



ARTICLE INFO

Received
March 26, 2021

Revised
June 01, 2021

Accepted
June 03, 2021

Published
July 05, 2021

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Keywords
Nonlinear optical materials
Density functional theory
4-methylphenyl)-(4-methylpiperidin-1-yl) methanone
Energy band gap
Molecular hyperpolarizability

How to cite
Oyenehin OE. Tuning the electronic and nonlinear optical properties of (4-methylphenyl) (4-methylpiperidin-1-yl) methanone and its substituted analogues. *Sci Lett* 2021; 9(2):49-54

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Tuning the Electronic and Nonlinear Optical Properties of (4-Methylphenyl) (4-methylpiperidin-1-yl) Methanone and Its Substituted Analogues

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Abstract

A lot of molecules have been reported for certain applications. However, the need to continuously search for novel materials with more promise is very important because of the competitive technological innovations. One of the ways to achieve this is to use valid theoretical methods that can effectively and accurately predict the properties of existing molecular entities and using these methods to predict the properties of hypothetical molecules. The compound (4-methylphenyl) (4-methylpiperidin-1-yl) methanone (MPMPM) has been reported for its nonlinear optical potentials; however, investigating their reactivity indices would lead to the understanding of the mechanism behind their suitability as nonlinear optical devices. The molecular backbone of MPMPM was altered by introducing some substituents that could alter molecular properties. MPMPM and its derivatives were, therefore, optimized with density functional theory and the time-dependent density functional theory using pure and hybrid correlations and a polar basis set, 6-31G(d). The energy band gaps of the substituted derivatives were lower than that of MPMPM while the dipole moments and hyperpolarizabilities were higher, indicating that they could serve as better alternatives for nonlinear optical applications.



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Introduction

Organic compounds have been investigated experimentally and theoretically for their use in nonlinear optical (NLO) devices due to the π -bonds in their moieties, non-centrosymmetric structure and donor-acceptor (D-A) configuration, which all facilitate intra-molecular charge transfer [1-5]. These materials shield human parts (eyes, skin, etc.) and other optical sensors from dangerous laser light by attenuating the incident laser beams [1]. Their use has become very important because of the growing use of intense lasers in the industry, military and medical sectors [1, 2]. These materials exhibit properties such as two/multi-photon absorption [3, 4], nonlinear scattering [5, 6], reverse saturation absorption [7, 8], etc. One of the ways to improve the NLO ability of a known compound is to derivatize it, especially by adding an electron donor at one end and an electron acceptor at the opposite end, this enhances asymmetric charge distribution [9-11]. Asymmetric charge distribution can be investigated by calculating the tensor components via quantum mechanical calculations [12-14]. This is used to calculate the dipole moments and hyperpolarizabilities, which are used to measure their harmonic generation efficiencies. For instance, the molecular first hyperpolarizability is used as a measure of the second harmonic efficiency of a molecule [12]. Density functional theory (DFT) methods have been employed while probing into molecular properties, it has been used in past and in recent times in different areas of materials science research [11, 12, 15-21]. In this study, 4-Methylphenyl (4-methylpiperidin-1-yl) methanone, (MPMPM; Fig. 1) was synthesized and reported for its NLO ability [22]. This work aimed to corroborate the experimental findings with theoretical method(s) and use the method(s) to predict the NLO properties of derivatized MPMPM to investigate the effect of some substituents on the NLO responses via DFT and TD-DFT calculations. Their NLO responses would be compared to that of urea crystals, a standard for NLO materials.

Materials and Methods

MPMPM and its derivatives were modeled and optimized using DFT with (i) a restricted Kohn-Sham self-consistent field (SCF) calculation (BLYP) and (ii) a restricted hybrid Hartree Fock-DFT SCF calculation (B3LYP) [23] using Pulay's direct inversion of the iterative subspace (DIIS) and geometric direct minimization [24] for both

correlations and a polar basis set, 6-31G(d) after generating their most stable conformers with the molecular mechanics force field. These levels of theory have been reported to be consistent with experimental trends [25]. The energies of the frontier molecular orbitals (FMOs), that is, energies of the highest occupied molecular orbital, E_{HOMO} and that of the lowest unoccupied molecular orbital, E_{LUMO} were calculated and used to get the values of the energy band gap, E_g (eq. 1), chemical hardness, η (eq. 2), chemical softness, σ (eq. 3) and the dipole moments (μ) (eq. 4). The molecular first hyperpolarizabilities, β were calculated from Kleimann's reduced 10 components from the $27 \times 3 \times 3 \times 3$ matrix (eq. 5) [26]. The absorption maxima (λ_{abs}), electronic transition energies/optical band gaps (E_{ex}) and oscillator strengths (f) were calculated using time-dependent density functional theory, TD-DFT method. all on Spartan 14 (v112, Wavefunction, Inc., Irvine.).

