

Substituent Effects on the Structural and Nonlinear Optical Properties of 1-[4-((E)-[4-(methylsulfanyl)phenyl]methylidene)amino]phenyl]ethanone and Some of its Substituted Derivatives- a Theoretical Method

O.E. Oyeneyin^{a,b,*}, I.A. Adejoro^{b,c} and T.O. Esan^b

^aDepartment of Chemical Sciences, Adekunle Ajasin University, Akungba-Akoko, Ondo State, Nigeria

^bDepartment of Chemistry, University of Ibadan, Oyo State, Nigeria

^cDepartment of Chemistry, University of Medical Sciences, Ondo, Ondo State, Nigeria

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This work investigates the structural and nonlinear optical properties of a D-A type 1-[4-((E)-[4-(methylsulfanyl)phenyl]methylidene)amino]phenyl]ethanone, MMP, in which charge transfer occurs from -SCH₃ donor to -COCH₃ acceptor group through methylidene backbone, and some of its modeled analogues using quantum chemical calculations with pure BLYP and hybrid B3LYP correlations with high basis sets, 6-31G* and 6-31+G* in gas phase to understand their structure-property relationship. The molecular properties such as FMOs energies, dipole moments (μ), polarizabilities (α), and molecular first hyperpolarizabilities (β) were calculated. The results showed that the molecular properties are enhanced upon substitution with different groups. The β value is a measure of the second order susceptibility of molecule; MMP has a β value of 2.44×10^{-30} esu (B3LYP), 3.75 times of urea (0.65×10^{-30} esu) and 2.61×10^{-30} (BLYP), 4.02 times that of urea. The experimental SHG efficiency of MMP is 4.13 times that of urea crystals of identical particle size, meaning that the BLYP correlation predicts the SHG efficiency and second order susceptibility more effectively than the B3LYP method. With 6-31+G*, B3LYP gave 2.83×10^{-30} esu, 4.35 over urea's (94.9%) while BLYP is 3.11×10^{-30} esu, 4.78 times that of urea (84.3%). Both basis sets gave expected results in the right order for the molecules, however, β value was increased for all analogous, confirming that they are better candidates for NLO applications than MMP. The electronic transitions were calculated with CAM-B3LYP.

Keywords: MMP, Density functional theory, Frontier molecular orbitals, Second order susceptibility, Molecular first hyperpolarizability

INTRODUCTION

Conjugated organic molecules with a donor part on one side and an acceptor part on the other side (D-A configuration) have become of scientific interest due to their important applications in photovoltaic, optoelectronic and optical limiting technologies [1-6]. They protect sensors and the human eyes from intense laser light owing to their optical limiting potentials [7,8]. A lot of π -conjugated organic molecules have been investigated for their nonlinear optical (NLO) behaviours [9-11]. NLO compounds exhibit large dipole moments (μ) [12], polarizabilities (α) and

molecular first hyperpolarizabilities (β) [1]. It is important to understand the relationship between NLO processes and molecular structure. The properties of molecules tend to change when a substituent group is introduced into their backbone; accordingly, molecules can be designed to meet certain applications. The frontier molecular orbitals (FMOs) can be altered by introducing electron donors and acceptors at either end of a conjugated molecule leading to the formation of dipoles and improve intramolecular charge transfer (ICT).

Different experimental methods are used to characterize nonlinear behaviors in molecules such as molecular beam methods [13], collision-induced scattering of light [14], Kerr-effect experiments [15], third-harmonic generation

*Corresponding author. E-mail: emmanueltoba90@gmail.com

techniques, THG [16] and electric field-induced second harmonic generation experiments, EFISHG [17,18]. Quantum mechanical methods have also been used to study NLO behaviors of certain materials [7,9,10]. Determining molecular polarizabilities and hyperpolarizabilities of molecules is very important in explaining their NLO properties theoretically. Quantum chemical calculations have been employed in past and recent times to either predict NLO behaviors of organic molecules [27,28] or used to corroborate experimental findings [7,9]. Density functional theory (DFT) programs have been employed in calculating molecular polarizabilities and hyperpolarizabilities [7,9,19], either with the finite field approach or with Kohn-Sham method [20,21]. The pure DFT method, BLYP and hybrid Becke Three Lee-Yang-Parr (B3LYP) methods have been employed in explaining the influence of the molecular and electronic structure, and solvent media on polarizabilities and hyperpolarizabilities. In nonlinear materials, the systems consist of net permanent dipole moment, that is, they are non-centrosymmetric, as seen in Fig. 1. Since understanding the electronic properties like the energy band gap from the frontier orbital energies guides the design of a new and appropriate structure for NLO materials, this work is aimed at predicting the structural and electronic properties of the investigated molecules using quantum chemical calculations. The B3LYP exchange correlation has been reported in the past and recent times for predicting and investigating the electronic properties of π -conjugated organic molecules [9,23,24]. However, the pure BLYP, although least explored, has been considered as a comparative option to predict molecular properties. Hence, both were chosen in order to validate which of them is broadly consistent with available experimental results. 1-[4-((E)-[4-(methylsulfanyl)phenyl]methylidene)amino)phenyl]ethanone has been synthesized and characterized for its NLO applications and was reported to be better than urea [26]. In this study, the structural and solvent dependence on the molecular, electronic and nonlinear optical properties of 1-[4-((E)-[4-(methylsulfanyl)phenyl]methylidene)amino)phenyl]ethanone and some of its substituted derivatives are investigated using quantum chemical DFT calculations with pure BLYP and hybrid B3LYP correlations using high basis sets, 6-31G* and 6-31+G* in gas phase in order to

understand their structure-property relationship. Hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP) was employed for electronic transitions, this method has proven to be the best for this type of calculations today [30,31].

