

THE IMPACT OF TORSIONAL ANGLES TO TUNE THE NONLINEAR OPTICAL RESPONSE OF CHALCONE MOLECULE: QUANTUM COMPUTATIONAL STUDY

IMPACTO DE LOS ÁNGULOS TORSIONALES EN LA RESPUESTA ÓPTICA NO LINEAL DE LA MOLÉCULA DE CALCONA: ESTUDIO CUÁNTICO COMPUTACIONAL

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The study of linear and nonlinear optical properties of molecules is essential for the design and construction of new optical devices that might be useful in electronic communication and photonic treatments. Hence, we have determined related nonlinear properties such as HOMO-LUMO, dipole moments, static polarizabilities, the anisotropy of polarizability, and first hyperpolarizabilities with the dihedral angles. Some dihedral angles can make switching behaviours in the two components of dipole moment and hyperpolarizability. The molecules with multi-torsional angles have nonlinear properties different than those who has a single torsional angle. The behaviours and results were compared with available theoretical data determined from different computational methods.

En el diseño y construcción de nuevos dispositivos ópticos potencialmente útiles en las comunicaciones ópticas son esenciales los estudios de las propiedades ópticas lineales y no lineales de las moléculas. Por ello, determinamos propiedades no lineales como el HOMO-LUMO, momentos dipolares, polarizabilidades estáticas, la anisotropía de la polarizabilidad y las primeras hiperpolarizabilidades en función de los ángulos dihedros. Las moléculas que presentan varios ángulos torsionales manifiestan propiedades no lineales diferentes a las que tienen solo un ángulo torsional. Los resultados y comportamientos obtenidos son comparados con la data teórica disponible a partir de diferentes métodos computacionales.

PACS: Nonlinear optical materials (materiales ópticos no-lineales), 42.70.Mp, = 42.70.Nq; ab initio calculations (cálculos ab initio), 31.15.A-; polarizability of molecules (polarizabilidad de las moléculas), 33.15.Kr

I. INTRODUCTION

As nonlinear optical (NLO) substances have amazing features, they play a real role in future technology demands, such as the using of photons as information carriers [1]. They have a high potential for designing photonic devices such as active wavelength filters, modulators, optical switches and for THz wave generation [2–4]. During the last decades, different theoretical techniques have been used to study and design a wide variety of NLO materials, which can be are organic, inorganic, and also organic-inorganic hybrids [5–9]. They are efficient in the fields of optoelectronics (EO), optical rectification (OR), and optical parametric oscillation (OPO) [10]. Also, they have good prospects for fabrication and integration into devices. Besides, they have low dielectric constants [11–14]. Furthermore, the transition metal (organometallic and coordination) complexes show a nonlinear response [15,16]. Due to the extensive structural diversity of organic materials and their remarkable NLO coefficients, they will be at the frontline in nonlinear applications [17–19]. Therefore, many works have been devoted to find materials with a massive second-order NLO response [20]. Strategies are used to modify the response of NLO organic donor- π -conjugated-acceptor (D- π -A) configuration [21–23] and many similar others, such as twisted- π -conjugated structures [24,25]. Another technique is to use chiral molecules or chiral complexes [26,27]. Based on

their non-centrosymmetric structures, they achieve the NLO response to be recognised. Also, it is well understood that the use of heavy metal atoms inside the chiral ligand shows the progression in the second-order NLO response (β) value due to the robust charge transfer (CT) of the NLO chromophores [20]. Due to the scope of NLO applications of chalcone and its derivatives, it has been researched during recent years [28,29]. It has also excellent transparency through blue-yellow transmittance [30,31]. Likewise, yellow colour crystals of chalcone derivatives (with methoxy phenyl terminal groups) have been grown, and they showed second harmonic generation (SHG) with efficiency 15 times larger than the urea molecule [32]. Moreover, the single crystals of pyridine-based chalcone derivatives showed efficient NLO in the visible and infrared ranges [33]. Many researchers focused on the side group(s) substitution strategy to enhance the nonlinear optical properties [34–37]. Also, on the inverse relationship between the energy gap and first static hyperpolarizabilities [35–37], while very few publications have been focused on determining how large is the influence of the rotation around the central axis of the nonlinear optical molecules [38–41]. Nevertheless, more computational data of nonlinear optical behaviour for different materials are required. In particular, it would seem desirable to evaluate the nonlinear optical responses of nanotubes according to their dimensions [42,43] and fullerenes [44,45]. In addition, the nonlinear optical