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad \text{eq. 1}$$

$$\eta = \frac{E_g}{2} \quad \text{eq. 2}$$

$$\sigma = \frac{1}{\eta} \quad \text{eq. 3}$$

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad \text{eq. 4}$$

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yyz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2} \quad \text{eq. 5}$$

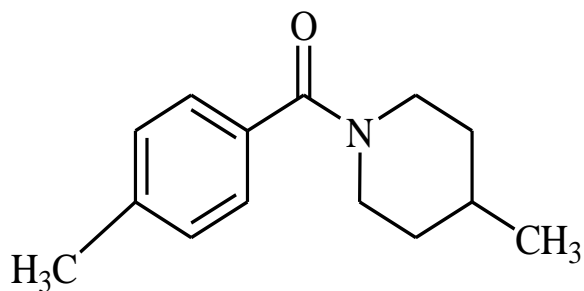


Fig. 1 4-Methylphenyl (4-methylpiperidin-1-yl) methanone (MPMPM) and its derivatives (different substituents were used to replace the methyl on phenyl ring). For example, -CHO replaced -CH₃ on the phenyl ring to become 4-CHO derivative (Table 1), CN became 4-CN and so on.

Results and discussion

Electronic properties

The electronic properties are presented in Tables 1 and Table 2 for DFT and TD-DFT methods. All substituted derivatives have lower E_g values than MPMPM with nitro and cyano acrylic acid substituted derivatives having the lowest values,

Table 1 Electronic and nonlinear optical properties of MPMPM and its substituted derivatives with B3LYP/6-31G*.

Molecules	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	η (eV)	σ (eV ⁻¹)	μ (D)	β (x10 ⁻³⁰ esu)
MPMPM	-6.19	-0.61	5.58	2.79	0.36	3.52	0.27
4-CHO	-6.55	-1.99	4.56	2.28	0.44	3.80	1.08
4-CH=C(CN)COOH	-6.63	-2.76	3.87	1.94	0.52	4.44	1.45
4-CN	-6.67	-1.79	4.88	2.44	0.41	5.73	2.64
4-NO ₂	-6.73	-2.58	4.15	2.08	0.48	5.87	1.44
4-NC	-6.58	-1.55	5.03	2.52	0.39	5.06	2.39

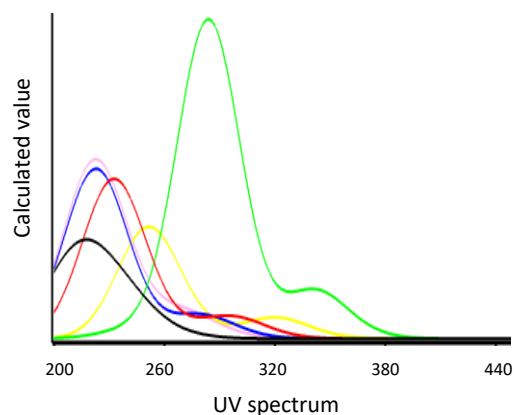
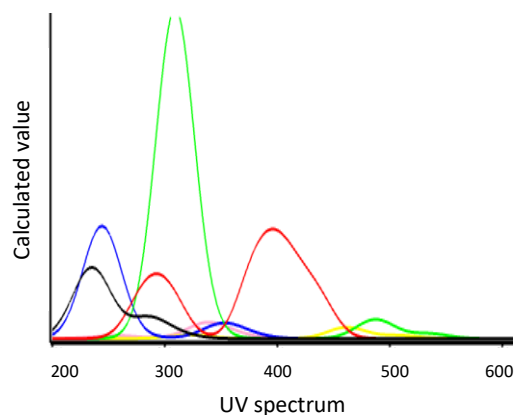
Table 2 Electronic and nonlinear optical properties of MPMPM and its substituted derivatives with BLYP/6-31G*.

