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NON-LINEAR OPTICAL PROPERTIES STUDY OF TWO HETEROCYCLIC COMPOUNDS

V.T. MUTTANNAVAR[a], RAVEENDRA. MELAVANKI[b*], P. BHAVYA[c], RAVIRAJ KUSANUR[d], N. R. PATIL[e] AND L. R. NAIK[f]

[a]Department of Physics, JSS Science RSH PU College, Vidyagiri Dharwad, Karnataka, India
[b]Dept. Of Physics, M S Ramaiah Institute of Technology Bangalore, Karnataka, India
[c]Dept. Of Physics, New Horizon College of Engineering, Bangalore, Karnataka, India
[d]Department of Chemistry, R.V. College of Engineering, Bangalore, Karnataka, India
[d]Dept. of Physics, B.V.B. College of Engg. & Tech. Hubli, Karnataka, India
[f]Department of Physics, Karnatak Univesity Dharwad, Karnataka, India

ABSTRACT

In an attempt towards understanding the relation between molecular structure-nonlinear optic activity (NLO) among heterocycles, with special reference to the identity, number and position of the heteroatom, semiempirical calculations were carried out. This paper reports the Non-linear optical properties of two heterocyclic compounds namely 3-[2-Oxo-2-(2-oxo-2H-chromen-3-yl)-ethylidene]-1,3-dihydro-indol-2-one (3OCEDI) and Quinolin-8-ol (QL). To understand the Non-Linear Optical properties of coumarin dyes we computed dipole moment (μ), electronic polarizability (α), and the mean was first hyperpolarizability (βo) using B3LYP density functional theory method in conjunction with 6-31G(d, p) basis set.All the calculations were carried out in gas phase and in acetonitrile medium. The optimized geometry of both compounds shows a 3D helical structure. The results indicate that given the same number and type of atoms and double bonds in a molecule, linear conjugation excels over cyclic or crossed conjugation in enhancing hyperpolarizabilities and it seems to be far more critical than a chiral centre.

KEYWORDS: *NLO, 3OCEDI, QL, DFT, dipole moment, polarizability, hyperpolarizability*

