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Short Communication

Crystal structure optimization, Semi-empirical quantum chemical calculations and Non-linear optical property of a thiazolo [3, 2-a] pyrimidine derivative

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Abstract

The crystal structure of the title molecule has been analyzed with the help of AM1 semi-empirical calculations to explain the crystal packing effect and the results were compared with earlier DFT analysis. The electric dipole moment (μ) and static first and second order hyperpolarizabilities (β and γ) have been computed using Time Dependent Hartree Fock (TDHF) method incorporated in MOPAC2009 program to inspect the microscopic non-linear optical behaviour of the title compound. This is in good agreement with the experimentally measured second harmonic generation efficiency of the compound which is 0.36 and 4.17 times to those of urea and KDP respectively, hence it suggests the non-linear optical behaviour of the material. The intramolecular charge transfer interactions result during the HOMO-LUMO transitions observed from the calculated energy values.

Keywords: Second harmonic generation, dipole moment, hyperpolarizabilty, non-linear optical property.

Introduction

The non-linear optics finds large intersection with experimental and theoretical physics, chemistry and engineering. It has attracted considerable interest not only due to its application in electro-optics, telecommunication etc., but also due to the fundamental research associated with charge transfer interaction, conjugation, polarisation and crystallization of material into non-centrosymmetric lattice. The material with which a light can exhibit non-linear optical (NLO) property is primarily controlled by its various order non-linear succeptibilities.

The crucial distinction between traditional materials and recent organic materials is revealed during the analysis of the origin of their non-linear succeptibilities. The large optical succeptibility, ultra fast response time and high optical threshold for organic materials compared to traditional materials like urea, potassium dihydrogen phosphate (KDP), theorem lead to the study of organic NLO materials.

The intrinsic properties to be optimized and compared for the NLO activity of the material at microscopic level are dipole moment (μ) and hyperpolarizabilities (β and γ).

From the crystal structural study on a series of pharmaceutically important thiazolo [3, 2-a] pyrimidine compounds designed to ascertain the influence of substitution pattern on crystal packing, the title compound, Ethyl (2Z,5R)-2-benzylidene-7-methyl-3-oxo-5-phenyl-2,3-dihydro-5H-[1,3] thiazolo [3,2-a] pyrimidine-6-carboxylate crystallized into non-centrosymmetric lattice may possess NLO behaviour. The crystallographic details along with the influence of different interactions on crystal packing effects have been discussed and published earlier[1].

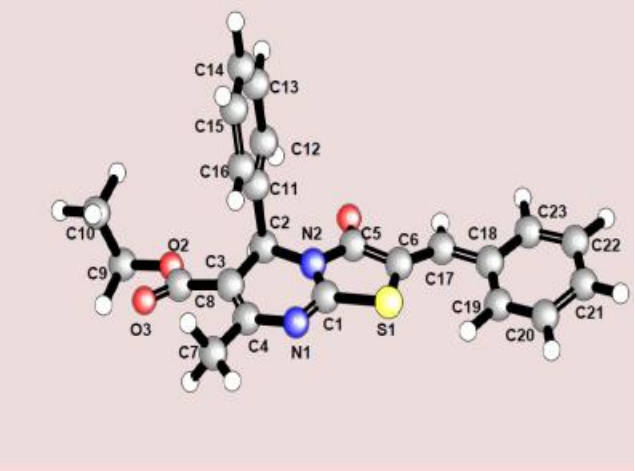

Figure- 1
Molecular structure with Atom labelling scheme

Figure 1 shows the molecular structure with atom labelling scheme. The present work relates the molecular structural features, hyperpolarizabilities and NLO response of material with the special emphasis on the role of intramolecular charge transfer mechanism in such a structure using HOMO-LUMO studies.

Material and Methods

Second harmonic generation efficiency measurement: The non-linear optical second harmonic generation efficiency of microcrystals was measured by Kurtz-Perry powder SHG method at Indian Institute of Science, Banglore, and India2. A Q-switched nanosecond pulsed (8 ns, 10Hz) Nd:YAG laser beam of 1064 nm wavelength and 5.6 ml power is used for the measurement. The grown single crystals of the compound were ground with particle size in the range 100-150 □m and packed in a microcapillary of uniform bore. The input laser beam was allowed to pass through the sample after reflection from the infra red reflector and the output from the sample was filtered by monochromator to separate the fundamental from the SHG signal. The second harmonic generated by randomly oriented microcrystals was focussed by a lens and detected by photomultiplier tube (Hammatsu RS 109). The emission of green light from the sample confirmed second harmonic generation. The crystalline powdered samples of urea and potassium dehydrogenate phosphate (KDP) with the same size as that of title compound is used as a reference.

Semi-empirical quantum chemical calculations: Austin Model 1 (AM1) is one of the popular semi-empirical methods for the calculation of electronic molecular properties such as ground state geometry, molecular energy and molecular polarizability. Austin Model 1 together with the restricted Hartree Fock closed shell wave function was used to perform semi-empirical quantum chemical calculations in order to optimize the experimental structure and to calculate hyperpolarizabilities using MOPAC2009 program[3].

