



Tuning Electronic and Nonlinear Optical Properties of Chalcone Derivatives-A Density Functional Theory and Time-Dependent Density Functional Theory Investigation

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Abstract Organic π -conjugated materials with excellent nonlinear optical (NLO) properties have attracted great interest owing to different applications in optical limiting technologies. -Br and -NO₂ substituted derivatives of 4-methylsulfanyl chalcone have been reported for their optical limiting applications via the third-order NLO properties. However, some electronic properties and second order NLO responses were not reported. This work therefore is aimed at investigating the electronic properties and molecular first hyperpolarizabilities of the molecules and newly modelled, yet to be synthesized ones both in gas phase and in dimethyl formamide (DMF).

Quantum chemical calculations were performed on the optimized structures of 4-methylsulfanyl chalcone derivatives with hybrid B3LYP/6-31G*. The ground state molecular properties like energies of the frontier molecular orbitals (FMOs), dipole moments (μ), polarizabilities (α), molecular first hyperpolarizabilities (β) were obtained. Time Dependent Density Functional Theory (TD-DFT) was employed to calculate their maximum absorption wavelengths (λ_{abs}), Excitation energies (E_{Ex}) and oscillator strengths (f).

The NLO responses of the molecules are in the order; -CH=C(CN)COOH > -NO₂ > -CHO > -Br. This is owing to the electron withdrawing nature of -CHO, -NO₂ and -CH=C(CN)COOH. The stronger the electron-withdrawing group, the stronger the push-pull effect which consequently leads to larger hyperpolarizability. The best NLO response possessed by -CH=C(CN)COOH substituted analogue may be attributed to its largest molecular size and consequently, its longest charge transfer axis. All modelled analogues are better than urea (0.65×10^{-30} esu), a standard for organic NLO materials in the order; -Br (2.03×10^{-30} esu), -CHO (5.11×10^{-30} esu), -NO₂ (7.34×10^{-30} esu) and -CH=C(CN)COOH (11.06×10^{-30} esu).

The inclusion of solvent was found to alter E_{g} , BLA, μ , β and λ_{abs} greatly. From the obtained results, the modelled analogues have proven to be good materials for applications as optical limiters.

Keywords π -conjugated organic molecules, Density functional theory, Frontier molecular orbitals, second order susceptibility, molecular first hyperpolarizability

1. Introduction

NLO materials can be applied in optoelectronic and photonic devices [1-3]. Combining donor (D) and acceptor (A) units in D- π -A type molecules and also introducing different electron donating and/or withdrawing groups into molecular backbones has made it endlessly possible to tune molecular properties to meet desired applicabilities [4,5]. A theoretical model/method may explain or corroborate experimental observations so well that it can be efficiently useful in predicting the properties of hypothetical, yet to be synthesized molecules; this is key in arriving at materials with optimal properties, the expectations of material scientists. D'Silva and co-workers have synthesized and studied the third-order NLO properties of 4-methylsulfanyl chalcone derivatives using picosecond



pulses and reported that they are desirable for NLO applications [6]. This work intends to use theoretical means to corroborate their findings and extend the work by comparing the behaviours of the molecules and newly modelled derivatives in gas phase and in DMF solution, just like in the experiment. Also, their second-order NLO properties will be investigated.

This work was designed in order to understand the molecular, electronic and NLO properties of 4-methylsulfanyl chalcone derivatives. The density functional theory (DFT) methods have proven to be successful in predicting and explaining molecular properties including the electronic and NLO properties of π -conjugated organic molecules. [7-11]. DFT methods that can predict and corroborate experimental findings [12] will be employed, these methods can then be used to predict the NLO potentials of substituted, yet to be synthesized derivatives in a bid to understand molecular behaviours and derive better NLO materials than existing ones. Throughout this study, the $-\text{SCH}_3$ group is used as the donor while $-\text{Br}$ (at 3- and 4- positions), $-\text{NO}_2$, $-\text{CHO}$ and $-\text{CH}=\text{C}(\text{CN})\text{COOH}$ were used as acceptors. The effects of DMF on the dipole moments, hyperpolarizabilities and absorption maxima were investigated using the Polarizable continuum model (PCM) calculations.