Molecules	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	η (eV)	δ (eV ⁻¹)	μ (D)	β (x10 ⁻³⁰ esu)
MPMPM	-4.82	-1.15	3.67	1.84	0.55	3.43	0.25
4-CHO	-5.21	-2.50	2.71	1.36	0.74	4.05	1.14
4-CH=C(CN)COOH	-5.31	-3.15	2.16	1.08	0.93	4.69	1.43
4-CN	-5.32	-2.26	3.06	1.53	0.65	5.83	2.65
4-NO ₂	-5.39	-3.09	2.30	1.15	0.87	5.99	1.43
4-NC	-5.23	-2.06	3.17	1.59	0.63	5.24	2.50

which could be attributed to the larger molecular weight of the substituted derivatives, mesomeric effects and/or conjugation length. The substituted derivatives are, therefore, more reactive than MPMPM. Nitro is a stronger electron-withdrawing group than the others (increase mesomeric effect) while cyano acrylic acid has the longest π -conjugation length and even the largest of all the molecules. The η and σ values are expected to have similar and reverse trends, respectively (eq. 2 and eq. 3). Consequently, all substituted derivatives have lower η values, with nitro and cyano acrylic acid having the lowest, while the highest σ values. Formation of instantaneous dipoles (tensor components) is usually enhanced by improved reactivity of molecules (the closer the HOMO-LUMO gap) and the μ values of the substituted molecules are higher than that of MPMPM (Tables 1 and 2) and all molecules under investigation. MPMPM showed higher μ values than urea (1.98 D) [27].

Hyperpolarizability

The β value is a measure of the second harmonic generation (SHG) efficiency of a NLO molecule. These values are higher in the substituted derivatives than MPMPM. A similar trend was observed in the two correlations used. The β value of urea (a standard for organic NLO materials) was calculated as 0.6498×10^{-30} esu [12]. From Table 1 and Table 2, all substituted derivatives have higher values than urea, this is because of the enhanced delocalization of charges brought about by the different substituents that reduced the HOMO-

**Fig. 2** Calculated UV spectra of the MPMPM and its substituted derivatives (MPMPM = black; 4-CHO = red; 4-CH=C(CN)COOH = green; 4-CN = blue; 4-NO₂ = yellow; 4-NC = pink) with hybrid correlation.**Fig. 3** Calculated UV spectra of the MPMPM and its substituted derivatives (MPMPM = black; 4-CHO = red; 4-CH=C(CN)COOH = green; 4-CN = blue; 4-NO₂ = yellow; 4-NC = pink) with pure correlation.

