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Theoretical Diagnostics of Second and Third-order Hyperpolarizabilities of Several Acid Derivatives

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Abstract: The density functional theory (DFT) at B3LYP/6-31G(d) level has been utilized to achieve the electric dipole moment (μ), static dipole polarizability (α) and first hyperpolarizability (β) values for ferulic acid (1) and chenodeoxycholic acid (2). The time-dependent Hartree-Fock (TDHF) technique as a powerful quantum chemical method has been implemented to reveal the dynamic α , β and third-order hyperpolarizabilities (γ) of the examined compounds. Our computational conclusions have been compared with the results of similar materials in the literature. The first and second frontier molecular orbitals (MOs) and their band gaps have also been investigated by means of DFT.

Keywords: Electric dipole moment, Second-order nonlinear optic, Third-order nonlinear optic.

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1 Introduction

To determine the magnitudes of first hyperpolarizabilities is quite important for the devices provided the second-

harmonic generation (SHG) and quadratic electro-optic responses. So, the push-pull type π -electron arrangements associated with aromatic chains and unsaturated bonds and also unsymmetrically substituted donors and acceptors have been especially designed to obtain the SHG processes [1]. It has been also shown that the molecules with octupolar symmetries are among the efficient molecular materials [2]. The third-order macroscopic NLO susceptibilities are directly related to their corresponding microscopic cubic responses. The images of biological structures are provided by the third-harmonic generation (THG) technique indicating the variations on the third-order NLO susceptibilities [3].

In this work, one of our aims is to focus on theoretically evaluating the second and third-order NLO behaviour of the title molecules in Figure 1. The μ , dispersion-free α and β values have been produced using DFT calculations. The dynamic dipole polarizabilities, quadratic and cubic hyperpolarizabilities have been also computed by means of ab-initio quantum mechanical approach (TDHF). Besides, the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) have been defined by DFT/B3LYP.

2 Theoretical Calculations

We have firstly performed the optimization studies on the examined structures. After the geometry optimizations, we have calculated the μ , static α and β for 1-2 utilizing the finite field (FF) procedure [4]. The GAUSSIAN03W [5] package program using DFT method at B3LYP/6-31G(d) level has carried out the computations of optimization, μ , static α and β . To build the molecular models of examined compounds shown in Figure 2, GaussView [6] program has been utilized as the interface program for GAUSSIAN03W [5]. The total electric dipole moments in terms of electric dipole moment components (μ_x, μ_y, μ_z), the orientationally averaged (isotropic) dipole polarizabilities $\langle\alpha\rangle$ and the magnitudes of β_{tot} (total

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Figure 1: Bond-line formulas of Ferulic acid (1) and Chenodeoxycholic acid (2).

first static hyperpolarizability) are evaluated as follows, respectively [7,8]:

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

$$\langle \alpha \rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (2)$$

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

The TDHF procedure of the GAMESS [9] package program has obtained the $\gamma(0;0,0,0)$ at $\omega = 0$ and $\alpha(-\omega; \omega)$, $\beta(-2\omega; \omega, \omega)$, $\gamma(-3\omega; \omega, \omega, \omega)$ values at $\omega = 0.04282$ atomic units (a.u.) ($\lambda = 1064$ nm) with 6-31G(d) basis set. The dispersion-free second hyperpolarizabilities are expressed as $\gamma(0;0,0,0)$. The SHG and THG groups, respectively, in TDHF method have generated the $\beta(-2\omega; \omega, \omega)$ and $\gamma(-3\omega; \omega, \omega, \omega)$ calculations at the studied ω frequencies.

Using the following equations, we have computed the $\beta - V$ (β vector) which is the vector part of the second-order hyperpolarizability and the averaged (isotropic) second hyperpolarizability $\langle \gamma \rangle$:

$$\beta - V = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (4)$$

where β_i ($i = x, y, z$) is given by:

$$\beta_i = (1/3) \sum_{j=x,y,z} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad (5)$$

$$\langle \gamma \rangle = (1/5) [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xyxy} + \gamma_{xxzz} + \gamma_{yyzz})] \quad (6)$$

The GAUSSIAN03W [5] package program at DFT/ B3LYP level with 6-31G(d) basis set has also derived the HOMOs,

