, in an induced polarization or induced dipole, μ^{ind} . When a molecule is subjected to very high intensity electric fields, the induced

polarization becomes the non-linear function of the field strength. The approximation to formulate the non-linear polarization is to expand the total dipole as a Taylor series,

$$\mu_i = \mu_i^0 + \alpha_{ij}E_j + \frac{1}{2!}\beta_{ijk}E_jE_k + \frac{1}{3!}\gamma_{ijkl}E_jE_kE_l + \dots$$

where μ_i^0 is the permanent ground state dipole moment, α_{ij} is the linear (or first-order) polarizability tensor, β_{ijk} is the second-order polarizability (or first hyperpolarizability), and γ_{ijkl} is the third-order polarizability (or second hyperpolarizability). At the macroscopic level, the response of a material under an electric field E is given by its volume polarization P,

$$P_i = P_i^0 + \chi_{ij}^{(1)} E_j + \frac{1}{2!} \chi_{ijk}^{(2)} E_j E_k + \frac{1}{3!} \chi_{ijkl}^{(3)} E_j E_k E_l + \dots$$

where P_i^0 is the permanent polarization, $\chi_{ij}^{(1)}$ is the linear susceptibility of an ensemble of the molecules, and $\chi_{ijk}^{(2)}$ and $\chi_{ijkl}^{(3)}$ are the second and third susceptibility, respectively. The electric field strength of the plane light wave, to understand the origin of the frequency doubling, can be expressed as,

$$P = (P_0 + \frac{1}{4} \chi^{(2)} E_0^2) + \chi^{(1)} E_0 \cos \omega t + \frac{1}{4} \chi^{(2)} E_0^2 \cos 2\omega t + \dots$$

This equation states that the polarization consists of a second-order dc field contribution to the static polarization (first term), a frequency component ω corresponding to the incident light frequency (second term), and a new frequency- doubled component, 2ω (third term). Therefore, an intense light beam passing through a second-order NLO material produces light at twice the input frequency, as well as a static field.

The second-order susceptibility should be written more precisely as a tensor of rank 3, including the frequency of the incident light $\chi^{(2)} = \chi_{ijk}^{(2)}(-\omega_3; \omega_1, \omega_2)$. The process associated with the Pockels effect, $\omega + 0 \rightarrow \omega$, can be viewed as a particular case of sum frequency generation where one light beam is substituted by a static dc electric field of magnitude E_2 (and $\omega_2 = 0$). The second-order term of the induced polarization simply becomes $\chi^{(2)} E_1 E_2 \cos \omega_1 t$; E_2 is associated with a voltage applied to the non-linear material. Then,

$$P = [\chi^{(1)} + \chi^{(2)} E_2] E_1 \cos \omega_1 t.$$

This expression demonstrates that an electric field can change the effective linear susceptibility by an amount linearly proportional to the second-order susceptibility $\chi^{(2)}$ multiplied by the applied E_2 . The application of a voltage to the material causes the optical beam to see a different refractive index than in the absence of the voltage. This, the linear electro-optic (LEO) or Pockels effect, is used to modulate the phase or the polarization state of light by changing the applied voltage [6].

3. Computational Details

The electronic structure and optimized geometry of the molecule were computed by the DFT method using the Gaussian 09 program [7] package employing basis set and Becke's three parameter (local, nonlocal, Hartree-Fock) hybrid exchange functional with Lee-Yang-Parr correlation functional (B3LYP) [8-10]. The basis set 6-311++g(d,p) augmented by d polarization functions on heavy atoms and p polarization functions on hydrogen atoms were used [11,12]. The geometry was fully optimized at the 6-31G(d,p) level of theory with standard thresholds defined by the 'Opt' keyword. For the computation of polarizability and hyperpolarizability 'Polar' keyword is used in the Gaussian 09 package. Visualization and confirmation of the calculated forms of the vibrations were done using the CHEMCRAFT program [13].

4. Geometry optimization

The initial geometry taken from crystallographic information file (CIF) of DMDMC was minimized without any constraint using B3LYP/6-311++g(d,p) level of theory and the optimized structural parameters were obtained. The ground state optimized structure of CPP is shown in Figure 1. From the theoretical values, it is found that some values slightly deviates from the experimental values. These differences are probably due to intermolecular interactions in the solid state. This structure is remarkably similar to one of the crystallographic asymmetric unit and hence these structural parameters are the basis for the calculation of the other parameters. The self consistent field energy of the stabilized geometry of the molecule, calculated by DFT method is - 1112.4276 au and the calculated dipole moment is 3.5532 Debye.