behaviour of nanotubes has been used in anti-cancer drugs [46, 47]. However, investigators have shown an increased interest in the nonlinear optical responses of the nitrogen bases of DNA and its mutations [48, 49], because these have not been considered in computational studies. The identification of the structure-property relationship and the NLO response origin of the aromatic molecules is an essential issue for achieving further understanding of their performance improvement. For this purpose, three issues of torsional angles were adopted. In principle, theoretical computations can provide a detailed description of the whole torsional potential, electronic and nonlinear optical properties. For conformational analysis of chalcone, a comprehensive review of literature can be found in a paper by Muhammad [49]. Our aim is, firstly, to perform *ab initio* computations for the most significant chalcone, in order to analyse the interplay of conjugative, steric and electrostatic interactions in determining torsional barriers of this molecule. Up to now, calculations on the torsional behaviour of chalcone has not been made. So, our aim is to cast light on the photophysical characteristics of chalcone molecules and the assessment of their configurations to find their nonlinear optical origin according to their microscopic structure.

II. COMPUTATIONAL DETAILS

The electric dipole moment μ of molecules is a quantity of fundamental interest in a structural molecule. While a molecule is subject to an external electric field ϵ , the molecular charge density may reset and so the dipole moment may change. This change can be described as the first derivative of the energy E to a component of the electric field (ϵ_i) that gives a component of the electric dipole moment: $\mu_i = (\partial E / \partial \epsilon_i)(\epsilon = 0)$. The polarizability can be understood as the gradient of the induced dipole: $\alpha_{ij} = (\partial^2 E / \partial \epsilon_i \partial \epsilon_j)(\epsilon = 0)$. The average static polarizability $\langle \alpha \rangle$ tensor is defined as $\langle \alpha \rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$, where α_{xx} , α_{yy} , and α_{zz} are the diagonal elements of the polarizability tensor matrix [50]. The anisotropic polarizability ($\Delta\alpha$) amplitudes are usually defined as $\Delta\alpha = [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2)]^{1/2}/2$. The equations for the calculation of molecular hyperpolarizability are given as follows: $\beta_{ijk} = (\partial^3 E / \partial \epsilon_i \partial \epsilon_j \partial \epsilon_k)(\epsilon = 0)$. The complete equation for calculating the magnitudes of β from Gaussian 09 output provides ten components of this matrix as β_{xxx} ; β_{xxy} ; β_{xyx} ; β_{yyx} ; β_{yyi} ; β_{xxz} ; β_{xyy} ; β_{xyy} ; β_{xzz} ; β_{yzz} ; β_{zzz} , reported in atomic units (AU) [51]. So that, $\beta_{tot} = [\beta_x^2 + \beta_y^2 + \beta_z^2]^{1/2}$, where $\beta_x = (\beta_{xxx} + \beta_{xxy} + \beta_{xzz})$, $\beta_y = (\beta_{yyx} + \beta_{yzz} + \beta_{yxx})$, $\beta_z = (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})$. The component of the first hyperpolarizability β_{tot} along the direction of the dipole moment is represented by β_μ which is usually defined as $\beta_\mu = (\mu_x \beta_x + \mu_y \beta_y + \mu_z \beta_z) / \mu$. The XY-plane hyperpolarizability (β_{xy} -plane) is given as β_{xy} -plane = $\beta_{xxx} + \beta_{xxy} + \beta_{xyy} + \beta_{yyx}$, which reflects the amount of β_{tot} in XY-plane of the molecule. Full geometry optimization of chalcone, (E)-1-(2,5-dimethylthiophen-3-yl)-3-phenylprop-2-en-1-one with methoxy group para-position, was performed (Fig. 1). Individual torsion potentials were obtained for the molecule as a function of inter-atom C₂ - C₈, C₈ - C₉, C₁₀ - C₁₁ dihedral angles, named as θ_1 , θ_2 , θ_3 respectively. During the scan process, the whole geometrical parameters were simultaneously relaxed, so that they were varied between