RAVEENDRA. MELAVANKI*

**Dept. Of Physics, M S Ramaiah Institute of Technology Bangalore,
Karnataka, India**

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INTRODUCTION

Heterocyclic chemistry is a very important branch of organic chemistry accounting for nearly one-third of modern publications. In fact, two thirds of organic compounds are heterocyclic compounds. A cyclic organic compound containing all carbon atoms in ring formation is referred to as a carbocyclic compound. If at least one atom other than carbon forms a part of the ring system then it is designated as a heterocyclic compound[1].Nitrogen, oxygen and sulfur are the most common heteroatoms but heterocyclic rings containing other hetero atoms are also widely known. An enormous number of heterocyclic compounds are known and this number is increasing rapidly. Accordingly, the literature on the subject is very vast. Heterocyclic compounds may be classified into aliphatic and aromatic. The aliphatic heterocyclics are the cyclic analogues of amines, ethers, thio ethers, amides, etc. Their properties are particularly influenced by the presence of strain in the ring. These compounds generally consist of small (3- and 4-membered) and common (5 to 7 membered) ring systems. The aromatic heterocyclic compounds, in contrast, are those which have a heteroatom in the ring and behave in a manner similar to benzene in some of their properties. Furthermore, these compounds also comply with the general rule proposed by Huckel. Besides the vast distribution of heterocycles in natural products, they are also the major components of biological molecules such as DNA and RNA. DNA is without doubt the most important macromolecule of life. Nucleotides, building blocks of our genes are derivatives of pyrimidine and purine ring structures. Chlorophyll and heme, the oxygen carriers in plants and animals respectively are derivatives of large porphyrin rings. Heterocycles are an important class of compounds, making up more than half of all known organic compounds. Heterocycles are present in a wide variety of drugs, most vitamins, many natural products, biomolecules, and biologically active compounds, including antitumor, antibiotic, anti-inflammatory, antidepressant, antimalarial, anti-HIV, antimicrobial, antibacterial, antifungal, antiviral, antidiabetic, herbicidal, fungicidal, and insecticidal agents[2,3]. Also, they have been frequently found as a key structural unit in synthetic pharmaceuticals and Agrochemicals. Some of these compounds exhibit a significant solvatochromic, photochromic, and biochemi-luminescence properties. Most of the heterocycles possess important applications in materials science such as dyestuff, fluorescent sensor, brightening agents, information storage, plastics, and analytical reagents. The practical application of coumarins and indoles are heavily centered in the pharmaceutical area. Many analogues of coumarins and indole derivatives have been synthesized in an effort to find substances with useful central nervous systems (CNS) activity[4]. Nonlinear optics is an important branch of science which took birth with the advent of highly intense laser systems. It is concerned with the study of the phenomena that result from highly intense light induced modifications in the optical properties of the materials. The field of nonlinear optics (NLO) explores the coherent coupling of two or more electromagnetic fields in a nonlinear medium[5-7]. The discovery of the important nonlinear effect, the second harmonic generation (SHG) introduced a new branch of experimental investigation in the area of laser-matter interaction. Study of nonlinear effects leads us to a new understanding of fundamental light-matter interaction. Implementation of the various NLO effects in the appropriate areas of technologies like optical communication, optical switching, optical data storage demands a detailed knowledge of the NLO processes and their dynamics. Nonlinear optics is observed with lasers which have high degree of spectral purity, coherence and directionality with which atoms and molecules can be irradiated with an electric field that is comparable to interatomic field. These fields are of the order of 10^{10} Vm^{-1} corresponding to an incident light of ~l00GWcm^{-2}. In practice it is possible to observe many nonlinear optical effects at much lower intensities due to enhancement of the nonlinear effect. If the induced diploes in the medium oscillate coherently, the field that they radiate can add together constructively to produce a much larger intensity. This condition is called phase matching and is often used to enhance nonlinear effects. If the frequency of the light lies nears the internal resonance frequency of the oscillating diploes, there is resonance enhancement of the nonlinearity. Multiphoton process is an example of such resonance enhancement[8]. The property of optical nonlinearity can be well understood by considering the dependence of dipole moment per unit volume or polarization P(t) of the material on the strength E(t) of the applied electric field. In the case of linear optics, the induced polarization has a linear dependence on the electric field strength which can be described as

$$P(t) = \chi^{(1)}E(t) \qquad (1)$$

where the constant of proportionality X is the linear optical susceptibility. When the electric field is significantly high, nonlinear interaction occurs and the observed nonlinear optical effects can be described by expressing the polarization P(t) as a power series in the field strength E(t) as

$$P(t)= \chi^{(1)}E(t) +\chi^{(2)}E^{2}(t) + \chi^{(1)}E^{(3)}(t) + \ldots\ldots\ldots \quad (2)$$

$$=P1(t)+P^{2}(t)+P^{3}(t)+ \quad \ldots\ldots\, .. \quad (3)$$

where□$^{(1)}$,□$^{(2)}$ are the second and third order nonlinear optical susceptibilities respectively. The second and third order polarizations can be expressed as