COMPUTATIONAL DETAILS

Quantum mechanical calculations were carried out on MMP and its substituted analogues with computational chemistry software on intel®Core (TM) i5-3317U CPU @1.70GHz 1.70Hz computer with the *ab initio* restricted pure BLYP and hybrid density functional theory (DFT) and the time dependent density functional theory (TDDFT) [20,21], B3LYP exchange- correlation method with 6-31G* and 6-31+G*[22]. The Coulomb Attenuated Method (CAM-B3LYP) was used for calculations of UV transitions, excitation energies (E_{ex}) and oscillator strengths (f). The DFT calculations were carried out only in gas phase. Structural optimization was done without any constraints, after convergence (that is, after reaching a minimum on the potential energy surface) to get the equilibrium structures of the molecules. The experimental data for MMP were used as a standard. It was observed that the theoretical methods employed correlated well with experimental observations. Such method(s) were employed in understanding structure-property relationships of other hypothetically modeled molecules. The energy band gaps (E_g) were all obtained from the difference between energies of the lowest unoccupied molecular orbitals (E_{LUMO}) and the highest occupied molecular orbitals (E_{HOMO}) while the chemical hardness (η) is half of E_g value and softness is the inverse of η [23,24]. Molecular parameters such as polarizabilities and hyperpolarizabilities were calculated. The dipole moments were also obtained using the same methods and used to explain intermolecular interactions. The molecular first hyperpolarizability (β) is a third-rank tensor that 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 [25] and is given by:

$$\beta_{eff} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \dots \dots \dots 1.01$$

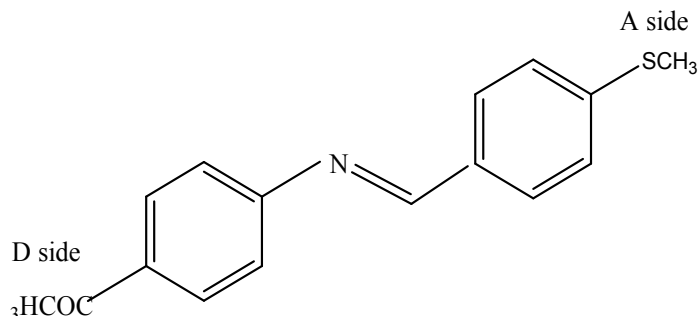


Fig. 1. Structure of 1-[4-((E)-[4-(methylsulfanyl)phenyl]methylidene)amino]phenyl]ethanone, MMP.

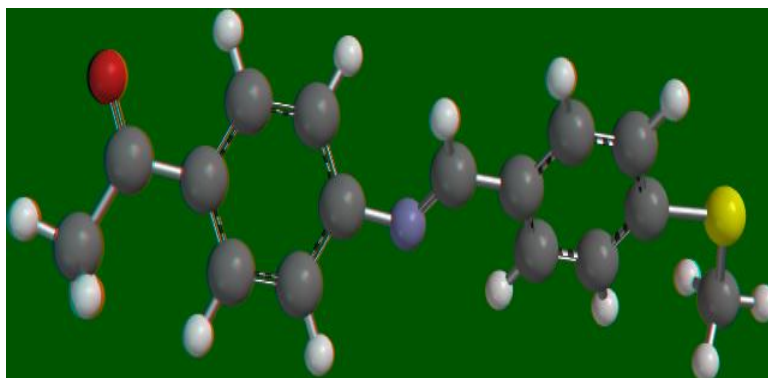


Fig. 2. Optimized structure of 1-[4-((E)-[4-(methylsulfanyl)phenyl]methylidene)amino]phenyl]ethanone.

The second order susceptibility of a nonlinear optical (NLO) material, χ^2 , strongly depends on β_{eff} value. The β_{eff} value increases with reduced E_g values and increased α values [9].

RESULTS AND DISCUSSION

Geometric Parameters

The geometric and electronic structure of MMP are used as references to compare with the properties of other substituted analogues (Fig. 2). For all molecules, molecular geometries were obtained after total optimization with BLYP and B3LYP/6-31G* (Tables 1-3) and 6-31+G* (Tables 4-6).

Different donor and acceptor substituents affect molecular properties, that may lead to a variation in their NLO efficiency. The existence of strong intramolecular charge transfer excitations in a non-centrosymmetric molecule is paramount in explaining their NLO responses

[31]. The energy band gap of molecules determines their reactivity and intramolecular charge transfer (ICT), and has been found to decrease with increased μ , α and β values [9,23,24]. E_g is, therefore, expected to be altered with different substituent groups. Hyperconjugation is always affected by the insertion of different substituent group(s) due to the increased steric and inductive effects. Consequently, the substituted derivatives are expected to possess higher dipole moments (μ), polarizabilities (α) and hyperpolarizabilities (β).