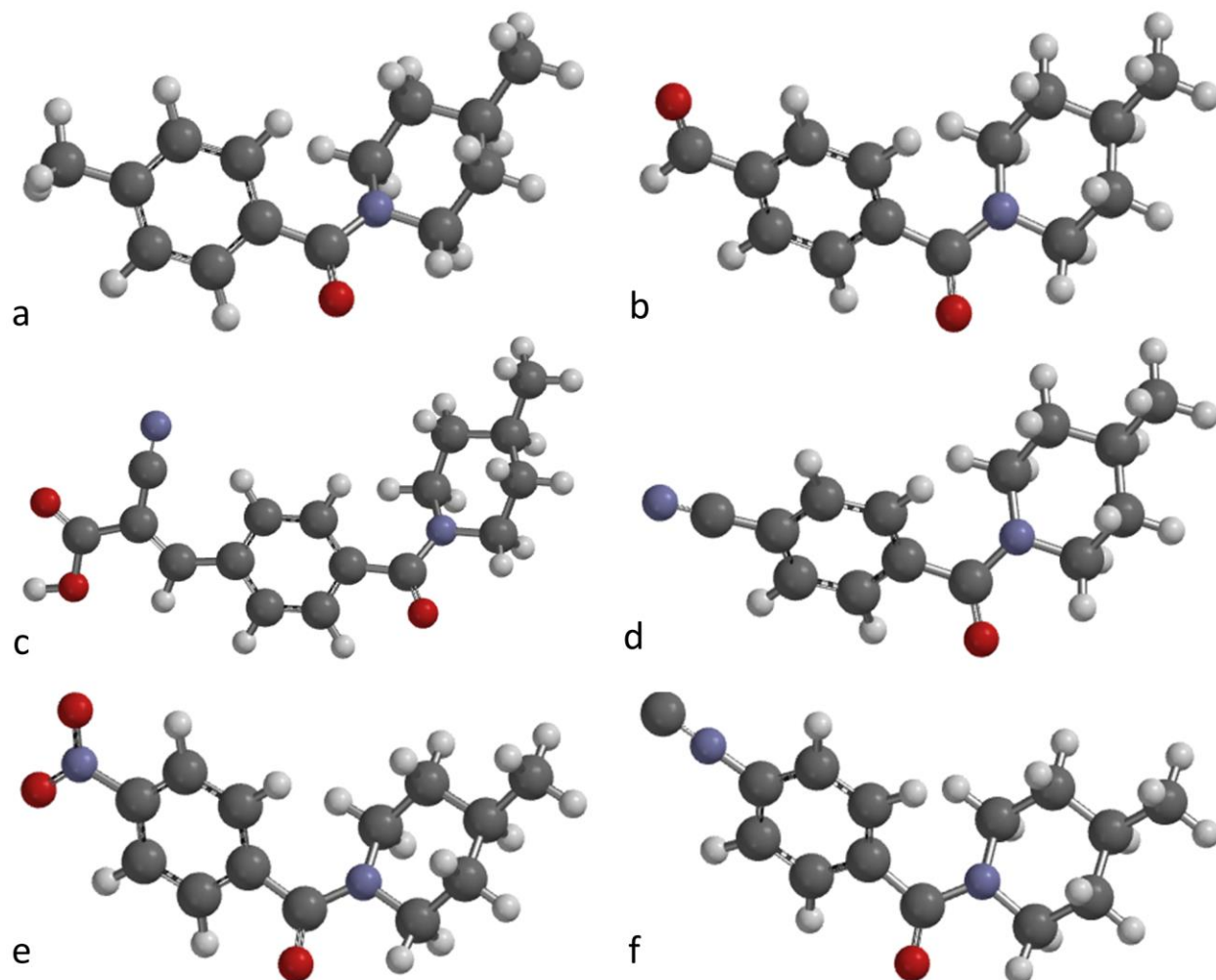


Fig. 4 Optimized (4-methylphenyl) (4-methylpiperidin-1-yl) methanone (MPMPM) (a); optimized cyano derivative (b); optimized 4-CHO derivative (c); optimized nitro derivative (d); optimized 4-cyano acrylic acid (e); and optimized isocyno derivative (f).

LUMO gap and improved intramolecular charge transfer (ICT). The chemical hardness and softness values provide information about the molecules' reactivity and electron transportation. All the substituted derivatives are softer than MPMPM as a result of the lower energy band gap. This consequently led to an increase in their dipole moment values and hyperpolarizabilities.

Electronic transitions

MPMPM was absorbed at 285 nm with BLYP correlation, while it was absorbed at 237 nm with B3LYP (Fig. 2 & Fig. 3). The absorption of 295 nm was ignored because of its zero-oscillator strength. The experimental λ_{abs} was 296 nm [22]. The band gap corresponding to the calculated λ_{abs} (BLYP) was 4.34 eV while the experimental band gap obtained was 4.19 eV. The calculated λ_{abs} (BLYP)

corresponding to 295 nm (4.21 eV) was ignored because of zero oscillator strength. The substituted derivatives bathochromically shifted the λ_{abs} (Fig. 4, & Tables S1-S6). Cyano acrylic acid substituted derivative shifted the λ_{abs} the most, followed by $-\text{NO}_2$. Similar results were observed in previous studies [28]. The red shift observed in 4- $\text{CH}=\text{C}(\text{CN})\text{COOH}$ is attributed to its conjugation length and also the strong inductive electron-accepting nature of nitro derivative than others [29, 30].

Conclusions

DFT and TD-DFT calculations were carried out on MPMPM and its substituted derivatives to obtain the ground state optimized geometry, FMOs energies, energy band gap, dipole moments and hyperpolarizabilities. The properties calculated

were used to explain their NLO properties and compared with the values of urea, a standard NLO material. The FMOs energies obtained show that the substituted derivatives are more reactive than MPMPM owing to lower energy band gaps. The dipole moments of the molecules were higher than that of urea while the hyperpolarizability values of the substituted derivatives were higher than that of urea in multiple folds. The hyperpolarizability of MPMPM and derivatives depends on the electronic structure of the molecule, as seen from the lower energy band gap, which increased charge transfer from the donor to the acceptor parts of the molecules. It is also evident that the hyperpolarizability was affected by the energy band gap. The substituted derivatives could be used as precursors in the development of better NLO materials. In this study, only the electronic components of the hyperpolarizability values were considered. The effect of field strength on nuclear positions was not considered.

Conflict of Interest

There are no conflicts of interest to declare.

Acknowledgment

We pay gratitude to Adekunle Ajasin University, Akungba-Akoko, Ondo State for creating an enabling environment for this research work.

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