$$P^{2}\ (t) = \chi^{(2)}E^{2}(t) \quad (4)$$

$$P^{3}\ (t) = \chi^{(3)}E^{3}(t) \quad (5)$$

The physical processes that occur due to second and third order polarizations are distinct from each other. Second order nonlinear effects occur only in noncentrosymmetric crystals. They are crystals which do not possess inversion symmetry. Liquids, gases, amorphous solids like glass and even many crystals display inversion symmetry and the □$^{(2)}$ value vanishes for such media and consequently they cannot exhibit second order nonlinear optical effects. On the other hand third order nonlinearity which is described by □$^{(3)}$ can occur both for centrosymmetric and non centrosyrnmetric media. Third order NLO effects are particularly interesting since they have great technological relevance and these effects are present in varying measure of strength in all materials irrespective of symmetry of materials. The third order optical susceptibility is considered to be a complex quantity having both real and imaginary components, $\chi^{(3)}=\chi_{R}^{(3)}+\chi_{1}^{(3)}$. The real and imaginary parts are related to □ and □ respectively where □ is the nonlinear refractive index in $cm^{2}W^{-1}$ and □ is the nonlinear absorption coefficient and is defined as $\alpha(1)=\alpha_{0}+\beta_{1}$. The nonlinear refractive index □ is one of the simplest quantities derived from □$^{(3)}$ and is a very complicated one in its most general form[6-7,9].

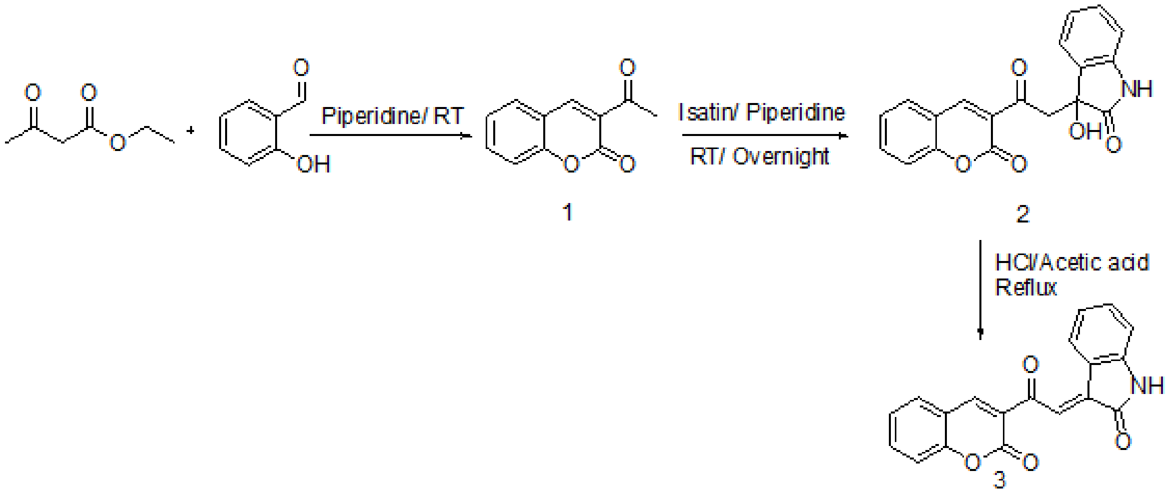
Theory/Computational Method

In the present study, the computations were carried out in ground state and gas phase to compute NLO properties like static dipole moment (μ), anisotropy of polarizability (Δα), mean polarizability (α), and first hyperpolarizabilities (β) by using DFT/B3LYP method with 6-31+G (d, p) basis set via Gaussian 09W [10] program. The Gauss view software database[11]was used for visualization.

MATERIALS AND METHODS

All the chemicals were procured from Sigma-Aldrich, Merck and were used without additional purification. The heterocyclic compound namely 3-[2-Oxo-2-(2-oxo-2H-chromen-3-yl)-ethylidene]-1,3-dihydro-indol-2-one (3OCEDI) is synthesized by standard methods and here we give the synthesis procedure for 3OCEDI.

Synthetic Procedure



Schematic diagram for synthesis of 3OCEDI

Step-I

Preparation of 3-acetyl coumarins

Ethyl acetoacetate (0.5 mole) and salicylaldehde (0.5 mole) ware stirred with 4-5 drops of piperidine. The reaction mixture kept for overnight at room temperature. The resulting yellow coloured solid washed with cold ethanol and dried. The crude product taken to the next step without further purification.