0 and 180° in 10° steps (Fig. 1). Accurate calculation of dipole polarizabilities requires the use of extended basis sets. Here, 6-311G (d,p) is a split-valence triple-zeta basis (Pople-type basis), which adds one set of d functions to heavy atoms plus p polarization functions for hydrogen [52–54]. The dipole moment, static polarizability and first static hyperpolarizability calculations are performed using density functional theory through the B3LYP functional using 6-311G (d,p) basis set [55–58]. The B3LYP functional is a combination of Becke's three-parameter hybrid exchange functional (B3) and the Lee-Yang-Parr correlation functional (LYP) [55, 56]. All computations were done using the Gaussian 09 package program [51].

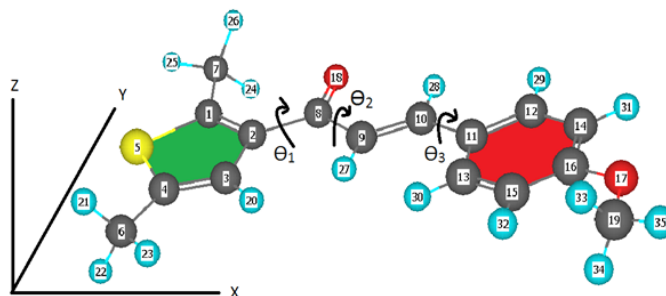


Figure 1. Optimised molecular geometry of the chalcone molecule at the B3LYP/6-311G(d,p) level of theory. θ_1 , θ_2 , θ_3 are the three torsional angles that were adopted.

III. RESULTS AND DISCUSSION

The variation of relative stability ΔE with the dihedral angles for chalcone is shown in Fig. 2. We checked the geometrical effect of these torsional angles, to add robustness to the NLO response of chalcone during its design [32]. The symmetry of the molecule imposes strictly equivalent minima for θ_3 only. At the same time, θ_2 showed the instability of the structure for the higher torsional angles, if they are compared with the results by Yoruk et al. [39]. So, any results for the torsional angle θ_1 and θ_2 beyond 150° will not be considered. In this work, we will focus on NLO properties because the torsional angles calculations of chalcone previously had not been studied. We reported the calculations of dipole moment, average polarizability, the anisotropy of polarizability and first static hyperpolarizability by changing the dihedral angle (θ_1 , θ_2 , θ_3) for chalcone. The variation of dipole moment, static polarizability and anisotropy of polarizability with the dihedral angles for chalcone is graphically shown in Figs. 3, 5, 7. The dipole moment (μ), which is given as $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$, illustrates the amount of intermolecular interactions, as shown in Fig. 3. The intermolecular interactions include the non-bonded type of dipole-dipole interactions. Furthermore, the higher dipole moments give stronger intermolecular interactions. The calculations show that θ_1 increases the total

dipole moment, unlike to the other angles θ_2 and θ_3 .