The minimizations were terminated at r. m. s. gradient less than 0.01 kJ mol^{-1} $Å^{-1}$ and optimized geometry together with dipolemoment vector is shown in figure 2. The comparision of the geometries optimized by density functional theory (DFT) and MOPAC2009 with the geometry observed from the crystal structure is given in table 1. The geometrically optimized molecule is then used to compute the static - values using time dependent Hartree Fock (TDHF) method incorporated in MOPAC2009 program.

β_{vec}, the vector component along dipole moment at zero frequency is defined as

$$\beta_{vec} = \frac{3}{5}\frac{\vec{\beta}\cdot\vec{\mu}}{|\vec{\mu}|} \ldots\ldots(1)$$

Where $\vec{\beta}\cdot\vec{\mu} = \beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z \ldots\ldots(2)$

And $\beta_i = \beta_{iii} + \beta_{ijj} + \beta_{ikk} \ldots\ldots(3)$

Where, □ i =x, j = y and k = z

$$\beta_{tot} = [\beta_x^2 + \beta_y^2 + \beta_z^2]^{1/2} \ldots\ldots(4)$$

Here, β_{tot} and β_{vec} are determined from the computed sensorial components. Due to 3D nature of molecule, Klein man symmetry relations and the squared norm of Cartesian expressions for β tensor were taken into account while calculating β_{vec} and β_{tot}. The calculated β and μ for the title molecule are given in table 2.

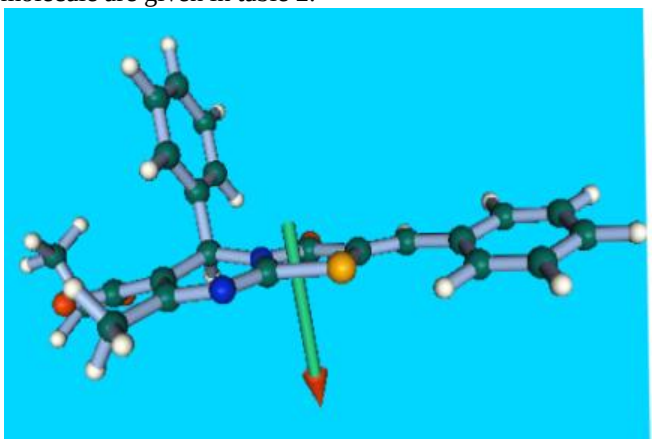

Figure-2
AM1 optimized molecule Showing dipole moment vector

Results and discussion

The semi-empirical AM1 calculated values for the optimized geometry together with DFT calculated and experimental values are listed in Table 1. The comparison of C-N-C and C-C-N bond angles for the fused thiazolopyrimidine system between experimental values (crystallographic information file), DFT and semi-empirical AM1 calculated values with small deviations confirm the screw-boat conformation of puckered pyramiding ring. The shortening of C = O distance between C8 and O3 atoms from the optimized geometrical value and the significant difference in the torsional angle around C3-C8 and O2-C9 bonds may be due to the involvement of these atoms in the intramolecular C-H…O and C-O…π □interactions.

The semi-empirical AM1 calculations also support presence of intermolecular C-H…S interaction characterized by C6-C17-C18-C19 torsional angle (9.8(4) ° (cif); 15.72° (AM1). The discrepancies in the bond distances and some other geometrical parameters between AM1 calculated and experimental values are also observed similar to that with DFT calculated model. Thus semi-empirical quantum chemical calculations also support the crystal packing interaction of title molecule. The TDHF calculations indicates that the three dimensional molecule possess no symmetry and has a point group C_1.

The second harmonic generation resulted from the randomly oriented microcrystals in a micro capillary tube through the emission of a green light of wave length 532 nm. The output of SHG signal generated from the title compound was measured as 100 mV in comparison with 24 mV and 274 mV outputs measured for the reference compounds KDP and urea

respectively. Thus, the title compound has SHG efficiency equals 4.17 and 0.36 times to that of KDP and urea respectively. The dipole moment (μ) and hyperpolarizabilities (β and γ) calculated by TDHF method are given in Table 2. The dipole moment vector is aligned diagonally across bc -plane of unit cell and normal to the plane extending to acetyl group on one side and to the benzene ring through C=C group on other side of the central fused pyrimidine system Which is shown in figure 1. The larger magnitude of dipole moment (μ) is due to the effective charge separation within the molecule.

The large first order hyperpolarizability (β) compared to that of urea also suggest non-linear optical behavior of the material in the solid state. The measure of non-linear optical response of a molecule β_{tot} has the dominance of β_{vec} and β_{oct} both given in table 2. In addition the third order hyperpolarizability (γ) has also significant contribution to the non-linear optical property due to its relatively large value.