Step-II

Preparation of 3-Hydroxy-3-[2-oxo-2-(2-oxo-2H-chromen-3-yl)-ethyl]-1,3-dihydro-indol-2-one

A mixture of 8-methoxy-3-acetyl coumarin (0.01 mole), isatin (0.01 mole) in absolute alcohol (100 ml) and two drops of piperidine was stirred for half an hour at room temperature. The reaction mixture was allowed to stand for overnight at room temperature. The solid separated was filtered andrecrystallised from alcohol-dioxane mixture to afford the title compound. Further the compound is characterised by ^{1}HNMR 7□93 (*s*, 1H, =CH), 8□70 (*s*, 1H, C4-H), 10□46 (*s*, 1H, NH, D2O exchangable), 7□83 (*d*, 1H, C5-H, *J* = 7□48 Hz), 7□73 (*t*, 1H, C6-H, *J* = 8□3 Hz), 7□40 (*t*, C7-H, *J* = 8□1 Hz), 8□45 (*d*, 1H, C8-H, 7□74 Hz), 6□87 (*d*, 1H, C4□-H, *J* = 7□8 Hz), 6□96 (*t*, 1H, C5□-H, *J* = 7□34 Hz), 7□40 (*t*, 1H, C6□-H, *J* = 7□2) , 7□42 (*d*, 1H, C7□-H, *J* = 7□2 Hz)

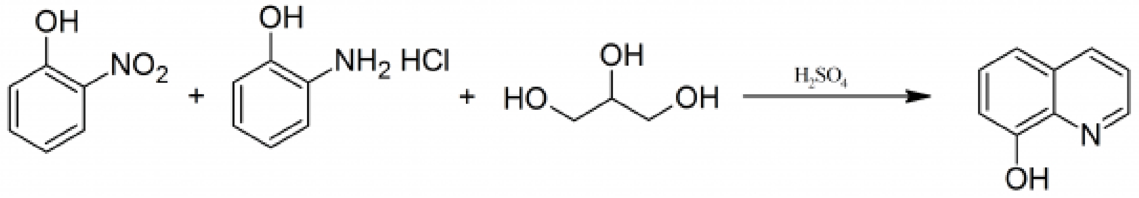
Step-III

Preparation of 3-[2-Oxo-2-(2-oxo-2H-chromen-3-yl)-ethylidene]-1,3-dihydro-indol-2-one

To the solution of 3-(3□-hydroxy-2□-oxoindolo) acetyl coumarin (**2**) (0□01 mole) in acetic acid (25 ml), 0□5 ml of concentrated hydrochloric acid was added. The reaction mixture was warmed on water bath for one hour and cooled to room temperature. The separated orange coloured precipitate was filtered and recrystallised from alcohol dioxane mixture to afford the ketone. Further the compound is characterised by ^{1}HNMR 8□87 (*s*, 1H, C4-H), 9□83 (*s*, 1H, =CH), 7□28–8□16 (*m*, 12H, Ar-H) . Further Quinolin-8-ol is synthesised as follows

Synthetic Procedure

It is prepared by gently boiling, for 3-4 hours, a mixture of 7 g of 2-nitrophenol, 15 g of 2-aminophenol hydrochloride, 25 g of glycerol and 20 g of sulfuric acid. The reaction mixture is diluted with water, made alkaline, and the 8-hydroxyquinoline distilled over in steam. 8-hydroxyquinoline melts at 73-74° C.



Schematic diagram for synthesis of QL

The molecular structures are given in Figure 1 (a) &(b).

RESULTS AND DISCUSSION

In an electric field Ei (ω), the non-linear optical properties of an isolated molecule can be expressed as a Taylor series expansion of the total dipole moment, μ_{tot}, influenced by the field

$$\mu_{tot} = \mu_0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \ldots,$$