Properties such as μ , α , β , UV-Vis absorption maxima (λ_{max}), and E_g will be fully established if these materials are better than 1-[4-((E)-[4-(methylsulfanyl)phenyl]methylidene)amino]phenyl] ethanone. This is the basis of this work. Different donor and acceptor groups affect molecular properties, that may lead to a variation in their NLO efficiencies.

Table 1. Electronic Properties of 1-[4-((E)-[4-(Methylsulfonyl)phenyl]methylidene)amino]phenyl]ethanone and Substituted Analogues with B3LYP and BLYP/6-31G* in Gas Phase

Molecules	E _{LUMO} (eV)	E _{HOMO} (eV)	E _g (eV)	η (eV)	S (eV ⁻¹)
B3LYP					
A-COCH ₃ , D-SCH ₃ , MMP	-1.94	-5.79	3.85	1.93	0.52
A-NO ₂ , D-SCH ₃	-2.44	-6.02	3.58	1.79	0.56
A-NO ₂ , D-NH ₂	-2.25	-5.80	3.55	1.78	0.56
A-CN, D-SCH ₃	-2.28	-5.94	3.66	1.83	0.55
A-CN, D-NH ₂	-2.03	-5.71	3.68	1.84	0.54
A-CH=C(CN)COOH, D-SCH ₃	-2.72	-6.08	3.36	1.68	0.59
BLYP					
A-COCH ₃ , D-SCH ₃ , MMP	-2.41	-4.88	2.47	1.24	0.81
A-NO ₂ , D-SCH ₃	-2.90	-5.11	2.21	1.11	0.90
A-NO ₂ , D-NH ₂	-2.51	-4.99	2.48	1.24	0.81
A-CN, D-SCH ₃	-2.53	-5.01	2.48	1.24	0.81
A-CN, D-NH ₂	-2.25	-4.79	2.54	1.27	0.79
A-CH=C(CN)COOH, D-SCH ₃	-3.12	-5.18	2.06	1.03	0.97

Frontier Orbital Energies and Related Properties

The E_g values of the molecules differ as different substituent groups were inserted. Molecules possessing the low E_g values are good candidates to exhibit large second harmonic generation (SHG) efficiency because charge transfer tends to be easier; this is confirmed by β values. The two molecular orbitals must overlap in the middle region of the electron density, for efficient charge transfer, that is, E_g values determine level of charge transfer and also possess large μ, α and β values.

Both methods used afford a comparison between the results obtained and see the trend which the molecular properties follow and to determine which of the methods is closer to experimental data. From Table 1, the experimental E_g values for MMP (A-COCH₃, D-SCH₃, MMP) were found to be 2.27 eV, 2.80 eV and 2.94 eV that were obtained from

three different experimental methods, from ε₂^{1/2}/λ vs. (1/λ) in Tauc's expression [26,27], direct and indirect band gap methods [26]. The B3LYP E_g value of MMP is 3.85 eV with 6-31G* basis set while its BLYP value is 2.47 eV with 6-31G*. This result is consistent with some other reports that the hybrid B3LYP overestimates E_g values while the pure BLYP underestimates it, though closer [37]. The E_g value in BLYP method (2.47 eV) is closer to Tauc's ε₂^{1/2}/λ vs. (1/λ) method value of 2.27 eV and underestimates the direct and indirect band gap values of 2.80 eV and 2.94 eV, while it is 3.85 eV with B3LYP. It is expected that the other substituted derivatives will have a different E_g value from MMP owing to different effects like the inductive and mesomeric effects from substituent groups, NO₂ acceptor group reduced E_g values, CN group also did the same with a greater reduction with CH=C(CN)COOH, which is a larger

Table 2. The Dipole Moments (μ), Polarizabilities (α), Hyperpolarizabilities (β) and λ_{\max} of 1-[4-((E)-[4-(Methylsulfonyl)phenyl]methylidene)amino]phenyl]ethanone and Substituted Analogues with B3LYP and BLYP/6-31G* in Gas Phase

Molecules	μ (D)	A ($\text{cm}^2 \text{V}^{-1}$)	B ($\times 10^{-30}$ esu)
B3LYP			
A-COCH ₃ , D-SCH ₃ , MMP	4.60	59.63	2.44
A-NO ₂ , D-SCH ₃	7.45	62.27	3.84
A-NO ₂ , D-NH ₂	10.10	61.08	4.78
A-CN, D-SCH ₃	7.04	62.05	5.45
A-CN, D-NH ₂	9.62	60.84	5.87
A-CH=C(CN)COOH, D-SCH ₃	11.49	66.98	8.98
BLYP			
A-COCH ₃ , D-SCH ₃ , MMP	5.05	58.17	2.61
A-NO ₂ , D-SCH ₃	7.99	62.80	4.03
A-NO ₂ , D-NH ₂	10.65	60.55	4.95
A-CN, D-SCH ₃	7.45	62.56	5.60
A-CN, D-NH ₂	10.06	60.33	6.05
A-CH=C(CN)COOH, D-SCH ₃	12.14	67.54	9.34