Density functional theory (DFT) methods have been used in predicting molecular polarizabilities and hyperpolarizabilities [7,13], with the Becke Three Lee Yang Parr (B3LYP) exchange correlation used most often [7,13]. The molecules were also calculated in dimethylformamide, DMF (dielectric constant, $\epsilon = 36.7$). This is to understand the changes conformations and hence, some molecular properties of the molecules in solution.

2. Computational Details

The molecules (figs. 1-5) were modelled using computational chemistry software. Optimizations were carried out on the most stable conformers of each molecule. The energy band gap (E_g), derived from the energies of the frontier molecular orbitals (FMO), dipole moments (μ), polarizabilities (α), first-order hyperpolarizabilities (β) were obtained after optimization with DFT methods with the hybrid correlation B3LYP functional using the 6-31G* basis set. Absorption maxima (λ_{abs}), electronic transition energies (E_{ex}) and oscillator strengths (f) were calculated using time-dependent density functional theory method (TDDFT).

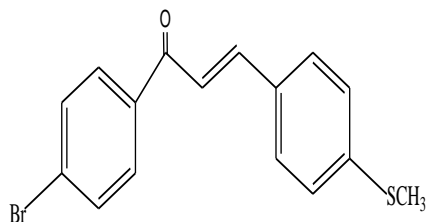


Figure 1: a

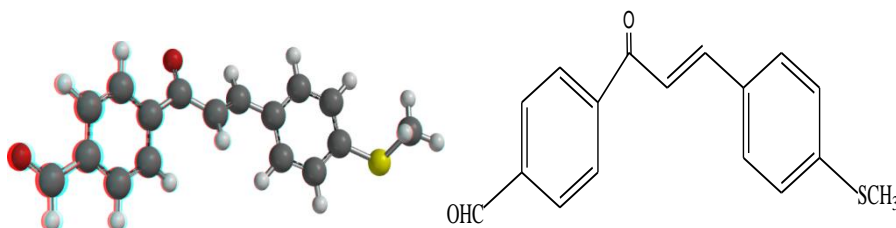


Figure 2: b

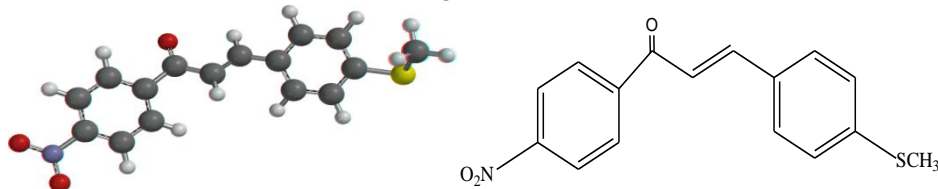


Figure 3: c



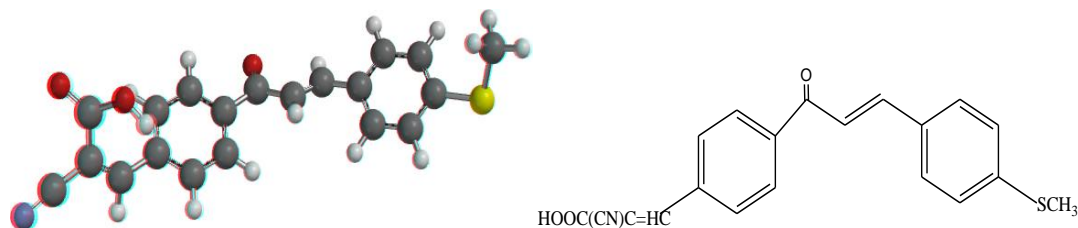


Figure 4: d

E_g values were all obtained from the difference between E_{LUMO} and E_{HOMO} (energies of the lowest unoccupied molecular orbital and the highest occupied molecular orbital). The polarizability, dipole moment and hyperpolarizability of a molecule usually increase with a decrease in E_g values [7,8,11,12]. The molecular first hyperpolarizability (β), a third-rank tensor, is described by a $3 \times 3 \times 3$ matrix from a reduced 27 components of the 3D matrix which becomes 10 components owing to Kleimann symmetry [12,13], given by:

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

The second order susceptibility of a nonlinear optical (NLO) material, χ^2 strongly depends on β_{eff} value. β_{eff} value increases with reduced E_g values and increased α and μ values [7,8]. And because the second harmonic generation (SHG) efficiency is a measure of the second order susceptibility, the SHG efficiency would be compared with β value. The molecules were optimized using B3LYP, a hybrid of the Hartree Fock (HF, 20%) and DFT methods. TDDFT was employed to obtain the electronic transitions in ground state S_0 . The molecules were also considered in solvent medium using the SM8 TD-B3LYP/6-31G* as implemented in Spartan. DMF was chosen, just like in experiments. Some bond lengths were selected from the area of substitution, C_4 , C_5 and C_6 and were used to calculate the bond length alternation (BLA). The BLAs of molecules tend to decrease with increased nonlinearity [12].

3. Results and Discussions

3.1 Results

The E_g , μ and α values were obtained after optimization of the molecules and presented in tables 1 and 2 while their β , λ_{abs} , excitation energies and oscillator strengths were presented in tables 3 and 4. The λ_{abs} values are for the two main transitions present in the molecules, π - π^* and n - π^* transitions, hence the reason for the two λ_{abs} , E_{Ex} and f values recorded. Br is an electron donating group making -Br substituted analogue a D-A-D type molecule while others groups (-NO₂, CHO and -CH=C(CN)COOH) are acceptors and are consequently, the A-A-D type as SCH₃ is acting as a donor in all [6]. It is therefore expected that the electronic and NLO properties of the later are to be better than the former, depending on the type of acceptor group. This is owing to the fact that D-A configuration favours efficient charge transfer taking place through donor to acceptor group. It has also been reported that nonlinearity is enhanced by the length of the charge transfer axis [14]. The molecules also reduced the BLA as E_g values are reduced (table 2).

3.2 Discussions

3.2.1 Structural dependence on the electronic properties of 4-methylsulfonyl chalcone derivatives

The E_g values on table 1 vary with different substituent groups with -Br substituted analogues having the highest value of 3.59 eV while others have smaller values (-CHO, 3.35 eV, -NO₂, 3.13 eV and -CH=C(CN)COOH, 2.98 eV). This is expected because the charge transfer in the A-A-D analogues is more rapid than in the D-A-D analogue and because -NO₂ is a stronger electron donor than -CHO, its value is smaller. The smallest value possessed by -CH=C(CN)COOH substituted analogue may be attributed to larger molecular size and longer charge transfer axis. This indicates that -CH=C(CN)COOH substituted analogue should possess the best NLO property, to be confirmed from μ , λ_{abs} and β values. The value of the dipole moment varies as the substituent's are added, -CH=C(CN)COOH (9.70 D) while -NO₂ (7.49 D), -CHO (4.84 D) and -Br (4.28 D), this is expected as E_g should increase with decreasing values of the dipole moments. The polarizability values are in the same order as the dipole moments, -CH=C(CN)COOH (69.30 cm²V⁻¹) while -NO₂ (64.59 cm²V⁻¹), -CHO (64.49 cm²V⁻¹) and -Br (64.21



cm^2V^{-1}). All these are indicative that the reactivity of these molecules are in the order $-\text{CH}=\text{C}(\text{CN})\text{COOH} > -\text{NO}_2 > -\text{CHO} > -\text{Br}$ and that the NLO responses has a big chance of following similar trend, to be ascertained by the β values.

3.2.2 Structural dependence on the NLO properties of 4-methylsulfanyl chalcone derivatives

The results of the molecular first hyperpolarizabilities are on table 2. The results are; $-\text{CH}=\text{C}(\text{CN})\text{COOH}$ (7.19×10^{-30} esu), $-\text{NO}_2$ (4.79×10^{-30} esu), $-\text{CHO}$ (3.32×10^{-30} esu) and Br (1.32×10^{-30} esu). This result confirmed that the trend $-\text{CH}=\text{C}(\text{CN})\text{COOH} > -\text{NO}_2 > -\text{CHO} > -\text{Br}$ holds. This correlates with E_g as earlier discussed and clearly shows that the strength and size of the electron-withdrawing groups influence NLO responses. The push-pull effects gets stronger with stronger electron-withdrawing group, consequently, larger hyperpolarizability values. Urea, a standard for other organic NLO materials has a β value of 0.65×10^{-30} esu [16]. This implies that all modelled analogues are better than urea as NLO materials in the order; $-\text{Br}$ (2.03), $-\text{CHO}$ (5.11), $-\text{NO}_2$ (7.34) and $-\text{CH}=\text{C}(\text{CN})\text{COOH}$ (11.06). $-\text{NO}_2$ analogue was earlier reported to show higher third order nonlinear susceptibility χ^3 than $-\text{Br}$ analogue [6] and was attributed to the fact that χ^3 increases with the presence of strong acceptor or donor groups. Charge transfer is also responsible for nonlinearity, table 1 and 2 show, from E_g and β values that the nonlinearity is a function of efficient charge transfer. $-\text{Br}$ derivative exhibited the least charge transfer, hence the least nonlinearity.

