Nano World Journal

https://doi.org/10.17756/nwj.2023-s5-044

Research Article

Open Access

Quantum Mechanical Density Functional Approach for the Studies of Nonlinear Optical and Reactivity Parameter of 5O.5 Liquid Crystal

Adrish Chakraborty[1], Ayon Bhattacharjee[1] and Debanjan Bhattacharjee[2*]

[1]Department of Physics, National Institute of Technology Meghalaya, Shillong, Meghalaya, India
[2]Department of Physics, Manipal University, Jaipur, Rajasthan, India

***Correspondence to:**
Debanjan Bhattacharjee
Department of Physics,
Manipal University,
Jaipur, Rajasthan, India.
E-mail: bhattacharjee8@gmail.com

Received: October 20, 2023
Accepted: December 21, 2023
Published: December 27, 2023

Citation: Chakraborty A, Bhattacharjee A, Bhattacharjee D. 2023. Quantum Mechanical Density Functional Approach for the Studies of Nonlinear Optical and Reactivity Parameter of 5O.5 Liquid Crystal. *NanoWorld J* 9(S5): S227-S230.

Copyright: © 2023 Chakraborty et al. This is an Open Access article distributed under the terms of the Creative Commons Attribution 4.0 International License (CCBY) (http://creativecommons.org/licenses/by/4.0/) which permits commercial use, including reproduction, adaptation, and distribution of the article provided the original author and source are credited.

Published by United Scientific Group

Abstract

This article emphasizes the nonlinear optical properties of 5O.5 liquid crystal compound. Generally, 5O.5 is a Schiff based compound and it shows different liquid crystalline phases with the variation of temperature. With changing temper-ature, the phases of the liquid crystal changes and it gives various important information about the ordering of the liquid crystal. The density functional theory (DFT) approach has been used to find the different parameters such as reactivity parameters and structural pa-rameters of the compound. Dipole moments, polarizability and non-linear optical (NLO) properties are essential to understanding different optical and physical behaviors of the liquid crystal are also reported in this article. The NLO properties of the compounds possess many properties which is useful for NLO based applications.

Keywords

Non-linear optical, Density functional theory, Liquid crystal

Introduction

Liquid crystals are partially organized fluids that exist between the states of crystalline solid and isotropic liquid. This is also known as a mesophase. They tend to have a regular alignment in one or more dimensions while maintaining the ability to move and flow like a liquid. Liquid crystals are anisotropic in nature, and as a result of their anisotropy, they have distinct optoelectrical properties in comparison to other materials [1-9]. The peculiar nature of the chemical has sparked the interest of experts, which are currently researching the properties of liquid crystals. Most calamitic liquid crystalline compounds are uniaxial in nature, although some researchers are currently focusing on bent-core or biaxial liquid crystalline compounds [1-5].

Depending on temperature and pressure, liquid crystals can exist in a variety of phases. Nematic, smectic, and cholesteric phases are the most common. The molecule alignment in a specific direction without a defined positional order distinguishes nematic liquid crystals. In layers, smectic liquid crystals have both directional alignment and positional order. Cholesteric liquid crystals have a helical structure with an axis that rotates.

Because of their exceptional properties that bridge the gap between the liquid and solid phases, liquid crystals have piqued the scientific community's curiosity. Because of its unusual mix of solid-like organization and fluid-like movement, liquid crystals are applied in a wide range of academic subjects [1-3]. Nanotechnology, LCD (liquid crystal display) technology, holography, optical fiber technology, optoelectronics, tunable lenses, optical switches, biosensors, and drug delivery systems are among the disciplines described above [4-10]. Display

technologies are one of the most important applications of liquid crystals. An electric field is used to adjust the alignment of liquid crystal molecules in LCD sections. The transmission of light through the liquid crystal layer may be controlled by modifying the mo-lecular alignment, allowing for the formation of images and text on screens.

The electrical configuration of molecules and materials can be determined using DFT, a powerful computational method. The goal is achieved by employing the concept of electronic density as a theoretical framework for solving the Schrodinger equation for systems containing many interacting particles. The use of DFT to the study of liquid crystal energy characteristics, electronic transitions, and optical properties has greatly improved our understanding of their NLO properties.

In this study, DFT simulations are utilized to analyze the NLO properties of liquid crystals. We would like to understand the underlying principles regulating NLO behavior in various liquid crystal systems using DFT's capacity to anticipate. The thorough analysis of these characteristics will improve our understanding of liquid crystals while also providing designers of modern photonic devices with fresh ideas for improving their usefulness and efficiency.