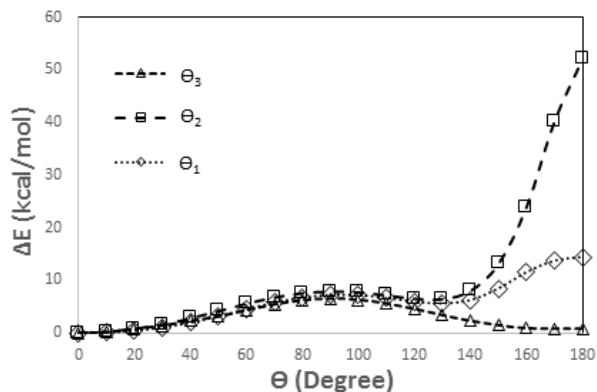


Figure 2. Dependence of ΔE with the angle, for the three dihedral angles (θ_1 , θ_2 , θ_3) corresponding to the chalcone molecule.

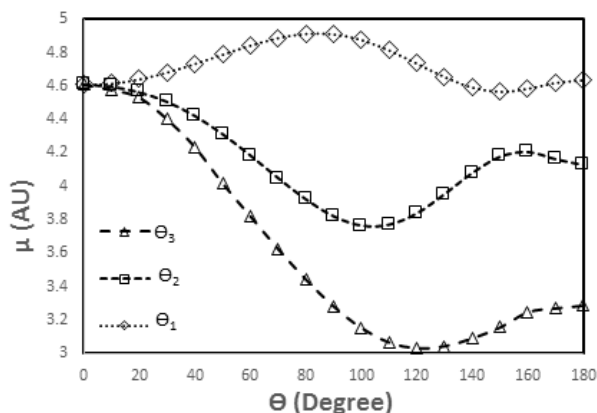


Figure 3. Dependence of the total dipole moments (μ) with the angle, for the three dihedral angles (θ_1 , θ_2 , θ_3), corresponding to the chalcone molecule.

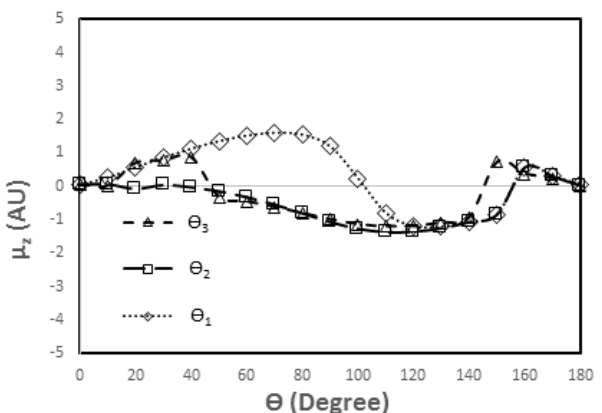
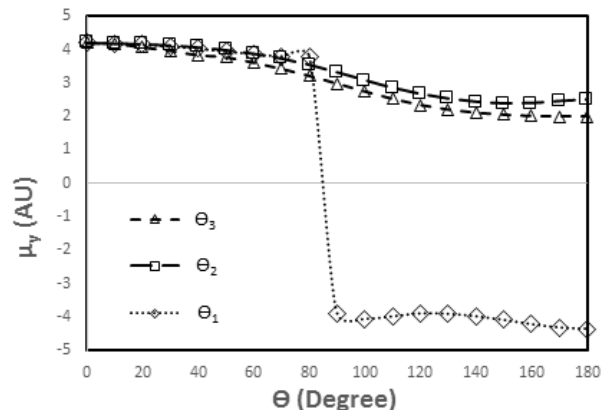
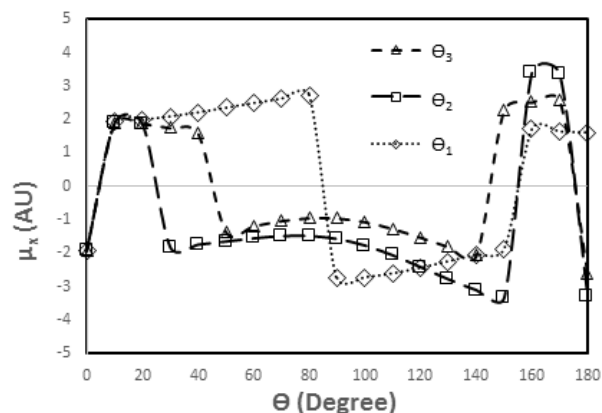


Figure 4. Dependence of the μ_x , μ_y and μ_z components of the dipole moment with the angle, for the three dihedral angles (θ_1 , θ_2 , θ_3), corresponding to the chalcone.