Table 3. The Vibrational Frequencies and Corresponding Mode Assignments of 1-[4-((E)-[4-(Methylsulfonyl)phenyl]methylidene)amino]phenyl]ethanone, MMP with B3LYP and BLYP/6-31G* in Gas Phase

Modes assignment	Wave numbers (Exp.) in cm^{-1}	Wave numbers (B3LYP/6-31G*) in cm^{-1}	Wave numbers (BLYP/6-31G*) in cm^{-1}
C-H _{str} (aromatic)	3046.21	3181-3225	3095-3139
=C-H _{str}	2915.37	3033	2935
-C-H _{str}	2862.19	3054-3169	2972-3085
-C=N	1669.80	1640	1621
C=C _{str} (arom. rings)	1582.05	1602, 1609	1567, 1593
Ar. ring vibrations	1549.62	1549	1532, 1540
C-H _{def}	1435.50	1391-1426	1297-1414
C-Har. Bend	1080.14 and less	1107 and less	1062 and less
-C=O _{str}	-	1734	1676

Experimental data [26].

Table 4. Electronic Properties of 1-[4-((E)-[4-(Methylsulfonyl)phenyl]methylidene)amino]phenyl]ethanone and Substituted Analogues with B3LYP and BLYP/6-31+G* in Gas Phase

Molecules	E_{LUMO} (eV)	E_{HOMO} (eV)	E_{g} (eV)	η (eV)	S (eV ⁻¹)
B3LYP					
A-COCH ₃ , D-SCH ₃ , MMP	-2.28	-6.04	3.76	1.88	0.53
A-NO ₂ , D-SCH ₃	0.28	-8.49	8.77	4.39	0.23
A-NO ₂ , D-NH ₂	0.79	-8.54	9.33	4.67	0.21
A-CN, D-SCH ₃	0.72	-8.38	9.10	4.55	0.22
A-CN, D-NH ₂	1.01	-8.18	9.19	4.59	0.22
A-CH=C(CN)COOH, D-SCH ₃	0.06	-8.44	8.50	4.25	0.24
BLYP					
A-COCH ₃ , D-SCH ₃ , MMP	-2.79	-5.18	2.39	1.19	0.84
A-NO ₂ , D-SCH ₃	0.00	-8.50	8.50	4.25	0.24
A-NO ₂ , D-NH ₂	0.19	-8.32	8.51	4.26	0.23
A-CN, D-SCH ₃	0.52	-8.38	8.90	4.45	0.22
A-CN, D-NH ₂	0.81	-8.17	8.98	4.49	0.22
A-CH=C(CN)COOH, D-SCH ₃	-0.17	-8.40	8.57	4.29	0.23

Table 5. The Dipole Moments (μ), Polarizabilities (α), Hyperpolarizabilities (β) and λ_{max} of 1-[4-((E)-[4-(Methylsulfonyl)phenyl]methylidene)amino]phenyl]ethanone and Substituted Analogues with B3LYP and BLYP/6-31+G* in Gas Phase

Molecules	μ (D)	α (cm ² V ⁻¹)	β ($\times 10^{-30}$ esu)
B3LYP			
A-COCH ₃ , D-SCH ₃ , MMP	5.11	63.67	2.83
A-NO ₂ , D-SCH ₃	7.84	61.07	4.46
A-NO ₂ , D-NH ₂	10.17	58.77	5.03
A-CN, D-SCH ₃	7.09	60.83	5.93
A-CN, D-NH ₂	9.48	58.62	6.09
A-CH=C(CN)COOH, D-SCH ₃	10.90	65.83	8.88
BLYP			
A-COCH ₃ , D-SCH ₃ , MMP	5.68	64.21	3.11
A-NO ₂ , D-SCH ₃	8.30	61.35	4.85
A-NO ₂ , D-NH ₂	10.72	59.13	5.42
A-CN, D-SCH ₃	7.34	61.07	6.19
A-CN, D-NH ₂	9.74	58.84	6.34
A-CH=C(CN)COOH, D-SCH ₃	10.92	66.14	9.05

Table 6. The Vibrational Frequencies and Corresponding Mode Assignments of 1-[4-((E)-[4-(methylsulfanyl)phenyl]methylidene)amino]phenyl]ethanone, MMP with B3LYP and BLYP/6-31+G* in Gas Phase

Modes assignment	Wave numbers (Exp.) in cm ⁻¹	Wave numbers (B3LYP/6-31+G*) in cm ⁻¹	Wave numbers (BLYP/6-31+G*) in cm ⁻¹
C-H _{str} (aromatic)	3046.21	3178-3222	3092-3135
=C-H _{str}	2915.37	3030	2933
-C-H _{str}	2862.19	3050-3161	2967-3076
-C=N	1669.80	1695	1613
C=C _{str} (arom. rings)	1582.05	1534-1595	1531, 1583
Ar. ring vibrations	1549.62	1543	1524
C-H _{def}	1435.50	1330-1503	1058-1295
C-Har. Bend	1080.14 and less	1103 and less	1055 and less
-C=O _{str}	-	1743	1647

Experimental [26].

group. It is expected that E_g values tend to decrease with higher molecular weight. This trend is repeated even in the different DFT methods. The chemical hardness, η is a direct consequence of the E_g values, and determines if a molecule can react more easily or not. The chemical softness is an inverse of η values and indicates which molecules react readily. A molecule with low E_g value is more polarizable and is generally reactive, with high electro-optic response and is usually termed a soft molecule [24]. The substituted molecules are softer than MMP while MMP is harder than them. The substituted molecules should, therefore, have higher ability to form instantaneous dipoles than MMP. The dipole moments (μ), polarizability (α) and hyperpolarizability (β) values are expected to be enhanced compared to MMP. The 6-31+G* result, however, gave a different trend for the modelled analogues.

