Canadian Journal of Pure and Applied Sciences
Vol. 10, No. 1, pp. 3771-3775, February 2016
Online ISSN: 1920-3853; Print ISSN: 1715-9997
Available online at www.cjpas.net

MOLECULAR STRUCTURE, ELECTRONIC AND SPECTRAL STUDIES OF COUPLED LIQUID CRYSTAL

S. Deepthi[1], Priyanka Bhatt[2], J. Anjali[2] and *Ch. Ravi Shankar Kumar[1]
[1]Department of Physics, GITAM University, Visakhapatnam, India
[2]Department of Chemistry, GITAM University, Visakhapatnam, India 530045

ABSTRACT

Optimization of supramolecular crystals with self assembling is assessed in coupled mesogenic liquid crystal reveal interesting characteristics in computation studies with Gaussian 03, Revision E.01 using MP2, extended 3-21G (d) basis set. Adsorption of liquid crystal CS with IO focuses interesting characteristic structural features with low shear. Studies of thermal and spectroscopic studies signify the former in confirmed transition peaks with altered energies and later ensured bonding with sharp peaks of stretching and bending vibrations in functional and fingerprint regions influenced on coupling. Interestingly the vital play of potential energies with shear gained importance in stable molecular configuration, dipole moment, atomic charges, moment of inertia, critical velocity, highest occupied molecular orbital energies and lowest unoccupied molecular energies in formation of complex.

Keywords: Moller–Plesset, DFT, molecular structure, electronic, Gaussian, supramolecular.

INTRODUCTION

Most studies with liquid crystals are proto type self organized (Brian *et al*., 2012), soft (Alejandro, 2010), supramolecular materials (Takashi Kato, 2003) are anisotropic functional materials (Pankaj *et al*., 2013) are organic and introduction of nano material has interesting features is subject of study. These mesogenic (Pankaj *et al*., 2013; Zakerhamidi *et al*., 2014; Rejith and Krishnan, 2013; Martin *et al*., 2010) anisotropic materials with nano particle coupled has emerged fascinating area of research in applications with metals (Dominic *et al*., 2013) semiconductors (Byron *et al*., 2014), ferro electrics (Hakobyan *et al*., 2014) and carbon related particles (Dhrubajyothi *et al*., 2014).These inherently possess structural features with interactions due to hydrogen bonding, metal coordination, hydrophobic forces, vanderwaalls forces, pi-pi and electrostatic interactions gained importance in molecules of longer length with ordering and mobility due to self organization with optimized geometry. Dipole moment, moment of inertia, Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO) energies (Subhapriya *et al*., 2014) are studied with enhanced properties of nano particles in liquid crystals. Improved physical, electrical and electro-optical properties of liquid crystals (Chaudhary *et al*., 2012) are referred with incorporation of metal into mesogenic. DFT frame work with quantum calculations is essential to model large systems providing promising approach for accurate parameters are currently realized. Optimization of structure in present observation of liquid crystal with nano particle (CSIO) possess significant impact on molecular properties further in study of spectral and electronic properties with minimum energy. Gaussian 03,Revision E.01 utilizes ab initio with MP2 extended 3-21G basis set (De Luca *et al*., 2008). Nano particle (IO) (Wei Wu *et al*., 2008) has implications on conformational studies with mesogenic CS (Vadim and Valdas, 2009).

*Corresponding author e-mail: rskchaval@gmail.com

MATERIALS AND METHODS

Cholestryl Stearate (CS) and iron oxide (IO) were purchased from Sigma Aldrich are used as such. Ultrasonication (Siva *et al*., 2013) is performed with PCi analytics 250 W ultrasonic processor with a 12 mm probe operating at a fixed frequency of 50 Hz ACsupply; 220V is synthesis route for homogenization with 100 mg of Cholestryl Stearate and 0.08 mg of iron oxide nano powder was dissolved in 30 ml of ethanol solution. The complex (CSIO) was dried for four days with yield of 90%. Chemical structures of CS Figure 1 and IO Figure 2 with bonded structure of complex in Figure 3 with illustrated optimized geometry in Figure 4.