Table 1: E_{LUMO} , E_{HOMO} , E_g , μ and α values of 4-methylsulfanyl chalcone derivatives with B3LYP/6-31G* in gas phase and in DMF

Molecules	E_{LUMO} (eV)	E_{HOMO} (eV)	E_g (eV)	μ (D)	$\alpha(\text{cm}^2\text{V}^{-1})$
VACUUM					
4-Br	-2.23	-5.82	3.59	4.28	64.21
4-CHO	-2.52	-5.87	3.35	4.84	64.49
4-NO₂	-2.85	-5.98	3.13	7.49	64.59
4-CH=C(CN)COOH	-3.04	-6.02	2.98	9.70	69.30
DMF					
4-Br	-2.17	-5.61	3.44	5.42	64.25
4-CHO	-2.40	-5.61	3.21	5.58	64.52
4-NO₂	-2.71	-5.72	3.01	8.97	64.66
4-CH=C(CN)COOH	-2.75	-5.62	2.87	12.36	69.32

3.2.3 Structural dependence on electronic absorption spectra of 4-methylsulfanyl chalcone derivatives

For a molecule to be considered a good NLO material, its absorption and emission properties must be very good. The calculated excitation energies and oscillator strengths are recorded in table 2. The molecules exhibit two absorptions as seen in their spectra, the excitation energies and oscillator strengths corresponding to these absorptions were therefore recorded for them. The results for $-\text{Br}$ substituted analogue for example, showed absorptions at 292 nm and 357 nm, with E_{Exs} of 4.25 eV and 3.47 eV respectively, with f values of 0.20 and 0.98 respectively. As $-\text{Br}$ was replaced with $-\text{CHO}$, a bathochromic shift occurred to 301 nm and 392 nm, with E_{Exs} of 4.12 eV and 3.16 eV respectively, with f values of 0.70 and 0.55. $-\text{NO}_2$ analogue also increased the λ_{abs} to 323 nm and 427 nm, with E_{Exs} of 3.83 eV and 2.90 eV respectively, with f values of 0.82 and 0.32 respectively while $-\text{CH}=\text{C}(\text{CN})\text{COOH}$ increased the most, as expected, to 337 nm and 453 nm, with E_{Exs} of 3.68 eV and 2.73 eV respectively, with f values of 1.14 and 0.30 respectively. The E_{Exs} decreases just as E_g values. These transitions are mainly due to $\pi-\pi^*$ and $n-\pi^*$. All these are indicative that these molecules could be tuned further to generate better NLO and optoelectronic properties.



Table 2: Hyperpolarizabilities (β), λ_{abs} Excitation energies and oscillator strengths of 4-methylsulfanyl chalcone derivatives with B3LYP/6-31G* in gas phase and in DMF

Molecules	BLA(Å)	$\beta(\times 10^{-30}$ esu)	λ_{abs} (nm)	E_{Ex} (eV)	f
VACUUM					
4-Br	0.2324	1.32	292, 357	4.25, 3.48	0.20, 0.98
4-CHO	0.1640	3.32	301, 392	4.12, 3.16	0.70, 0.55
4-NO₂	0.1618	4.79	323, 427	3.83, 2.90	0.82, 0.32
4-CH=C(CN)COOH	0.1609	7.19	337, 453	3.68, 2.73	1.14, 0.30
DMF					
4-Br	0.2331	1.67	290, 372	4.27, 3.33	0.18, 0.94
4-CHO	0.1638	3.77	308, 408	4.03, 3.04	0.68, 0.57
4-NO₂	0.1611	5.73	339, 471	3.66, 2.59	0.89, 0.23
4-CH=C(CN)COOH	0.1608	12.72	343, 478	3.61, 2.63	1.17, 0.29