Dipole Moments and Polarizabilities

MMP has dipole moment values of 4.60 D and 5.05 D with B3LYP and BLYP methods, respectively. All other substituted derivatives increased μ values, with the stronger NO_2 acceptor having higher values than CN, and a further increase with the insertion of a better NH_2 donor than SCH_3 . $\text{CH}=\text{C}(\text{CN})\text{COOH}$, D-SCH₃ has the highest values that could be due to its weight and longer conjugation. Similar trend was observed in the polarizability values, Table 2. This trend is also observed using the 6-31+G* basis set for μ values, but failed to predict α values as expected.

The β value is a measure of second order susceptibility of molecule; MMP has a β value of 2.44×10^{-30} esu (B3LYP), 3.75 times of urea (0.65×10^{-30} esu) [9] and 2.61×10^{-30} (BLYP), 4.02 times that of urea. The experimental SHG efficiency of MMP is 4.13 times that of urea crystals

of identical particle size [26], meaning that the BLYP correlation predicts the SHG efficiency and second order susceptibility more effectively than the B3LYP method. With 6-31+G*, B3LYP gave 2.83×10^{-30} esu, 4.35 over urea's (94.9%) while BLYP is 3.11×10^{-30} esu, 4.78 times that of urea (84.3%). However, both basis sets gave expected results in the right order for the molecules, that is, all substituted analogues increased β value, confirming that they are better candidates for NLO applications than MMP, with *A-CH=C(CN)COOH*, *D-SCH₃* proving the best in that it has the lowest optical/energy band gap, highest value of dipole moment, polarizability and hyperpolarizability. The best result for molecular first hyperpolarizability is with BLYP/6-31G*.

UV Absorptions

The extent of absorption of a compound provides information about the type of electronic transition(s) present in the molecule. The TD-DFT methods were used in calculating the absorption maxima (λ_{abs}) using CAM-B3LYP (Table 7-12). The various transitions associated with them were indicated, all due to π - π^* and n - π^* transitions, with the absorptions with the highest λ_{abs} attributed to n - π^* . MMP contains absorption wavelengths of 267 nm and 298 nm (both due to H-L transitions) with 6-31G* and 272 nm and 302 nm (assigned to H-1-L and H-L transitions, respectively). The λ_{abs} predicted are in close agreement with experimental λ_{abs} of <400 nm [26]. All substituted molecules were bathochromically shifted, with *A-CH=C(CN)COOH*, *D-SCH₃* shifting the most, obviously owing to extra conjugation length. The vibrational frequencies were also studied to ascertain which of the two methods is closer, from the results in Table 3, it is evident that the BLYP method corroborates well with experimental observations in both basis sets.

CONCLUSIONS

Investigation was made on the structural and electronic properties, as well as the optical properties of 1-[4-((E)-[4-(methylsulfonyl)phenyl]methylidene)amino]phenyl] ethanone, MMP, to find a theoretical method that corroborates its experimental findings, and also investigate the properties of similar hypothetical molecules by varying

the substituent groups. The ground state dipole moments, polarizabilities, hyperpolarizabilities and the optical/energy band gaps of MMP and substituted analogues were theoretically investigated using the density functional triple parameter hybrid model theory (DFT/B3LYP) and the pure BLYP correlation with 6-31G* and 6-31+G*. BLYP and B3LYP/6-31G* levels were found to be the calculation of choice because of their level of accuracy and reliable computation costs. The optical band gaps were electronically and sterically enhanced by the type of substituent groups introduced into the molecule's backbone. The reactivities and NLO responses were enhanced owing to a general decrease in optical band gaps (HOMO-LUMO gap) and an increase in molecular first hyperpolarizabilities of the substituted analogues compared to MMP, this may be due to enhanced charge transfer interaction between the donor and acceptor group as a result of increased size, planarity and maybe extra conjugation, like in *A-CH=C(CN)COOH*, *D-SCH₃*. *A-CH=C(CN)COOH*, *D-SCH₃* appears to exhibit the most chemical reactivity. MMP has a β value of 2.44×10^{-30} esu (B3LYP), 3.75 times of urea (0.65×10^{-30} esu) [9] and 2.61×10^{-30} (BLYP), 4.02 times that of urea. The experimental SHG efficiency of MMP is 4.13 times that of urea crystals of identical particle size [26], meaning that the BLYP correlation predicts the SHG efficiency and second order susceptibility more effectively than the B3LYP method. With 6-31+G*, B3LYP gave 2.83×10^{-30} esu, 4.35 over urea's (94.9%) while BLYP is 3.11×10^{-30} esu, 4.78 times that of urea (84.3%). However, both basis sets gave expected results in the right order for the molecules, that is, all substituted analogues increased β value, confirming that they are better candidates for NLO applications than MMP, with *A-CH=C(CN)COOH*, *D-SCH₃* proving the best in that it has the lowest optical/energy band gap, highest value of dipole moment, polarizability and hyperpolarizability. The best result for molecular first hyperpolarizability is associated with BLYP/6-31G*. These materials have shown their potential to be as optical limiters.