Experimental Techniques

Confirmed transition temperatures @ 1^0C min^{-1} is carried with CS and CSIO with differential scanning calorimetry (Mettler-Toledo) and textures observed with polarizing optical microscope (Olympus BX-51) at same rate. The spectral analysis involves finger print and functional groups were identified with vibration assignments of Fourier Transform Infrared Spectroscopy (Thermo-Nicolet 6700). Absorption

and isolation of these individuals were recorded in confirmation of energies with UV spectrophotometer (Analytikjena SPECORD S-600).

Computational Techniques

Optimized structures of combining rigid geometry (CS) with spacer lead to large self assembled complex (CSIO) with vital features inherently provide distribution of atomic charges, bond lengths, bond angles, dipole moments and energies involved in frontier orbital's. Elucidation of optimized geometry of individuals and complexes was performed by *ab initio* method to obtain the stable molecular conformation using Gaussian 03, Revision E.01 using Moller–Plesset perturbation theory (MP2) with an extension of 3-21G basis set.

RESULTS AND DISCUSSION

Molecular properties derived from computation are electronic energies, molecular structures, and vibrational frequencies further with standard molecular coordinates and normal vibration modes of individual atoms within molecular sub fragments. Studies with Moller-Plesset perturbation theory is free from false interaction energies of electrons during their correlation with considerable effect on molecular geometries applicable for long chain molecules as relevant to nano doped molecules with liquid crystals. With 3-21 G (d) basis set in electronic structure calculations as linear combinations of Gaussian functions with a spilt valence basis set of two sets of functions in the valance region provide a more accurate representation of the orbital's in computation. The computed parameters with individuals and complexes are (a) Atomic coordinates (b) atomic distances and angles (c) HOMO/LUMO Eigen values (eV), (d) Mulliken atomic charges (short) and (e) dipole moments.

Atomic coordinates, atomic distances, dipole moments angles and computed parameters of optimized molecule of individuals and complexes listed in Table 1 are the z-matrix descriptions with internal coordinates of each obtained from a line of z-matrix denoting the lowest energy of the structure. The increased bond length signifies the tendency to increase shear influencing rotational parameters dipole moment, moment of inertia and critical velocities due short range forces between iron and oxygen. The presence of higher electronegative oxygen atom and increased molecular mass reduce the rotation along the director favors increased dipole moment, moment of inertia with reduced critical velocity stabilized with the substantial improvement in energy.

Frontier orbital's signifies localization of LUMO energies to a good electrophile site and the localization of HOMO energies to a good nucleophile site with energies depicted in Table 2. A low electron density molecule is nucleophile that attacks the sites of other molecules and former with high electron density. The localization of electron density provides highest occupied molecular orbitals (HOMO) configure molecular with electron donor interactions and lowest unoccupied molecular orbitals (LUMO) with acceptors characterized by LUMO-HOMO energy gap (frontier gap). A low frontier gap suggests the easy surpassing of electron within the individuals or the complexes that enhances the polarizabilty with interaction resulting in high chemical reactivity and low kinetic stability of molecules (Subhapriya *et al*., 2014).

Correlation with differed energy gap (LUMO-HOMO) with corresponding wavelength with UV studies specify reduced gap on complexation (6.974 eV, 450nm) than CS (7.557 eV, 244nm) enabling a proper conjugation with optimized structure. The Mulliken distribution of atomic charges responsible for redistribution due to interaction between fragments vary between 1.675 and 1.632 in IO varies with oxygen from -0.432 to -0.546 and -0.675 to -0.569 for carbon in CSIO is tabulated in Table 3.