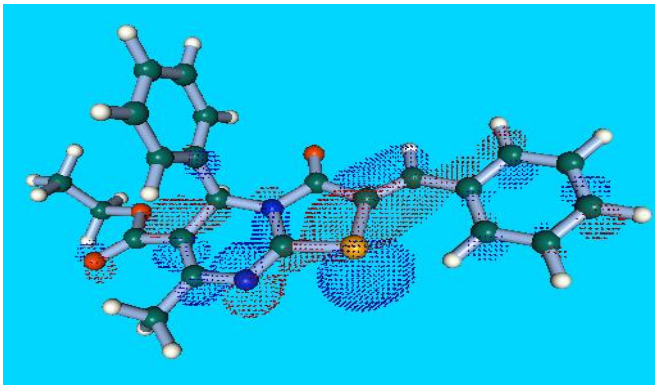

Figure- 3
Homo composition of molecular orbital

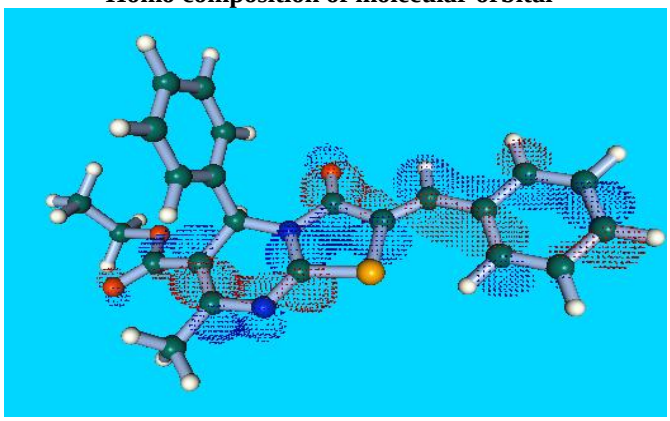

Figure-4
Lumo composition of molecular orbital

The semi-empirical quantum chemical calculations using MOPAC2009 are also employed to compute the different form of energies such as heat of formation, transition energies, ionization potential etc. These values are listed in Table 3. The analysis of restricted Hartree Fock wave function indicates that the transition from ground to first excited state is described by one electron transition from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). The frontier molecular orbital HOMO is localized with the large concentration around the atoms of central fused pyrimidine system shown in figure 3, whereas LUMO is located near the most of the coplanar atoms including benzylidene moiety of the molecule (figure 4). An electron transition from HOMO to LUMO through an absorption of energy equal to homo-lumo energy gap equals to7.323 eV reflects the chemical activity of a molecule thereby resulting intermolecular charge transfer between the atoms of the molecule.

Conclusion

The optimized geometry of title molecule using DFT and AM1 semi-empirical computations reveals the involvement of atoms in short intermolecular C-H…S, C-H…O and C-O…π interactions for the crystalline environment of the molecule. The dipole moment and hyperpolarizabilities have been computed by TDHF method from AM1 optimized geometry of the molecule using MOPAC2009 program. The computed value suggest the non-linear optical behaviour of the material at microscopic level and is supported by the experimental SHG efficiency measurements. The dipole moment vector (μ) aligned diagonally across bc-plane of unit cell has large magnitude. The intramolecular charge transfer results within the atoms of molecule during HOMO-LUMO transition.

Acknowledgements

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Table-1
Selected geometrical parameters

(a) Bond lengths (Å)			
Bond	Experimental (cif)	DFT calculated	AM1 calculated
O2-C8	1.332(2)	1.387	1.371
O2-C9	1.451(4)	1.485	1.435
O3-C8	1.184(3)	1.236	1.237
C9-C10	1.404(5)	1.530	1.509
(b) Bond angles (°)			
Bonds	Experimental (cif)	DFT calculated	AM1 calculated
C1-N2-C5	116.65(19)	118.42	114.30
C2-N2-C5	123.33(17)	121.72	125.73
N2-C2-C3	108.29(17)	108.48	110.61
N2-C1-N1	126.9(2)	126.55	125.68
(c) Torsional angles (°)			
Bonds	Experimental (cif)	DFT calculated	AM1 calculated
C8-O2-C9-C10	115.0(4)	78.57	80.29
C4-C3-C8-O3	11.4(3)	3.01	19.52

Table-2
Dipolemoment and hyperpolarizabilities

(a) Dipolemoment (D)			
μ_x	μ_y	μ_z	μ
- 0.291	-3.750	- 1.455	4.033
(b) First order hyperpolarizabity (× 10^{-30} esu)			
β_x	β_y	β_z	–
-16.513	-21.363	-2.223	-
β_{tot}	β_{vec}	β_{oct}	–
27.092	16.26	10.23	-
(c) Second order hyperpolarizabity (× 10^{-35} esu)			
γ_{av} = 9.2869			

Table-3
Energy values from Semi-empirical calculations

Heat of formation	0.987 Kcal /mol (4.129 KJ)
Total energy	-4787.552 eV
Electronic Energy	-38163.892 eV
Core-Core repulsion	33376.340 eV
No of filled levels	73
Ionization potential	8.666 eV
Homo-Lumo energies	-8.666 eV, - 1.343 eV.