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Table 7. The Absorptions (nm), Oscillator Strengths (f), Transitions and Percentage Contributions (%) of 1-[4-((E)-[4-(methylsulfonyl)phenyl]methylidene)amino]phenyl]ethanone (A-COCH₃, D-SCH₃, MMP)

	λ_{abs} (nm)	f	Transitions	%	λ_{abs} (nm)	f	Transitions	%
	CAM-B3LYP/6-31G*				CAM-B3LYP/6-31+G*			
1	224.72	0.1280	H -> L+1	31%	232.94	0.0985	H -> L+1	29%
			H-1 -> L	23%			H -> L+3	12%
			H-5 -> L	17%			H-1 -> L	11%
			H-1 -> L+1	10%			H-1 -> L+1	11%
2	247.14	0.0048	H-3 -> L	55%	252.02	0.0058	H-3 -> L	53%
			H-1 -> L+3	19%			H-1 -> L+4	21%
			H -> L+3	12%			H -> L+4	11%
3	248.64	0.0051	H -> L+2	46%	255.55	0.0274	H -> L+2	49%
			H-4 -> L	35%			H-4 -> L	30%
4	266.75	0.5557	H-> L	34%	272.81	0.3621	H-1 -> L	35%
			H-1 -> L	29%			H -> L	27%
			H-5 -> L	19%			H-5 -> L	17%
5	298.37	0.9157	H -> L	56%	304.49	1.0079	H -> L	60%
			H-1 -> L	25%			H-1 -> L	22%
6	307.83	0.0037	H2 -> L+1	47%	308.29	0.0190	H-2 -> L+1	44%
			H-2 -> L	42%			H-2 -> L	41%

Table 8. The Absorptions (nm), Oscillator Strengths (f), Transitions and Percentage Contributions (%) of A-NO₂, D-SCH₃

	λ_{abs} (nm)	f	Transitions	%	λ_{abs} (nm)	f	Transitions	%
	CAM-B3LYP/6-31G*				CAM-B3LYP/6-31+G*			
1	249.74	0.0064	H-3 -> L H-1 -> L+2	63% 18%	256.62	0.0085	H-3 -> L H-1 -> L+2	64% 16%
2	249.86	0.0010	H-> L+3 H-2 -> L H-2 -> L+1	43% 25% 20%	257.31	0.0079	H-> L+3 H-2 -> L+1 H-2 -> L	39% 17% 15%
3	270.65	0.2836	H-> L H-1 -> L H-1 -> L+1 H-4 -> L	27% 22% 18% 12%	274.07	0.0016	H-8 -> L H-8 -> L+1	69% 23%
4	272.56	0.0057	H-7 -> L H-7 -> L+1	59% 27%	276.01	0.1456	H-1 -> L H-1 -> L+1 H-> L H-4 -> L	26% 21% 20% 10%
5	300.56	1.1089	H-> L H-1 -> L	52% 29%	309.00	1.1932	H-> L H-1 -> L H-> L+1	53% 26% 12%
6	307.44	0.0001	H-5 -> L H-5 -> L+1	54% 27%	312.61	0.0034	H-5 -> L H-5 -> L+1	65% 23%

Table 9. The Absorptions (nm), Oscillator Strengths (f), Transitions and Percentage Contributions (%) of A-NO₂, D-NH₂

	λ_{abs} (nm)	f	Transitions	%	λ_{abs} (nm)	f	Transitions	%
	CAM-B3LYP/6-31G*				CAM-B3LYP/6-31+G*			
1	248.58	0.0068	H -> L+3 H-2 -> L+1 H-2 -> L	54% 20% 16%	256.87	0.0045	H-3 -> L H -> L+4 H-1 -> L+2	57% 13% 12%
2	249.83	0.0056	H-3 -> L H-1 -> L+2 H -> L+2	66% 17% 10%	257.42	0.0115	H -> L+4 H-2 -> L+1 H-3 -> L	37% 13% 12%
3	267.48	0.1689	H-1 -> L H-1 -> L+1 H -> L	27% 23% 22%	271.39	0.0919	H-1 -> L H-1 -> L+1 H -> L	28% 26% 18%
4	271.99	0.0020	H-7 -> L H-7 -> L+1	71% 22%	273.68	0.0029	H-7 -> L H-7 -> L+1	75% 17%
5	299.74	1.1642	H -> L H-1 -> L	61% 22%	308.03	1.1730	H -> L H-1 -> L H -> L+1	61% 21% 11%
6	307.18	0.0023	H-5 -> L H-4 -> L H-5 -> L+1 H-4 -> L+1	36% 35% 12% 10%	312.53	0.0151	H-5 -> L H-4 -> L H-5 -> L+1	57% 18% 13%

Table 10. The Absorptions (nm), Oscillator Strengths (f), Transitions and Percentage Contributions (%) of A-CN, D-SCH₃