The liquid crystal exhibit enantiotropic twisted nematic texture at 71.26^0C confirmed with transition temperature differed by 5^0C in CSIO with decreased energy. Concentration of 1.4% by IO has reduced remarkable effect on the texture. Interpretation of FTIR reveal upward spectral shifts of O-H and CH_3 (~20 cm^{-1}) with and downward shift (~30 cm^{-1}) in finger print region with sharp peaks reveal bonding nature with increased bonding index(BI>1) with mesogenic. Absorption studies of interactions in complex exhibit characteristic wavelength (450 nm) with reduced energy than liquid crystal. Despite experimental studies for transition temperature, texture, enthalpy, associated bonding conformational studies provide significant explanation for attributed changes with optimized geometry depicted in Table 4.

CONCLUSION

Studies with MP2/3-21G basis set reveal significant changes that play vital role in study of molecular structure, electronic and spectral properties. Significant features viz (i) Complex exhibit abrupt change in the dipole moment, moment of inertia and atomic charges. (ii) low frontier gap arises with reduced enthalpy has little influence on shear.(iii)variation in spectral shifts reveal molecular bonding with sharp peaks (iv)Though experimental studies could not reveal change in texture, satisfactory explanation of conformational changes has remarkable effect in molecular, electronic and spectral properties. Computational studies with MP2 succeeded in explaining significantly the interactions for longer structures with optimized geometry.

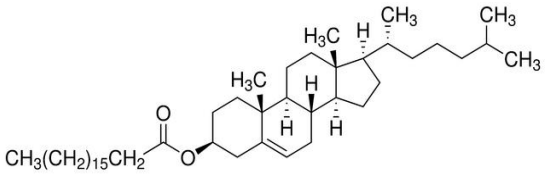

Fig. 1. Molecular Structure of CS.

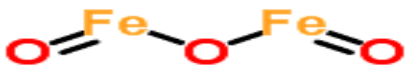

Fig. 2. Molecular Structure of IO.

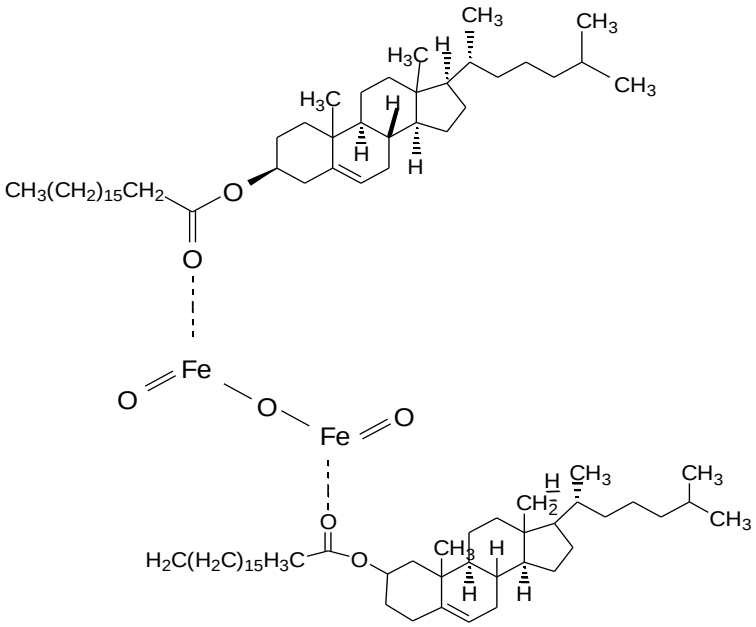

Fig. 3. Bonded structure of complex.