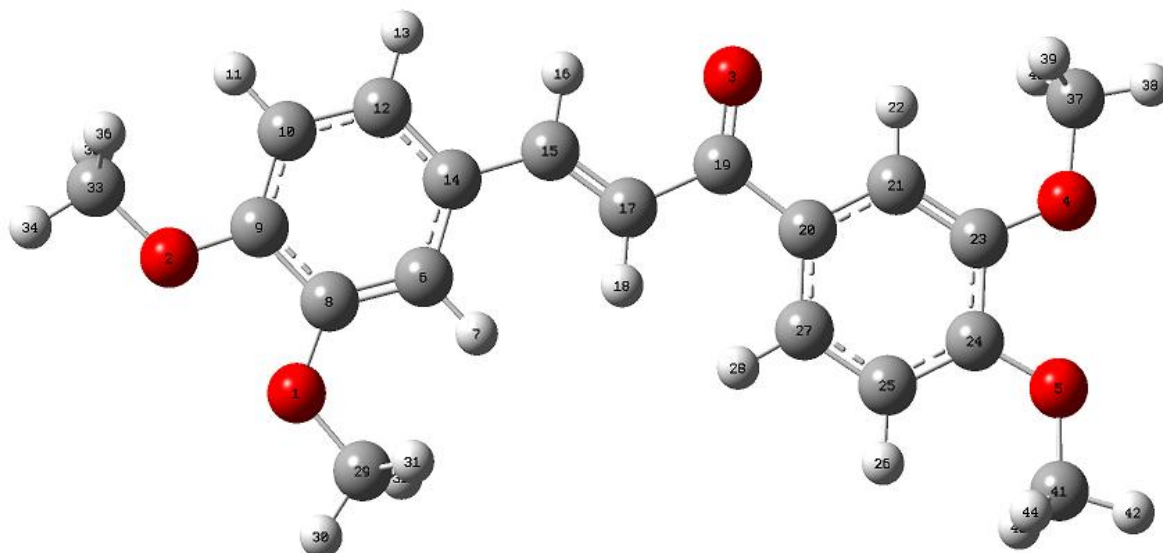


Figure 1

The molecular structure consists of two rings which are planar with dihedral angle C6-C14-C15-C17 = -0.0218 and C27-C28-C19-C17= 0.0094. Due to high electronegativity of the oxygen than carbon, the carbonyl group is polar and has substantial dipole moments. The carbonyl group is also planar with respect to the Ring2 with a dihedral angle O3-C19-C17-C15= -0.0036. The methoxy groups are also planer with respect to the associated rings. Such high degree of planarity in structure increases electron negativity within the π - conjugated molecular system, which results in nonlinear properties of the molecule.

5. Homo-Lumo analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. HOMO and LUMO are used to determine the molecular reactivity and the ability of a molecule to absorb light. The energy gap between the highest occupied and the lowest unoccupied molecular orbital are largely responsible for the chemical, spectroscopic and optical properties of the molecules [14, 15]. The HOMO–LUMO energy gap of CPP was calculated at B3LYP/6-311++g(d,p) level using DFT theory. The ionization energy and electron affinity can be expressed through HOMO and LUMO energies as (1 a.u = 27.211396 eV)

$$I = -E_{HOMO} = 5.7661 \text{ eV and}$$

$$A = -E_{LUMO} = 2.1244 \text{ eV.}$$

$$\text{Energy gap} = E_{HOMO} - E_{LUMO} = 3.6417 \text{ eV}$$

It clearly indicates that charge transfer takes place within the molecule, which increases molecular activity of the molecule. Figure 2 displayed the HOMO & LUMO states and the energy gap. Using the HOMO and LUMO energies, the Global hardness η , Electron chemical potential μ and Global electrophilicity index ω are given by the following relations, as proposed by Parr et al. [16].

$$\eta = (E_{HOMO} - E_{LUMO}) / 2 = 1.8208 \text{ eV and}$$

$$\mu = (E_{HOMO} + E_{LUMO}) / 2 = 3.9452 \text{ eV.}$$

$$\text{Global electrophilicity index } \omega = \frac{\mu^2}{2\eta} = 4.2742 \text{ eV}$$