	λ_{abs} (nm)	f	Transitions	%	λ_{abs} (nm)	f	Transitions	%
	CAM-B3LYP/6-31G*				CAM-B3LYP/6-31+G*			
1	215.35	0.0007	H -> L+4	75%	224.47	0.2350	H-4 -> L	27%
							H -> L+1	26%
							H-1 -> L	18%
2	218.90	0.2087	H-4 -> L	34%	231.47	0.0004	H -> L+4	44%
			H-1 -> L	29%			H -> L+5	13%
			H -> L+1	12%				
3	241.22	0.0004	H-3 -> L	41%	246.02	0.0002	H-3 -> L	37%
			H-1 -> L+2	29%			H-1 -> L+2	32%
			H -> L+2	16%			H -> L+2	16%
			H-3 -> L+1	11%			H-3 -> L+1	11%
4	249.25	0.0039	H -> L+3	44%	255.88	0.0234	H -> L+3	45%
			H-2 -> L	40%			H-2 -> L	34%
5	272.06	0.4735	H -> L	34%	272.72	0.2902	H-1 -> L	39%
			H-1 -> L	32%			H -> L	26%
			H-4 -> L	18%			H-4 -> L	16%
6	305.77	0.9627	H -> L	58%	301.72	1.0565	H -> L	64%
			H-1 -> L	25%			H-1 -> L	21%

Table 11. The Absorptions (nm), Oscillator Strengths (f), Transitions and Percentage Contributions (%) of A-CN, D-NH₂

	λ_{abs} (nm)	f	transitions	%	λ_{abs} (nm)	f	transitions	%
	CAM-B3LYP/6-31G*				CAM-B3LYP/6-31+G*			
1	206.47	0.0362	H -> L+1 H-4 -> L H-1 -> L	43% 27% 13%	220.04	0.0847	H -> L+1	42%
2	212.26	0.0814	H -> L+1 H-4 -> L H-1 -> L	31% 20% 20%	236.70	0.0030	H -> L+3	64%
3	241.09	0.0001	H-3 -> L H-1-> L+2 H -> L+2	39% 26% 22%	246.24	0.0001	H-3 -> L H-1 -> L+2 H -> L+2	35% 24% 23%
4	248.00	0.0190	H -> L+3 H-2 -> L	51% 29%	255.79	0.0579	H -> L+4 H-2 -> L H -> L+1	38% 23% 13%
5	261.96	0.4337	H-1 -> L H -> L H-4 -> L	36% 28% 22%	266.18	0.2923	H-1 -> L H -> L H-4 -> L	42% 21% 21%
6	291.25	1.0295	H -> L H-1 -> L	64% 21%	296.50	1.0691	H -> L H-1 -> L	69% 17%

Table 12. The Absorptions (nm), Oscillator Strengths (f), Transitions and Percentage Contributions (%) of A-CH=C(CN)COOH, D-SCH₃

	λ_{abs} (nm)	f	Transitions	%	λ_{abs} (nm)	f	Transitions	%
	CAM-B3LYP/6-31G*				CAM-B3LYP/6-31+G*			
1	250.42	0.0017	H -> L+3 H-2 -> L+1 H-2 -> L	36% 25% 19%	246.43	0.0027	H-6 -> L H -> L+1 H-6 -> L+1	44% 12% 11%
2	252.12	0.0068	H-3 -> L H-6 -> L H-1 -> L+2	22% 17% 13%	256.75	0.0017	H -> L+3 H-2 -> L+1 H-2 -> L	41% 23% 16%
3	253.16	0.0057	H-3 -> L H -> L+1 H-1 -> L	27% 21% 12%	259.15	0.0030	H-3 -> L H-1 -> L+2 H -> L+2	57% 20% 11%
4	263.34	0.0215	H-6 -> L H -> L+1 H-1 -> L	24% 13% 11%	265.68	0.0248	H -> L+1 H-1 -> L H-1 -> L+1	38% 19% 12%
5	274.08	0.1632	H-1 -> L+1 H -> L H-1 -> L H-4 -> L	23% 19% 17% 16%	278.54	0.1206	H-1 -> L H-1 -> L+1 H -> L H-4 -> L	25% 21% 18% 13%
6	315.95	1.5242	H -> L H-1 -> L	56% 27%	323.97	1.5525	H -> L H-1 -> L	57% 26%