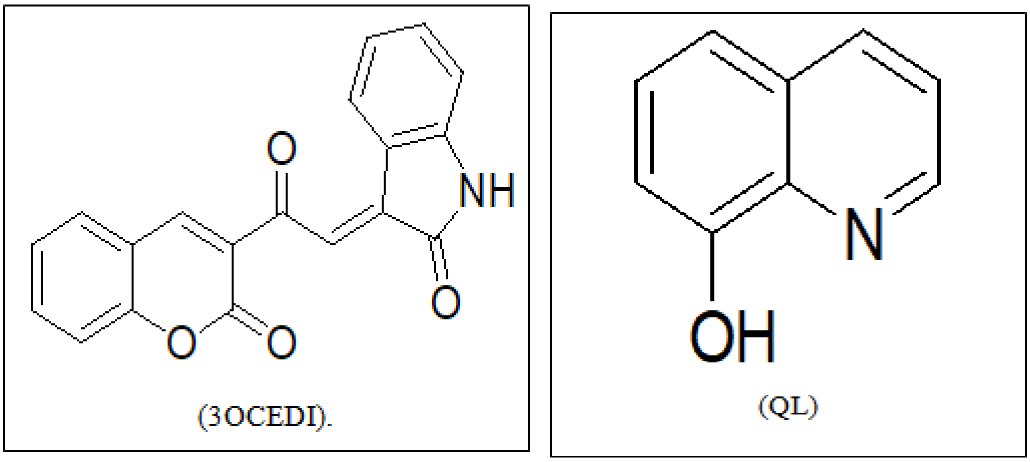
Where μ_0 is the permanent dipole moment, α is the linear polarizability and $\beta_{ijk}$are the first order hyperpolarizability tensor components. In the present discussion, we can compute the μ, α, Δα and (β) as described in the following equations.

1) Dipole moment $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$
2) Static polarizability$\alpha_0 = \alpha_{xx} + \alpha_{yy} + \alpha_{zz}/3\alpha_0 = \alpha_{xx} + \alpha_{yy} + \alpha_{zz}/3$
3) Total polarizability $\Delta\alpha = 2^{-1/2}\ [(\alpha_{xx}-\alpha_{yy})^2 + (\alpha_{yy}-\alpha_{zz})^2 + (\alpha_{zz}-\alpha_{xx})^2 + 6\ \alpha^2_{xz}]^{½}$
4) First order hyperpolarizability $\beta = (\ \beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$

Where $\beta_x = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})$

$\beta_y = (\beta_{yyy} + \beta_{xyy} + \beta_{yxx})$
$\beta_z = (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})$

The obtained values from Gaussian output are recorded in atomic units (a. u). These values have been expressed in terms of standard units by using 1 a.u = 2.5412 Debye for μ, 1 a.u. = $0.1482 X 10^{-24}$ esu for α and 1 a.u. = $8.6393 X 10^{-33}$ esu for β. The total static dipole moment (μ), the anisotropy of the polarizability Δα, the mean polarizability α and the mean first-order hyperpolarizability (β) of the molecule (3OCEDI) are recorded in Table.1. To investigate the NLO properties of organic compounds, urea is being considered as prototypical molecule. For this reason, urea is computed as the same basis level for comparative purpose. The computed total dipole moment of (3OCEDI) is 4.5652D, which is 1.1735 times larger than the that of the urea (μ =3.8903D) and the mean polarizability α of the 3OCEDI molecule is $41.8446 X 10^{-24}$ esu and the first order hyperpolarizability (β) of the 3OCEDI molecule is $10.713 \ X \ 10^{-30}$ esu, which is 17.229 times greater than that of urea (β_{tot}= $0.6218 \ X 10^{-30}$esu). The total static dipole moment (μ), the anisotropy of the polarizability Δα, the mean polarizability α and the mean first-order hyperpolarizability (β) of the molecule (QL) are recorded in Table.2. The computed total dipole moment of QL is 3.1503D, which is 0.8097 times larger than the that of the urea (μ =3.8903D) and the mean polarizability α of the 3OCEDI molecule is $17.2847 X 10^{-24}$esu and the first order hyperpolarizability (β) of the QL molecule is $2.6092 X 10^{-30}$ esu, which is 4.1962 times greater than that of urea (β_{tot} = $0.6218 \ X 10^{-30}$esu). The computed total dipole moment of (3OCEDI) is 1.1735 times larger and the mean polarizability α of the 3OCEDI molecule is $41.8446 X 10^{-24}$ esu and the first order hyperpolarizability (β) of the 3OCEDI molecule is 17.229 times greater than that of urea. Whereas, the computed total dipole moment of QL is 0.8097 times larger than the that of urea and the mean polarizability α of the QL molecule is $17.2847 X 10^{-24}$ esu and the first order hyperpolarizability (β) of the QLmolecule is 4.1962 times greater than that of urea.