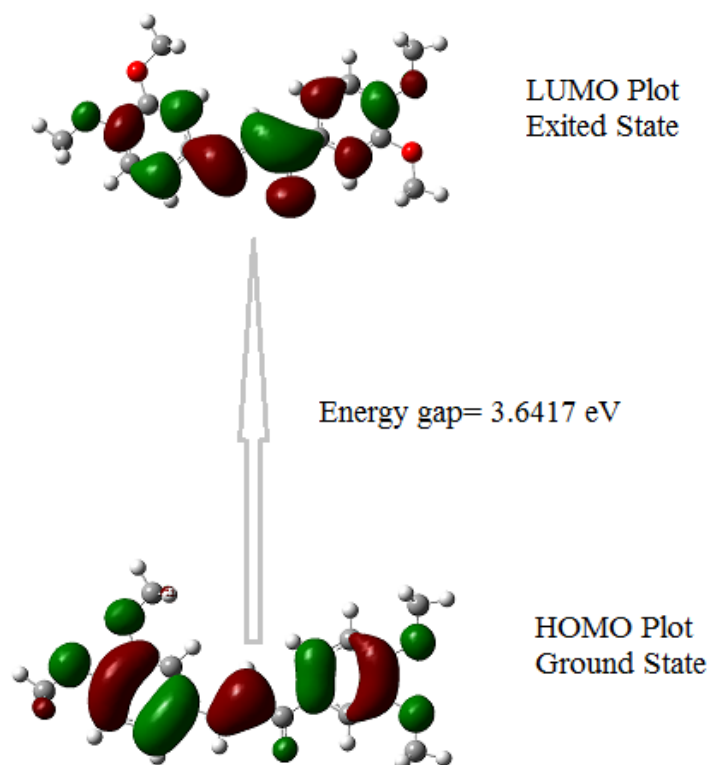


Figure 2

6. Nonlinear properties

The first order and second order hyperpolarizabilities have been calculated at DFT level by finite field approach [17], which is currently one of the methods for obtaining numerically accurate NLO responses. The components of b are defined as the coefficients in the Taylor series expansion of the energy in the external field. The first order hyperpolarizability is a third rank tensor that can be described by $3 \times 3 \times 3$ matrix. The 27 components can be reduced to 10 components due to Kleinman symmetry [18]. The total static dipole moment μ , the mean polarizability α_0 and the mean first hyper polarizability β_0 , using the x, y and z components are defined as

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) / 3$$

The nonlinear properties of the titled molecule were calculated using Gaussian09 software. For this Polar keyword was used. The dipole moment μ and the mean polarizability α_0 is found to be 3.5551 Debye and -19.2107×10^{-24} esu respectively. The first order hyper polarizability β was also calculated using the finite field approach theory. The components of first hyperpolarizability can be calculated using the following equation:

$$\beta_i = \beta_{ijk} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

Using the x, y and z components, the magnitude of the first hyperpolarizability tensor can be calculated using the following equation:

$$\beta_{total} = \sqrt{(\beta_x^2 + \beta_y^2 + \beta_z^2)}$$

where components of β are given by following relations

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

The first order hyperpolarizability of the title compound is calculated and is found to be 2.472×10^{-30} esu. The calculated first order hyperpolarizability of the title compound is 12.6 times that of the standard NLO material urea (0.1947×10^{-30} esu) [19].

The mean static second order hyperpolarizability (γ) for MDMC has been calculated by using the relation [20-23] $\langle \gamma \rangle = \left(\frac{1}{5}\right) [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]$ found to be -3.09×10^{-36} esu. Thus we can conclude that the title molecule is an attractive object for future studies of nonlinear optical properties.

(The conversion factor of α , β and γ in atomic unit are 1 atomic unit (a.u.) = 0.1482×10^{-24} electrostatic unit (esu) for α , 1 a.u. = 8.6393×10^{-33} esu for β and 1 a.u. = 5.0367×10^{-40} esu for γ .)

Table 1: Total static dipole moment (μ), the mean polarizability (α_0), the anisotropy of the polarizability ($\Delta\alpha$), the mean first order hyperpolarizability (β) and the mean Second order hyperpolarizability (γ) for DMDMC.

Property	B3LYP/6-311++G(d,p)	Property	B3LYP/6-311++G(d,p)	Property	B3LYP/6-311++G(d,p)
μ_x	1.7321 Debye	β_{xxx}	-232.6318 a.u.	γ_{xxxx}	-15675.03 a.u.
μ_y	3.1073 Debye	β_{xyy}	-47.9323 a.u.	γ_{yyyy}	-2355.97 a.u.
μ_z	0.1197 Debye	β_{xzz}	-5.6057 a.u.	γ_{zzzz}	-189.57 a.u.
μ	3.5551 Debye	β_{yyy}	67.2120 a.u.	γ_{xxyy}	-2738.38 a.u.
α_{xx}	-116.2000 a.u.	β_{yzz}	4.3789 a.u.	γ_{xxzz}	-3045.73 a.u.
α_{yx}	-14.4626 a.u.	β_{yxx}	73.6679 a.u.	γ_{yyzz}	-462.01 a.u.
α_{yy}	-125.7693 a.u.	β_{zzz}	0.2953 a.u.	Static γ	-3.09×10^{-36} e.s.u.
α_{zx}	0.0114 a.u.	β_{zxx}	2.6910 a.u.		
α_{zy}	0.0012 a.u.	β_{zyy}	0.5459 a.u.		
α_{zz}	-17.2842 a.u.	β	286.199 a.u.		
α_0	-19.2107×10^{-24} esu	β	2.472×10^{-30} esu		
$\Delta\alpha$	4.0338×10^{-24} esu				

7. Conclusion

Density functional theory (DFT) computations using (B3LYP) level with 6-311++g(d,p) basis set gave the optimized structure of DMDMC molecule. Molecular energy gap of MDMC was found as 3.6417 eV by HOMO-LUMO analysis. The low energy gap confirmed the charge transfer within the molecule. Optical absorption spectrum was recorded for the given crystal and it is found that it has minimum absorption in the entire visible region. It's found that first order hyperpolarizability and second order hyperpolarizability of the molecule is 2.472×10^{-30} esu and -3.09×10^{-36} esu respectively. This nonlinear optical analysis reveals the NLO behavior of the material.

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