Polarizability and hyperpolarizability in liquid crystals are regulated by factors such as molecular form, size, and arrangement within the material. Researchers may build liquid crystal materials with precise optical properties by regulating these parameters, making them advantageous in a variety of applications such as LCDs and electro-optic devices.

Polarizability and hyperpolarizability are critical factors for understanding liquid crystal optical behavior and designing new technologies based on their unique qualities. To describe the behavior of liquid crystal materials to external electric fields and light, researchers frequently use techniques such as optical spectroscopy, electric field-induced birefringence measurements, and nonlinear optical measurements.

Gaussian 09, a renowned and flexible quantum chemistry software program, is used in this study to carry out accurate and reliable DFT calculations. By using theoretical simulations, our goal is to definitively link the molecular structure to the nonlinear optical response of liquid crystals. The advancement of novel applications in the field of nonlinear optics will be aided by this research paper [11-14].

Materials and Methods

The nO.m family of liquid crystals under investigation is made up of calamitic-shaped molecules that exhibit nematic order. This arrangement is defined by the parallel alignment of the long axes of the molecules while preserving their fluid-like motion. Calamitic molecules are made up of connecting elements, terminal segments, and core units. A pair of benzene rings joined by a C=N bond make up the basic elements of this structural arrangement. Hydrocarbon chain terminal segments make up terminal segments. The core is directly connected to one terminal, while the other terminal is connected to the core via an oxygen connection.

The first part of our research involves running DFT simulations to find the optimum structures of nO.m liquid crystals. We employ the widely utilized B3LYP functional, which combines Becke's three-parameter exchange functional with Lee, Yang, and Parr's correlation functional. Because of its ability to balance accuracy and computing cost, the 6-31G basis set was chosen. These calculations are carried out with the assistance of the software package Gaussian 09, which has a reputation for reliability in quantum chemical simulations.

Following the optimization of the structures, our research focuses on the NLO capabilities of the 5O.5 calamitic liquid crystal. Our research focuses on important NLO phenomena such as dipole moment, polarizability, and hyperpolarizability [1-5, 11, 13].

Results and Discussion

A technique described previously was utilized to manufacture the sample 5O.5 used in this work. Figure 1 and table 1 show the chemical makeup and phase changes of the liquid crystalline molecule 5O.5.

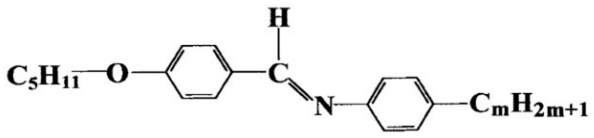

Figure 1: Molecular structure of the compound 5O.5, n = 5, m = 5.

Figure 2: Optimized structure of 5O.5 liquid crystalline molecule.

Table 1: Phase transition temperature of 5O.5 liquid crystal compound.

5O.5	Temperature
C-G	28 °C
G-SmF	47 °C
SmF-SmC	49 °C
SmC-SmA	53.1 °C
SmA-N	54.4 °C
N-I	78.8 °C

Geometric structure

The optimal structure of 5O.5 was found using the DFT approach with a functional B3LYP/6-31G(d,p) basis set, as illustrated in figure 2. The lowest energy of 5O.5 is computed and discovered to be -1025.152345 Hartree.

NLO and reactivity analysis

The energy gap of the molecule is critical for understand-

ing its stability and reactivity. Higher levels of the compound's energy gap (Eg) often behave like a hard solid. In general, the energy gap of nO.m series liquid crystal compounds is lower. Lower gap values need less energy to interact with the molecule and are therefore easier to polarize using electric and magnetic fields. And this is highly beneficial for a variety of applications.

NLO-based novel applications include optical computing, optical storage, and the creation of higher-order harmonic signals, among others. In the presence of a sufficiently powerful light source, molecules with anisotropic polarizability experience a transition from a state of high potential energy to a state of low potential energy. When there is a π bridge separating an electron donor group and an electron acceptor group, a key structural criterion for a molecule to show optical nonlinearity is met.

Due to their elongated conjugated molecular structure and propensity to align along the direction of an applied electric field, liquid crystalline molecules exhibit strong optical nonlinear effects. Here, we compute the B3LYP/6-31G(d) level components of the polarizability and hyperpolarizability tensors. DFT calculations are used to determine the total molecular dipole moment, total polarizability, asymmetry parameters, anisotropic polarizability, and first-order hyperpolarizability, which are all presented in table 2 [15-19].