Furthermore, the role of θ_1 is evident in the two dipole components (μ_x and μ_y) during the operation of switching between the angles $80^\circ \sim 90^\circ$, as shown in Fig. 4. Another significant molecular characteristic in the electronic properties is its average polarizability $\langle \alpha \rangle$, where it is enhanced with the increase of the torsional angles θ_2 and θ_1 , as illustrated in Fig. 5. Likewise, this will increase the molecule's refractive index too. The θ_2 and θ_3 were in good agreement with Ayar et al. [41] up to dihedral angles of 90° approximately, while θ_1 was dissimilar. The behaviour of the torsional angles is reported in Fig. 6.

The other NLO properties for this molecule is the anisotropic polarizability $\Delta\alpha$ which depends on the direction of the electric field. It was found to be significantly smaller than the average polarizability $\langle \alpha \rangle$, as indicated in Fig. 7. There, it can be seen that the torsional angles (θ_2 and θ_3) enhanced the polarizability parallel to the symmetry axes of the molecule, as compared to the perpendicular polarizability. Only θ_1 compares well with the results in [39].

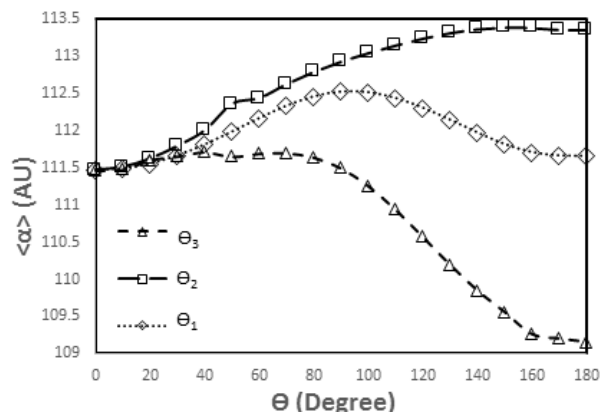


Figure 5. The variation of polarizability $\langle \alpha \rangle$ with the dihedral angles (θ_1 , θ_2 , θ_3) for chalcone molecule.