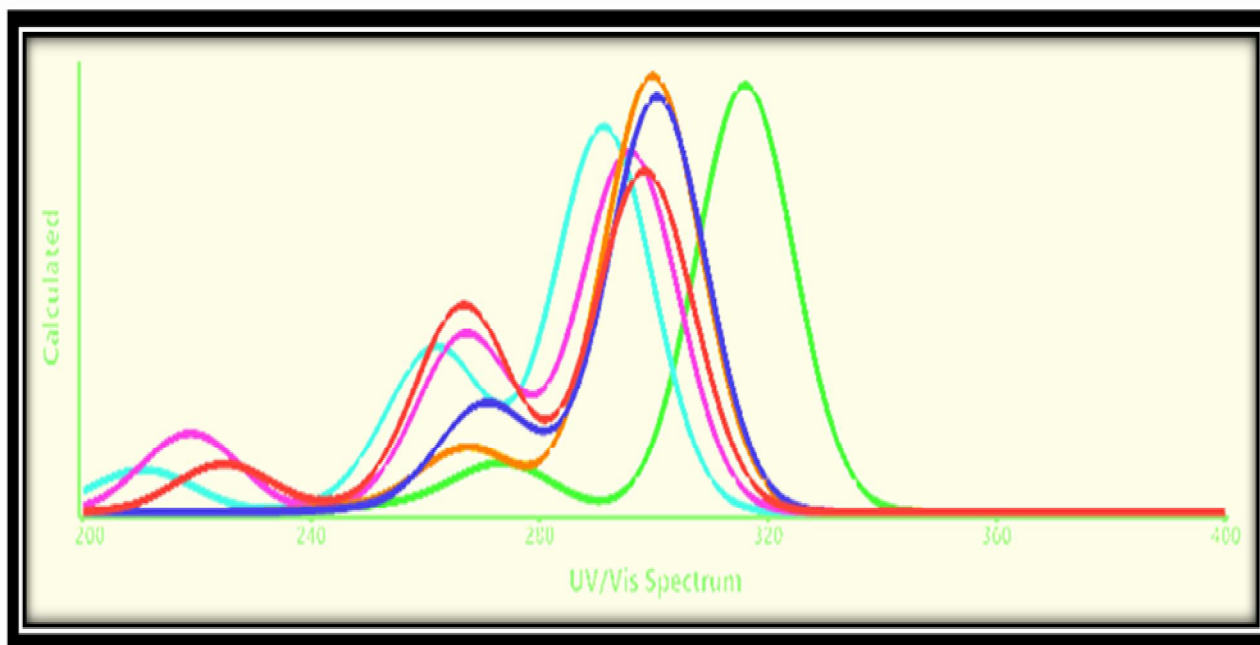


Fig. 3. UV spectra of all molecules with CAM-B3LYP/6-31G*. MMP (red), A-NO₂, D-SCH₃(blue), A-NO₂, D-NH₂ (orange), A-CN, D-SCH₃ (violet), A-CN, D-NH₂ (light green), A- CH=C(CN)COOH₂, D-SCH₃ (deep green).

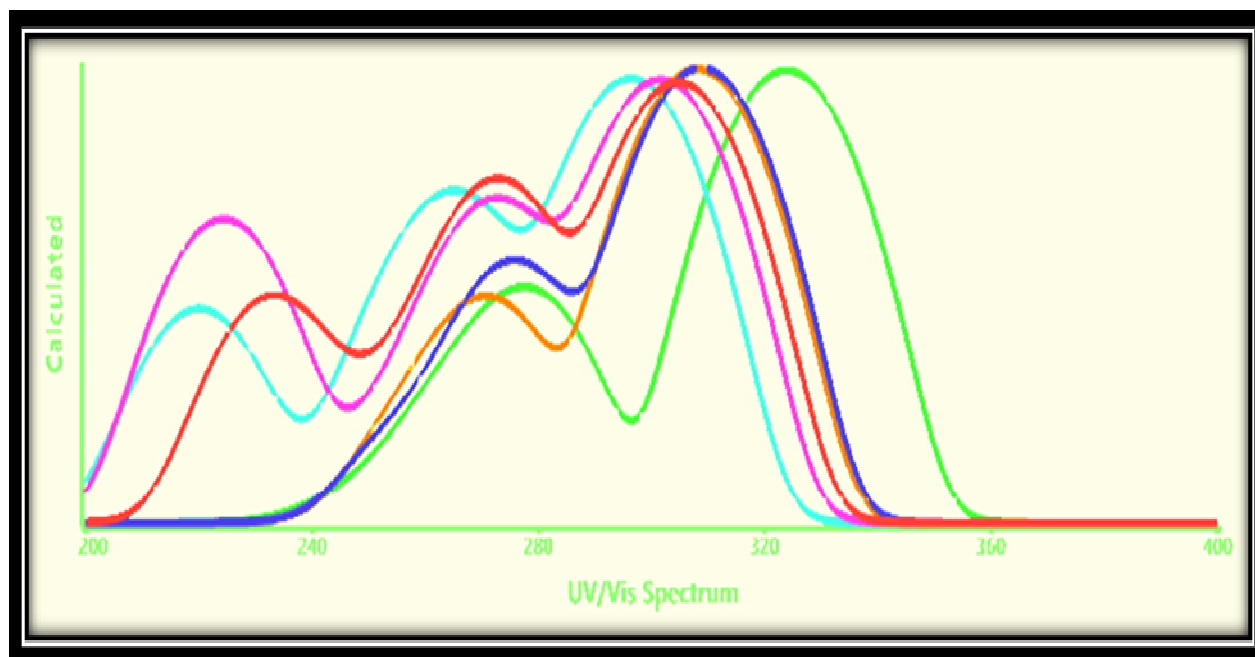


Fig. 4. UV spectra of all molecules with CAM-B3LYP/6-31+G*. MMP (red), A-NO₂, D-SCH₃ (blue), A-NO₂, D-NH₂ (orange), A-CN, D-SCH₃ (violet), A-CN, D-NH₂ (light green), A- CH=C(CN)COOH₂, D-SCH₃ (deep green).

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