In addition to the asymmetry parameter (η), isotropic polarizability (iso), anisotropic polarizability (Δ_α), total molecular dipole moment (μ_{total}), total polarizability (α_{total}), and first-order hyperpolarizability (β_o), table 2 shows the reduced components of the polarizability and hyperpolarizability tensors [18]. The computation has been carried out using B3LYP functionals. The components of dipole moment, polarizability, and hyperpolarizability have larger magnitudes, as shown by the data in table 2. This is due to the compound's narrower energy gap. The molecule then displays enhanced NLO properties, which are calculated using the formulas below:

$$\mu_{total} = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \quad (1)$$

$$\alpha_{total} = \frac{1}{\sqrt{2}} \text{ x } \sqrt{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xy}^2 + 6\alpha_{xz}^2 + 6\alpha_{yz}^2} \quad (2)$$

$$\eta = \frac{\alpha_{xx} - \alpha_{zz}}{\alpha_{xx} - \alpha^{iso}} \quad (3)$$

$$\Delta\alpha = \alpha_{xx} - \frac{\alpha_{yy} + \alpha_{zz}}{2} \quad (4)$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \quad (5)$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \quad (6)$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz} \quad (7)$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz} \quad (8)$$

$$\beta_0 = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (9)$$

Table 2: Asymmetry parameter (η), isotropic polarizability (iso), anisotropic polarizability (Δα), total molecular dipole moment (μ_{total}), total polarizability (α_{total}), and first-order hyperpolarizability (β_0).

Parameters		DFT (6-31(d))
Dipole moment (μ) (in Debye)	μ_x	-2.5501
	μ_y	1.7023
	μ_z	-1.0662
	μ_{total}	3.2462
Polarizability (in Debye-Å)	α_{xx}	-122.1418
	α_{yy}	-153.2826
	α_{zz}	-148.9178
	α^{iso}	47.14913
	Δα	-119.9594
	η	-0.15816
	α_{total}	29.20406
Hyperpolarizability (in Debye-Å2)	β_{xxx}	-191.4202
	β_{xxy}	14.5236
	β_{xyy}	-12.9313
	β_{yyy}	-8.8921
	β_{XX}	-10.1077
	β_{xyz}	-4.3327
	β_{yyz}	1.1587
	β_{xzz}	2.3508
	β_{yzz}	-0.9297
	β_{zzz}	2.7666
	β_x	-202.0007
	β_y	4.7019

Table 2 shows asymmetry parameter (η), isotropic polarizability (iso), anisotropic polarizability (Δα), total molecular dipole moment (μ_{total}), Total polarizability (α_{total}), and first-order hyperpolarizability (β_0).

Conclusion

NLO studies of the 5O.5 molecule's lowest energy configuration have provided information about its intramolecular activity. The molecule has a nonlinear structure, which was determined by looking at its ideal shape, and the higher value of its hyperpolarizability indicated that it has significant nonlinear features. In the fields of optics, materials science, and liquid crystals, the phrases polarizability and hyperpolarizability are fundamental concepts. Liquid crystals are rare materials that combine the properties of crystalline solids and liquids. Their molecular structure, which lets them to respond to external electric fields, makes them valuable in display technologies, optical devices, and other uses.

Acknowledgements

None.

Conflict of Interest

None.