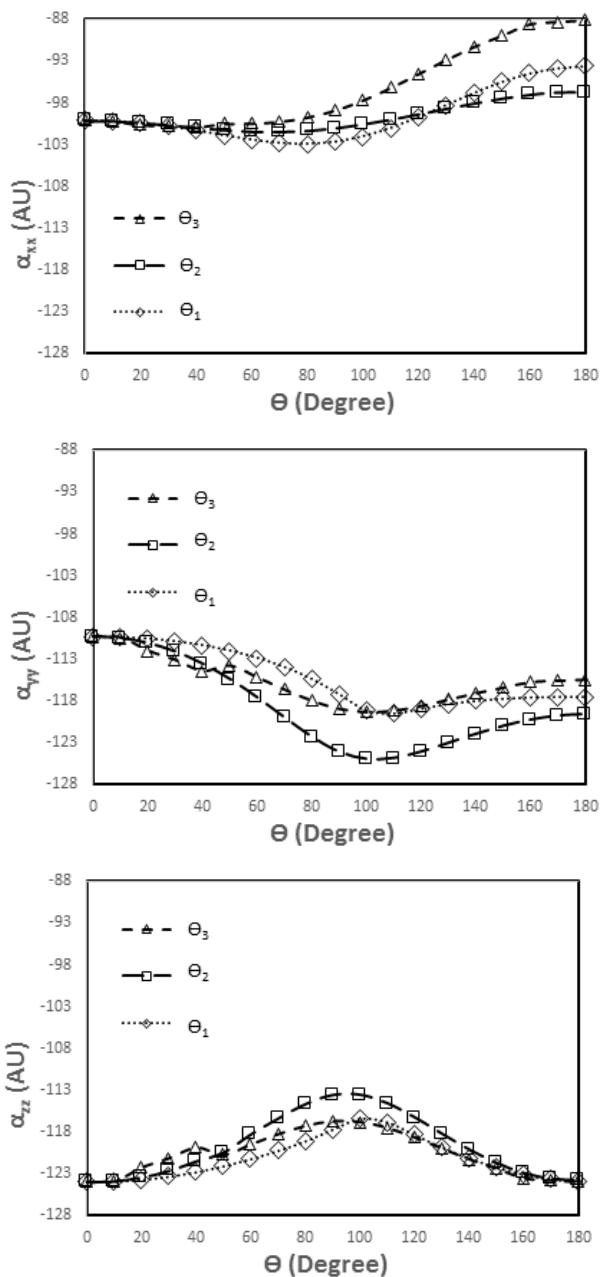


Figure 6. Dependence on the angle, of the static polarizability components (α_{xx} , α_{yy} and α_{zz}) corresponding to the three dihedral angles (θ_1 , θ_2 , θ_3), for the chalcone molecule.

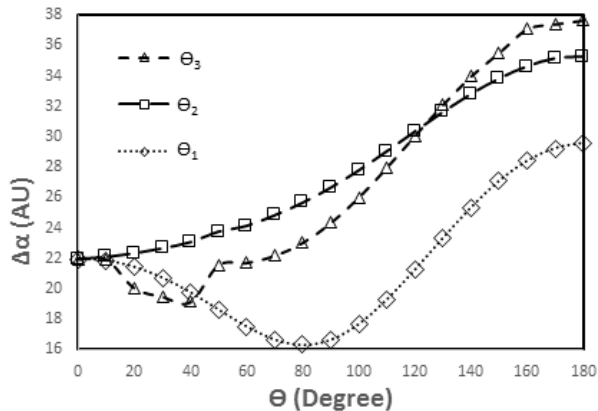


Figure 7. The variation of anisotropy of polarizability $\Delta\alpha$ with the angle, studied for the three dihedral angles (θ_1 , θ_2 , θ_3) for chalcone molecule.

The theoretical resolution of molecular hyperpolarizability (β_{tot}) is considered useful in explaining the relationship between molecular fabrication and non-linear optical properties. There is a maximum in the total hyperpolarizability β_{tot} for chalcone for dihedral angle θ_1 , as evident from the Fig. 8. If we examine variations of β_{μ} , which is the hyperpolarizability along the direction of the dipole moment, with the dihedral angles we can infer there is high synchronisation between them, see Fig. 9.

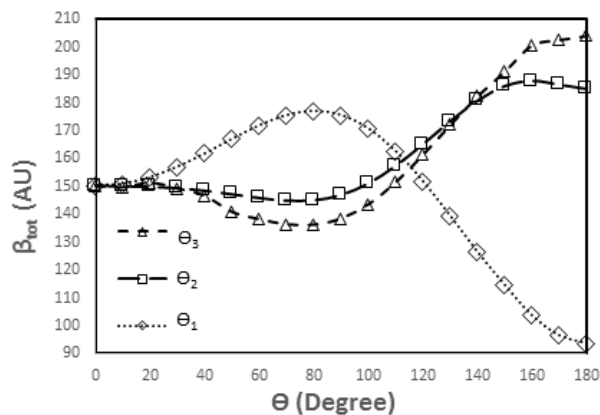


Figure 8. Angular variation of first static hyperpolarizability β_{tot} for the three dihedral angles (θ_1 , θ_2 , θ_3) for the chalcone molecule.