LUMOs and HOMO-LUMO energy band gaps. The HOMO-LUMO energy gaps (E_g) are achieved by the following expression:

$$E_g = E_{LUMO} - E_{HOMO} \quad (7)$$

3 Computational Results And Discussion

Table 1 lists the electric dipole moments of the title molecules. It has been found that the μ values of 1-2 are almost same for both studied acids (Table 1). The μ value for 1 has been calculated ($\mu = 4.583$ D) by Sebastian et al. utilizing ab-initio quantum mechanical techniques [10]. Our computed data on μ of 1 (Table 1) is almost 1.6 times lower than the estimated value in Ref. [10]. The μ value of 1 was calculated utilizing DFT technique by Kumar et al. as $\mu = 3.22$ D [11]. The reported μ of 3.22 D by Ref. [11] is in good agreement with our calculated value of 2.807 D (Table 1). Calaminici et al. calculated the dipole moment ($\mu = 3$ D) with DFT method of a phosphonic acid stilbene derivative containing the conjugated stilbene backbone, which is *p*-substituted by a methoxy electron donor group and *p'*-substituted by a phosphonic acid electron acceptor moiety [12]. Our computed data on μ for 1-2 (Table 1) are quite close to the evaluated result by Ref. [12]. It has been found that the DFT results on μ values of 1-2 have given rather consistent results with the computed DFT data for similar structures in Refs. [11,12], while the other technique (ab-initio method) used in Ref. [10] yield a numerical diversity.

Tables 2-4, respectively, show a few important computed components for the static dipole polarizabilities, first and second hyperpolarizabilities of 1-2. The dispersion-free $\langle \alpha \rangle$ values in Table 2 have an apparent reduction in sort order $2 > 1$. The static $\langle \alpha \rangle$ value of a

Figure 2: Molecular models of Ferulic acid (1) and Chenodeoxycholic acid (2).
Ethical approval: The conducted research is not related to either human or animal use.

Table 1: The calculated electric dipole moments μ (Debye) and dipole moment components for 1-2 using DFT method at B3LYP/6-31G(d) level.

Compound	μ_x	μ_y	μ_z	μ
1	2.559	1.155	0.000	2.807
2	-1.642	-1.563	1.507	2.722

Table 2: Some selected components of the static $\alpha(0;0)$ and $\langle\alpha\rangle(0;0)$ ($\times 10^{-24}$ esu) values for 1-2 computed by DFT method at B3LYP/6-31G(d) level.

Compound	α_x	α_y	α_z	$\langle\alpha\rangle$
1	33.401	18.661	7.084	19.715
2	47.733	34.709	30.253	37.565

Table 3: Some selected components of the static $\beta(0;00)$ and $\beta_{tot}(0;00)$ ($\times 10^{-30}$ esu) values for 1-2 computed by DFT method at B3LYP/6-31G(d) level.

Compound	β_{xxx}	β_{yyy}	β_{yyz}	β_{xzz}	β_{zzz}	β_{tot}
1	-20.295	-0.423	-0.008	-0.014	-0.004	21.272
2	0.567	-0.045	-0.105	-0.239	0.380	0.709

Table 4: All static $\gamma(0;0,0,0)$ components and $\langle\gamma\rangle(0;0,0,0)$ ($\times 10^{-37}$ esu) values for 1-2 computed by TDHF method with 6-31G(d) basis set.

	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}	$\langle\gamma\rangle$
1	407.420	4.716	-0.233	11.592	1.443	0.761	87.899
2	33.003	2.967	0.323	3.858	0.598	0.106	9.084

phosphonic acid stilbene derivative with a conjugated stilbene backbone was computed by DFT with a triple zeta

valence basis set (TZVP) to be 41.854×10^{-24} esu [12]. The calculated static $\langle\alpha\rangle$ value reported by Calaminici et al. [12] are about 2 and 1.1 times, respectively, higher than that of 1 and 2 in Table 2. The static first hyperpolarizability of a phosphonic acid stilbene derivative containing a conjugated stilbene backbone was reported at DFT/TZVP level to be 44.075×10^{-30} esu by Ref. [12]. Our result on β_{tot} for 1 (Table 3) is almost a factor of 2 lower than the presented data by Calaminici et al. [12]. To change the basis sets (TZVP) in the same method (DFT) for a similar acid reported by Ref. [12] has found out numerically discrepancies with the static $\langle\alpha\rangle$ and β results of 1-2 (DFT method and 6-31G(d) basis set). It is seen from Table 4 that the dispersion-free $\langle\gamma\rangle$ values show a reduction in sort order $1 > 2$.