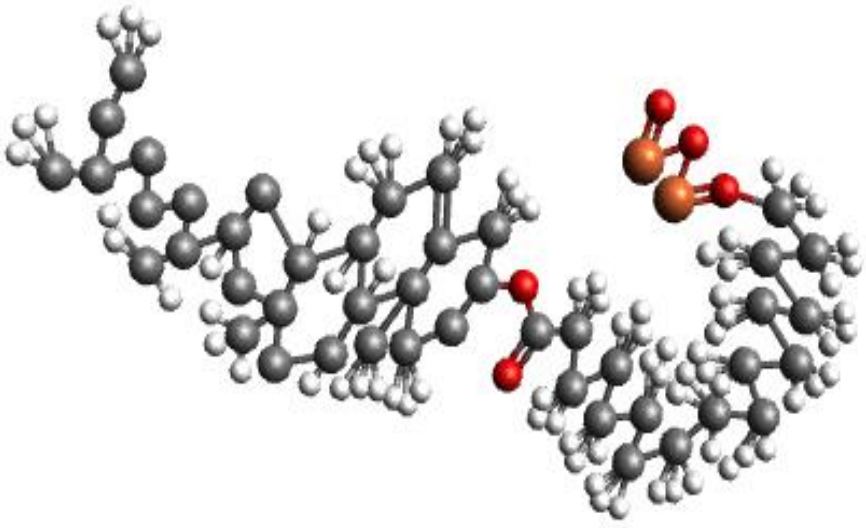

Fig. 4. Optimized structure of complex.

Table 1. Computational parameters.

Name of the compound	Bond length (A^0)	Bond angle$^{(0)}$	Dipolemoment (D)	Moment of inertia ($1X10^{-45}$) $kg.m^2$	Critical velocity ω (rad/s)
CS	1.395	152.2	4.8635	101.2	9.9
CSIO	1.667	153.4	5.98754	110.5	9.3
IO	3.568	80.46	6.7070	23.7	117.1

Table 2. Energies of individuals and complex.

Name of the compound	LUMO(eV)	HOMO(eV)	LUMO-HOMO(eV)
CS	-1.879	-5.678	7.557
CSIO	-1.978	-4.987	6.974
IO	-0.422	-2.159	4.879

Table 3. Atomistic distribution of individuals and Complex.

Name of the compound	Atomic charges(upper limit)				Atomic charges(lower limit)			
	O	C	H	Fe	O	C	H	Fe
CS	-0.432	-0.675	-0.92		-0.38	-0.54	-0.14	
CSIO	-0.546	-0.569	-083		-0.58	-0.86	-0.89	
IO				1.675				1.632

Table 4. Conformational studies of individual and complex.

Name of the compound	DSC(phase(^{0}C) $[\Delta H\ J/g]$		FTIR(cm^{-1})				UV(abs) (nm)
			O-H	CH_3 (stretching)	CH_3 (bending)	Fe	
CS	N(71.26) (2.43)	C(61.3) (71.47)	3449 (2.09)	2905 (2.79)	1377 (2.35)	1397 (1367)	0.3(244)
CSIO	N(76.49) (1.64)	C(71.9) (1.96)	3469 (2.07) BI:1.09	2924 (2.795) BI:0.99	1343 (1.725) BI:1.36	1075 (1012)	0.8(450)

ACKNOWLEDGEMENTS

The authors acknowledge Spectroscopy/Analytical Test Facility Entrepreneurship Centre, Society for Innovation and Development, Indian Institute of Science, Bangalore for providing experimental facilities and Prof. K. Ramakrishna Deptartment of Chemistry, GITAM University Visakhapatnam for technical support of Gaussain**.**

REFERENCES

Alejandro, DR. 2010. Liquid crystal models of biological materials and processes. Soft Matter. 6(15):3402-3429.

Brian, RW. and Douglas, LG. 2012. Nanoporous polymer materials based on self-organized, bicontinuous cubic lyotropic liquid crystal assemblies and their applications. Polymer Journal. 44:461-468.

Byron, HF., Zachary, A., Kyle, BJ., Papanikolas, M. and Thomas, JM. 2014. Driving Force Dependent, Photo induced Electron Transfer at Degenerately Doped, Optically Transparent Semiconductor Nanoparticle Interfaces. Jor. Am. Chem. Soc. 136(45):15869-15872.