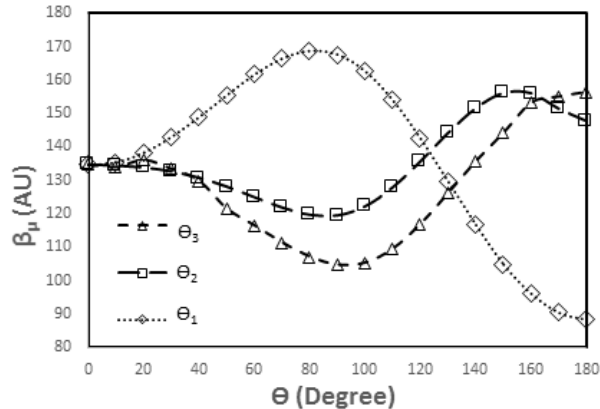


Figure 9. Angular variation of β_{μ} with the dihedral angles (θ_1 , θ_2 , θ_3) for the chalcone molecule.

The variation of the XY-plane hyperpolarizability (β_{xy} -plane), which is given as β_{xy} -plane = $\beta_{xxx} + \beta_{xxy} + \beta_{xyy} + \beta_{yyy}$, illustrates the amount of β_{tot} in the XY-plane of a molecule, as shown in Fig. 10. Only the torsion angle θ_1 peaked as β_{tot} in the XY-plane. So, is expected that θ_1 will improve the charge transfer along the plane of the central molecule axis.

The variation of HOMO–LUMO energy gap with the dihedral angles (θ_1 , θ_2 , θ_3) for chalcone is given in Fig. 11. Hyperpolarizability is associated with molecular electronic distribution under the influence of the electrical field depending on loosely or tightly bound electrons. Therefore, there is an approximate inverse relationship between the hyperpolarizability and HOMO–LUMO energy gaps, as we can see in Figs. 8 and 11, respectively. Generically, the inverse relationship between the energy gaps and the hyperpolarizabilities may be more depending on the substitution effects and position of some side groups [34–37]. The change in energy gap with the dihedral angles was within 50 % of the value which reported by Alyar et al. [41].

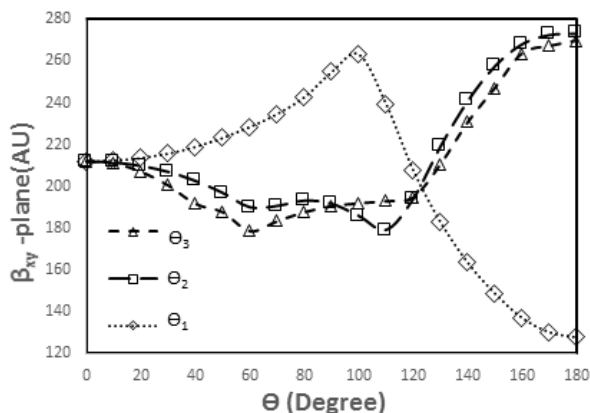


Figure 10. XY-plane of hyperpolarizability (β_{xy} -plane) due to the dihedral angles (θ_1 , θ_2 , θ_3) for the chalcone molecule.

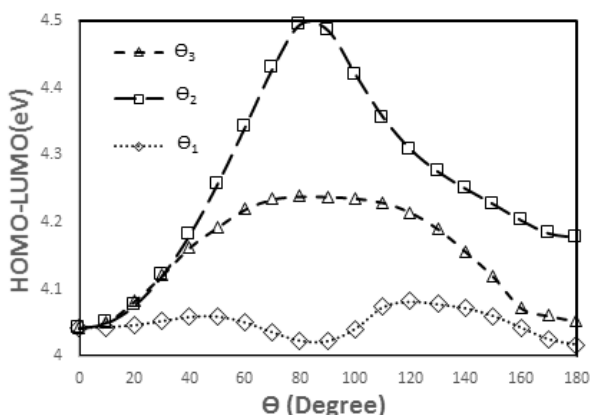


Figure 11. The angular variation of the HOMO-LUMO energy gap for the three dihedral angles (θ_1 , θ_2 , θ_3) for the chalcone molecule.