References

1. Pramanik A, Das MK, Das B, Żurowska M, Dąbrowski R. 2015. Electro-optical properties of a new series of fluorinated antiferroelectric orthoconic liquid crystalline esters. *Liq Cryst* 42(3): 412-421. https://doi.org/10.1080/02678292.2014.996792
2. Nandi R, Vikram K, Singh SK, Singh B, Singh RK. 2013. Synthesis and mesomorphic investigation of calamitic liquid crystalline system ethyl-[4-(4′-decyloxy) benzoyloxy]-benzoate (4-EDBB): a temperature dependent micro-Raman study and DFT calculations. *Vib Spectrosc* 69: 40-48. https://doi.org/10.1016/j.vibspec.2013.09.002
3. Nandi R, Singh HK, Singh SK, Singh B, Singh RK. 2014. Mesomorphic, micro-Raman and DFT studies of new calamitic liquid crystals; methyl 4-[4-(4-alkoxy benzoyloxy)benzylideneamino]benzoates. *Spectrochim Acta A Mol Biomol Spectrosc* 128: 248-256. https://doi.org/10.1016/j.saa.2014.02.112
4. Lin F, Tong X, Wang Y, Bao J, Wang ZM. 2015. Graphene oxide liquid crystals: synthesis, phase transition, rheological property, and applications in optoelectronics and display. *Nanoscale Res Lett* 10: 1-6. https://doi.org/10.1186/s11671-015-1139-1
5. Tadokoro C, Nihira T, Nakano K. 2014. Minimization of friction at various speeds using autonomous viscosity control of nematic liquid crystal. *Tribol Lett* 56: 239-247. https://doi.org/10.1007/s11249-014-0404-2
6. Cognard J. 1990. Lubrication with Liquid Crystals. In Biresaw G (ed) Tribology and the Liquid-Crystalline State. American Chemical Society Symposium Series, Washington, DC, pp 1-47.
7. Zhang LP, Wang XL, Pang QQ, Huang YP, Tang L, et al. 2017. Solvent-responsive floating liquid crystalline-molecularly imprinted polymers for gastroretentive controlled drug release system. *Int J Pharm* 532(1): 365-373. https://doi.org/10.1016/j.ijpharm.2017.09.008
8. Guo C, Wang J, Cao F, Lee RJ, Zhai G. 2010. Lyotropic liquid crystal systems in drug delivery. *Drug Discov Today* 15(23-24): 1032-1040. https://doi.org/10.1016/j.drudis.2010.09.006
9. Mo J, Milleret G, Nagaraj M. 2017. Liquid crystal nanoparticles for commercial drug delivery. *Liq Cryst Rev* 5(2): 69-85. https://doi.org/10.1080/21680396.2017.1361874
10. Carlton RJ, Hunter JT, Miller DS, Abbasi R, Mushenheim PC, et al. 2013. Chemical and biological sensing using liquid crystals. *Liq Cryst Rev* 1(1): 29-51. https://doi.org/10.1080/21680396.2013.769310
11. Govindarajan M, Karabacak M. 2012. Spectroscopic properties, NLO, HOMO–LUMO and NBO analysis of 2, 5-Lutidine. *Spectrochim Acta A Mol Biomol Spectrosc* 96: 421-435. https://doi.org/10.1016/j.saa.2012.05.067
12. Thamarai A, Vadamalar R, Raja M, Muthu S, Narayana B, et al. 2020. Molecular structure interpretation, spectroscopic (FT-IR, FT-Raman), electronic solvation (UV–Vis, HOMO-LUMO and NLO) properties and biological evaluation of (2E)-3-(biphenyl-4-yl)-1-(4-bromophenyl) prop-2-en-1-one: experimental and computational modeling approach. *Spectrochim Acta A Mol Biomol Spectrosc* 226: 117609. https://doi.org/10.1016/j.saa.2019.117609
13. Avcı D, Başoğlu A, Atalay Y. 2010. *Ab initio* HF and DFT calculations on an organic non-linear optical material. *Struct Chem* 21: 213-219. https://doi.org/10.1007/s11224-009-9566-1
14. Bhattacharjee D, Dabrowski R, Bhattacharjee A. 2018. Theoretical investigation of nonlinear optical and vibrational properties of two liquid crystalline compounds. *J Mol Liq* 255: 80-92. https://doi.org/10.1016/j.molliq.2018.01.157
15. Schmitt K, Herr RP, Schadt M, Fünfschilling J, Buchecker R, et al. 1993. Strongly non-linear optical ferroelectric liquid crystals for frequency doubling. *Liq Cryst* 14(6): 1735-1752. https://doi.org/10.1080/02678299308027712
16. Ara MM, Dehghani Z. 2019. Improvement of the third order nonlinear optical properties of nematic liquid crystal under the influence of different compositional percentage of doped SWCNT and the external electric field. *J Mol Liq* 275: 281-289. https://doi.org/10.1016/j.molliq.2018.11.069
17. Alejo-Molina A, Hardhienata H. 2016. The role of Kleinman symmetry in the simplified bond hyperpolarizability model. *IOP Conf Ser Earth Environ Sci* 31(1): 012020. https://doi.org/10.1088/1755-1315/31/1/012020
18. Chaitanya K, Ju XH, Heron BM, Gabbutt CD. 2013. Vibrational spectra and static vibrational contribution to first hyperpolarizability of naphthopyrans—a combined experimental and DFT study. *Vib Spectrosc* 69: 65-83. https://doi.org/10.1016/j.vibspec.2013.09.010
19. Rao NV, Pisipati VG. 1983. Phase-transition studies in polymesomorphic compounds. 1. Density studies in N-(pn-hexyloxybenzylidene)-pn-butylaniline. *J Phys Chem* 87(5): 899-902. https://doi.org/10.1021/j100228a040