Tables 5-7, respectively, give a few important calculated components for dynamic dipole polarizabilities, second and third-order hyperpolarizabilities of 1-2. The dynamic $\langle\alpha\rangle$ and $\langle\gamma\rangle$ values display the same reduction in sort order $2 > 1$ (for $\langle\alpha\rangle$ values) and $1 > 2$ (for $\langle\gamma\rangle$ values) as their corresponding static ones (see Tables 2,4,5,7). Song et al. obtained the dynamic β value of 35×10^{-30} esu using Hyper-Rayleigh scattering (HRS) technique at 532 nm for 5-(3,4-dimethoxybenzylidene) barbituric acid [13]. The quadratic hyperpolarizability of non-aromatic amino acid lysine was measured by means of HRS at 800 nm to be 0.3×10^{-30} esu [14]. The theoretical $\beta - V$ values for 1 ($\beta - V = 32.428 \times 10^{-30}$ esu) and 2 ($\beta - V = 0.196 \times 10^{-30}$ esu), respectively, in Table 6 are in accordance with the experimental results of similar acids in the literature reported by Refs. [13,14]. Our computed results on dynamic first hyperpolarizabilities could be compared with the result of urea which is well-known an efficiency standard in order to find out second-order NLO characterization. The $\beta - V$ values for 1 and 2, respectively, have been obtained 72 times higher (for 1) and 2.3 times lower (for

Table 5: Some selected components of the frequency-dependent $\alpha(-\omega; \omega)$ and absolute values of $\langle \alpha \rangle(-\omega; \omega)$ ($\times 10^{-24}$ esu) at $\omega = 0.04282$ a.u. for **1-2** computed by TDHF method with 6-31G(d) basis set.

Compound	α_{xx}	α_{yy}	α_{zz}	$\langle \alpha \rangle$
1	21.936	12.318	2.392	12.215
2	25.933	20.374	17.628	21.311

Table 6: Some selected components of the frequency-dependent $\beta(-2\omega; \omega, \omega)$ and $\beta - V$ ($\times 10^{-30}$ esu) values at $\omega = 0.04282$ a.u. for **1-2** computed by TDHF method with 6-31G(d) basis set.

Compound	β_{xxx}	β_{yyy}	β_{zzz}	β_x	β_y	β_z	$\beta - V$
1	10.401	-0.421	0.000	31.718	6.746	-0.000	32.428
2	0.036	0.021	0.071	0.023	-0.144	0.130	0.196

Table 7: Some selected components of the frequency-dependent $\gamma(-3\omega; \omega, \omega, \omega)$ and absolute values of $\langle \gamma \rangle(-3\omega; \omega, \omega, \omega)$ ($\times 10^{-35}$ esu) at $\omega = 0.04282$ a.u. for **1-2** computed by TDHF method with 6-31G(d) basis set.

Compound	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}	$\langle \gamma \rangle$
1	7.509	0.062	-0.002	0.145	0.020	0.008	1.601
2	0.359	0.032	0.004	0.041	0.006	0.001	0.099

2) than the quadratic hyperpolarizability of urea ($\beta_{urea} = 0.45 \times 10^{-30}$ esu) reported by Ledoux et al. [15]. The dynamic $\langle \gamma \rangle$ values for the title molecules are about factors of 1.25 higher (for **1**) and factors of 12.8 lower (for **2**) than the cubic hyperpolarizability of para-nitroaniline (*p*-NA) ($\gamma_{p-NA} = 1.271 \times 10^{-35}$ esu) given in [16] which is one of the reference materials utilized in third-order NLO area. Since the NLO parameters, their magnitudes and frequency dependences for **1-2** are determined by ab-initio and DFT levels of theory, these levels of understanding and such theoretical insights make viable computer-aided molecular design of new NLO materials in the future. It is shown that the non-zero μ values for **1-2** might cause microscopic quadratic and cubic hyperpolarizabilities with non-zero values derived by the numerical second-derivatives of the electric dipole moments to extent the implemented field. The presented data on dynamic $\beta - V$ and $\langle \gamma \rangle$ with non-zero values predict that the title compounds might acquire microscopic second and third-order NLO responses. As was to be expected from the comparisons with the urea standard, compound **1** might also possess macroscopic second-order NLO responses with non-zero

Table 8: The calculated HOMO-LUMO energy (a.u.) and HOMO-LUMO band gap E_g values for **1-2** using DFT method at B3LYP/ 6-31G(d) level.