We examined the variations of hyperpolarizability components (β_x , β_y and β_z) with the dihedral angles for the chalcone molecule, so only β_x and β_y are sensitive to the variation of the dihedral angle θ_1 compared with θ_2 and θ_3 , as illustrated in Fig. 12. Furthermore, β_x and β_y showed the same behaviour of μ_x and μ_y , as shown in Fig. 3.

IV. CONCLUSIONS

We have performed a theoretical study of torsional angles, electronic and nonlinear optical properties such as dipole moment, HOMO-LUMO energy gap, average static polarizability, the anisotropy of polarizability and static hyperpolarizability values for chalcone molecule, which were computed at the B3LYP/6-311G(d,p). Some of our results do not agree completely with previous results, where molecules with one dihedral angle only are studied. Additionally, we have observed that the energy gap, average polarizability and anisotropy of polarizability depend lightly on the dihedral angle. Some dihedral angles displayed switching behaviours in the two components of the dipole moment and hyperpolarizability, which are in the molecular plane. Furthermore, the dipole moment and hyperpolarizability had an equivalent dependence on the dihedral angles. However, the hyperpolarizability is massively dependent on

the dihedral angle. These results are potentially useful for the design of chalcone-in-molecule-based technologies.

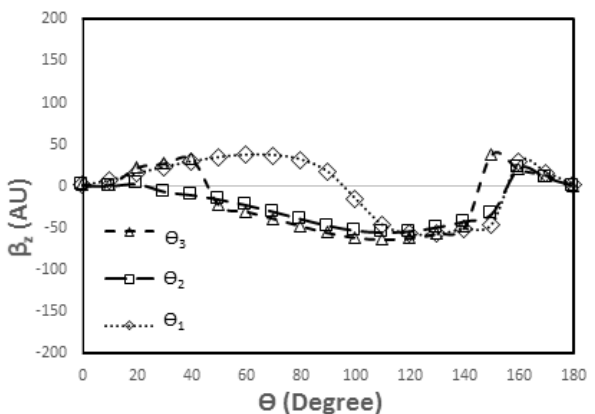
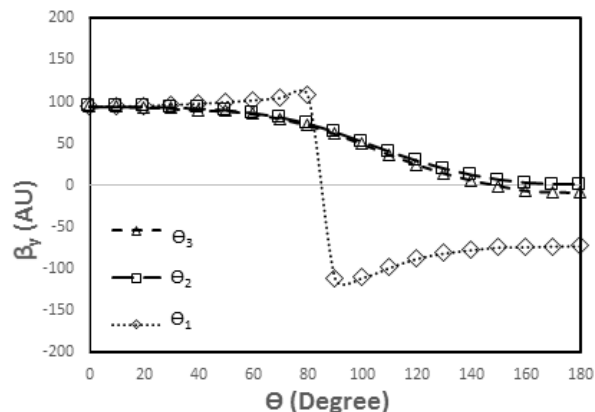
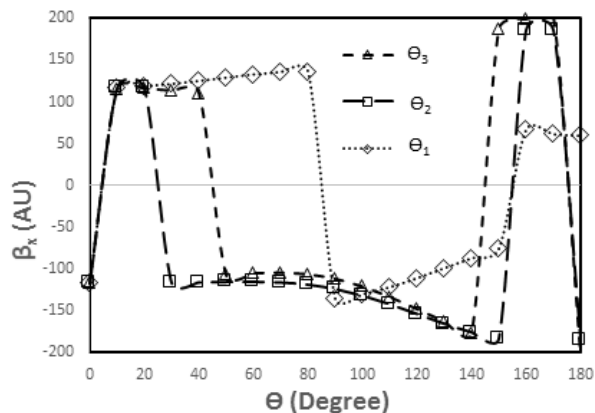


Figure 12. The angular variation of β_x , β_y , and β_z as a function of the dihedral angles (θ_1 , θ_2 , θ_3) for the chalcone molecule.

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