(a) (b)

Figure 1
(a) The Molecular structures of (3OCEDI)
(b) (QL)

Table 1
Electric dipole moment, polarizability and first hyper polarizability of 3-[2-Oxo-2-(2-oxo-2H-chromen-3-yl)-ethylidene]-1,3-dihydro-indol-2-one (3OCEDI).

	a.u	esu(x10^{-24})		a.u	esu(x10^{-33})
α_{xx}	471.8176	69.92336	β_{xxx}	636.8202	5501.6807
α_{xy}	-1.6312	-0.2417	β_{yxx}	-379.3551	-3277.3625
α_{yy}	249.5963	36.9901	β_{xyy}	269.5523	2328.7431
α_{xz}	-13.3665	-1.9809	β_{yyy}	-313.8070	-2711.0728
α_{yz}	2.1573	0.3197	β_{zxx}	-181.5326	-1568.3145
α_{zz}	125.6429	18.6202	β_{xyz}	-35.9864	-310.8973
α_0	282.3523	41.8446	β_{zyy}	32.6494	282.0679
$\Delta\alpha$	304.6765	45.1530	β_{xzz}	36.4990	315.32581
μ_x	0.5255		β_{yzz}	-96.5877	-834.4501
μ_y	-1.6502		β_{zzz}	-9.8478	-85.0780
μ_z	-0.4774		β_0	1240.12	10.713 X 10^{-30}
μ	1.7965	4.5652 Debye			

Table 2
Electric dipole moment, polarizability and first hyper polarizability of Quinolin-8-ol (QL)

	a.u	esu(x10^{-24})		a.u	esu(x10^{-33})
α_{xx}	153.0112	22.6762	β_{xxx}	163.4129	1411.7730
α_{xy}	18.9872	2.81390	β_{yxx}	43.1923	373.1512
α_{yy}	128.1448	18.9910	β_{xyy}	86.1881	744.6048
α_{xz}	-11.3290	-1.6789	β_{yyy}	-65.1239	-562.6249
α_{yz}	15.5626	2.3063	β_{zxx}	-22.7399	-196.4568
α_{zz}	68.7381	10.1869	β_{xyz}	9.3370	80.6651
α_0	116.6313	17.2847	β_{zyy}	-18.5253	-160.0456
$\Delta\alpha$	77.5226	11.4888	β_{xzz}	21.2370	183.4728
μ_x	0.4088		β_{yzz}	-50.1435	-433.2047
μ_y	-0.7154		β_{zzz}	-71.2957	-615.9449
μ_z	-0.9262555		β_0	302.0231	2.6092 X 10^{-30}
μ	1.2397	3.1503 Debye			

CONCLUSIONS

From above findings, we can conclude that 3OCEDI has higher NLO applicability while both 3OCEDI and QL molecule may be studied in future for detailed nonlinear optical properties.

AUTHOR CONTRIBUTION STATEMENT

First author V.T. Muttannavar: He is the research student who's contribution is conduction of experiment and preparation of manuscript.Sdcond author Raveendra. Melavanki is the corresponding Author of this manuscript. He has reviewed the article.Third author P. Bhavya is the research student who's contribution is to synthesize the title molecules. Fourth author Raviraj. Kusanur is the chief chemist who's contribution is to supervise the synthesis and yield and checked all the chemical tests. Fifth author N. R. Patil contribution is to carry out the DFT calculations using Gaussian software 09. Sixth author L. R. Naik is research supervisor of first author and helped in preparation of the manuscript.

CONFLICT OF INTEREST

Conflict of interest declared none.

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