	1	2
HOMO	-0.20926	-0.25174
LUMO	-0.05859	0.01445
$E_g[\text{HOMO-LUMO}]$	0.15067	0.26619
HOMO-1	-0.24793	-0.25346
LUMO+1	-0.00207	0.06196
$E_g[(\text{HOMO}-1)-(\text{LUMO}+1)]$	0.24586	0.31542

values in NLO measurements. So, compound **1** could be a promising material having quadratic electro-optic responses in second-order NLO applications, such as SHG experiments. Hence, compared with compound **2**, compound **1** may fulfill many of quadratic optical nonlinearity requirements and could have potential applications in NLO and electro-optic devices.

Table 8 presents the computed first and second frontier MO energies and also band gaps for **1-2**. Figure 3 shows the first and second frontier MOs. Since the charge transfer stimulations containing HOMO and LUMO affect the second and third-order optical nonlinearities, the lower HOMO-LUMO energy band gaps should generate the higher first and second hyperpolarizability values. In this work, the HOMO-LUMO and (HOMO-1)-(LUMO+1) energy band gaps have a reduction in sort order $2 > 1$, while the calculated values of dynamic $\beta - V$ and $\langle \gamma \rangle$ show an inverse reduction in sort order $1 > 2$ (see Tables 6-8). It is obvious that the HOMO-LUMO energy band gaps and hyperpolarizabilities introduce an opposite correlation [17]. The LUMO for **1** is localized on almost the whole molecule, while the HOMO is mainly localized on methoxy and hydroxyl groups, consequently the HOMO $\rightarrow$ LUMO transition implies an electron density transfer to aromatic part and propenoic acid of π -conjugated system from methoxy and hydroxyl group (Figure 3). The HOMO, HOMO-1, LUMO+1 for **2** are located over the benzene rings. By contrast, the LUMO of **2** is mainly located over the side chain (Figure 3).

4 Conclusions

We have determined the dispersion-free and frequency-dependent dipole polarizabilities, quadratic and cubic hyperpolarizabilities utilizing DFT and TDHF approaches, respectively. The microscopic second and third-order

Figure 3: The frontier and second frontier molecular orbitals of Ferulic acid (1) and Chenodeoxycholic acid (2).

optical nonlinearity behaviour for 1-2 have been confirmed by the non-zero hyperpolarizability values computed in this work. We have also made the comparisons for μ , static and dynamic α , β , γ results of the title compounds with the corresponding NLO parameters of similar structures previously reported in the literature. The applied computational techniques (DFT and TDHF) in this paper presented quite comparable results with the reported data in the literature. It has been shown that some numerical discrepancies between our results and the obtained data in the literature for similar acid derivatives could originate from different methods or basis sets preferred in the computations. One can also see from the comparisons on NLO efficiencies of 1-2 related to reference compounds (urea and *p*-NA) that compound 1 with quite high $\beta - V$ result offers a successful quadratic NLO behaviour. Both various chemical reactions and also resonance phenomena belonging to the structural properties for 1-2 could be understood with information of the HOMOs, LUMOs and HOMO-LUMO band gaps. To investigate the charge transfer properties of the examined structures, the HOMO and LUMO energies have been found out by means of DFT. One can benefit from the first and second frontier MOs determined here for the title compounds to explain their molecular structures and

reactivities. Besides, since the better hyperpolarizability responses are attained by the systems with rather low HOMO-LUMO band gaps, in this work, HOMOs, LUMOs and HOMO-LUMO band gaps for 1-2 have been obtained to define their NLO properties. Our computational results on first and second frontier MOs for 1-2 justify the relationship between HOMO-LUMO band gaps and NLO responses, supporting an inverse behaviour.

Conflict of interest: Authors declare no conflict of interest.

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