Chaudhary, A., Malik, PM. and R. and Raina, KK. 2012. Electrooptic and dielectric studies of silica nano particle doped ferro electric liquid crystal in Sm C Phase Phase Transitions. 85(3):244-254.

Dominic, B., Franziska, M., Martin, F., Steffen, K., Richard, K., Dietmar, B., Martin, W., Elie, P. and Stefano, P. 2013. Transition-Metal-Doped Zinc Oxide Nanoparticles as a New Lithium-Ion Anode Material. Chem. Mater. 25(24):4977-4985.

Dhrubajyothi, B., Hyean-Yeol, P., Min-Sik Kim, Hyuck-Soo choi, Shaukatali, NI. and Jong-Sung, Y. 2014. Nitrogen-Doped Carbon Nano particles by Flame Synthesis as Anode Material for Rechargeable Lithium- Ion Batteries. Langmuir. 30:318-324.

De Luca, G., Egan, M., Emsley, JW., Foord, EK., Longeri, M. and Pileio, G. 2008. Do the molecules which form discotic liquid crystals have disc-like structures? The conformation of a simple model compound, 1, 2- dihydroxydiacetylbenzene, determined from the NMR spectra of samples dissolved in liquid crystalline Solvents. Liquid Crystals. 35(2):205-212.

Hakobyan, MR., Alaverdyan, RB., Hakobyan, RS. and Yu, S. 2014. Chilingaryan, Enhanced physical properties of nematics doped with ferroelectric nano particles. Armenian Journal of Physics. 7(1):11-18.

Martin, U., Brandy, K., Hao, Q., Torsten, H. and Heinz, SK. 2010. Electro convection in nematic liquid crystals *via* nanoparticle doping Nanoscale. 2(7):1118-1121.

Pankaj, KT., Abhishek, KM., Kamal, KP. and Rajiv, M. 2013. Study on Dielectric and Optical Properties of ZnO Doped Nematic Liquid Crystal in Low Frequency Region. Chemical Rapid Communications. 1(1):20-26.

Pankaj, KT., Abhishek, KM., Shashwati, M., Swadesh, KG. and Rajiv, M. 2013. Improved dielectric and electro-optical parameters of ZnO nano-particle (8% Cu2+) doped nematic liquid crystal. Journal of Molecular Structure. 1035:371-377.

Rejith, SG. and Krishnan, C. 2013. Synthesis of cadmium-doped copper oxide nanoparticles Optical and structural Characterizations. Advances in Applied Science Research. 2(4):103-109.

Subhapriya, P., Sadasivam, K., Madhu, MML. and Vijayanand, PS. 2014. Experimental and theoretical investigation of p-n alkoxy benzoic acid based liquid crystals - a DFT approach. Spectro Chemica Acta. 123:511-523.

Siva, VKT., Karthikeyeni, S., Vasanth, S., Arul, G., Bupesh, G., Ramesh, R., Manimegalai, M. and Subramanian, P. 2013. Synthesis of Silver-Doped Zinc Oxide Nanocomposite by Pulse Mode Ultrasonication and Its Characterization Studies. Jor. of Nanoscience. Id. 785064-7.

Takashi, K. 2000. Molecular Self-Assembly Organic Versus Inorganic Approaches structure and Bonding Part-1Springer-Verlag Berlin Heidelberg. 96:95-146.

Vadim, M. and Valdas, V. 2009. Research of Tribological Properties of Mineral Motor Oil with Cholesteryl Stearate Additive. Solid State Phenomenon. 147-149:552-557.

Wei, W., Quanguo, H. and Changzhong, J. 2008. Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalization Strategies. Nanoscale Res Lett. 3:397-415.

Zakerhamidi, MS., Shoarinejad**,** S. and Mohammadpour, S. 2014. Fe_3O_4 nanoparticle effect on dielectric and ordering behavior of nematic liquid crystal host. Jor. Mol. Liquids. 191:16-19.

Received: Oct 2, 2015; Accepted: Nov 30, 2015