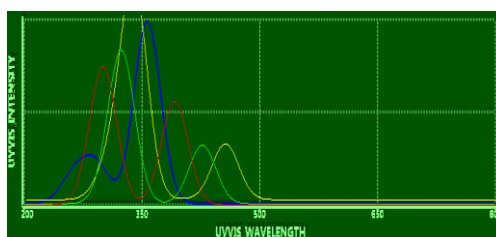


Figure 5: Absorption wavelengths of the molecules with B3LYP in vacuum

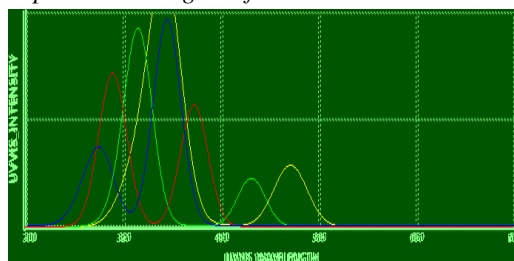


Figure 6: Absorption wavelengths of the molecules with B3LYP in DMF

NB: Blue = -Br analogue, Red = -CHO analogue, Green = -NO₂ analogue and yellow = -CH=C(CN)COOH analogue

3.3 Solvent effects

Many calculations for isolated molecules are generally likened to experiments in gas phase. However, these experiments take place in solutions. The external applied field is usually screened by solvents and consequently induces changes in the electronic and NLO properties of a molecule, the solute [15]. It has been reported that the optical properties of molecules can be drastically changed in solvent media. The dipole moment, hyperpolarizability and λ_{abs} are usually altered to great extents [12,15]. This was observed in the results in tables 1 and 2 as the dipole moments are increased in DMF as compared to the gas phase calculations. The hyperpolarizability and λ_{abs} values are also increased in the solvent than in gas phase while the trend of the results in gas phase is retained. The increase in λ_{abs} in DMF is indicative that the molecules show positive solvatochromism.

4. Conclusion

In a bid to design materials that meet certain applications, it is necessary to tune the properties of molecular systems. Theoretical chemistry affords this opportunity in that one could use a theoretical method to verify and corroborate experimental findings.



The structural and solvent dependence on the electronic and nonlinear optical properties of 4-methylsulfanyl chalcone and modelled analogues using quantum chemical calculations with hybrid B3LYP correlation and a basis set, 6-31G*. The ground state molecular properties like the frontier orbitals (FMOs) energies, dipole moments (μ), polarizabilities (α), molecular first hyperpolarizabilities (β) were obtained. Time Dependent Density Functional Theory (TDDFT) was employed to calculate their maximum absorption wavelengths (λ_{abs}), Excitation energies (E_{Ex}) and oscillator strengths (f).

The molecular properties investigated are Frontier molecular orbitals (FMOs), energy band gap (E_g), dipole moment (μ), polarizability (α), first hyperpolarizability (β) and UV absorptions (λ_{abs}) using B3LYP with the large polar 6-31G* basis set.

It was discovered that the NLO properties of these molecules could be modeled in vacuum/gas phase and in solutions. The inclusion of solvent was found to alter E_g , μ , β and λ_{abs} greatly. The multipolar decomposition (dipolar and octapolar) of α and β -tensor components was developed by the Kleinmann's symmetry model with the TD-DFT calculations. All calculations were carried out using quantum mechanical software.

This result confirmed that the molecules NLO responses follow the trend; $-\text{CH}=\text{C}(\text{CN})\text{COOH} > -\text{NO}_2 > -\text{CHO} > -\text{Br}$. This is owing to the electron withdrawing nature of $-\text{CHO}$, $-\text{NO}_2$ and $-\text{CH}=\text{C}(\text{CN})\text{COOH}$ and their withdrawing strength. The stronger the electron-withdrawing group, the stronger the push-pull effect which consequently leads to larger hyperpolarizability value. The best NLO response possessed by $-\text{CH}=\text{C}(\text{CN})\text{COOH}$ substituted analogue may be attributed to its largest molecular size and consequently, its longest charge transfer axis. The molecules have proven to be good materials for optical limiting applications.

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