The Vibrational Spectroscopy of 8OCB (4-n-octyloxy-4′-cyanobiphenyl) and 9OCB (4'-nonyloxy-biphenyl-4-carbonitrile) Liquid Crystal Molecules study using Density Functional Theory

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Abstract

In this article, we deal with IR and Raman spectroscopy of 8OCB (4-n-octyloxy-4′-cyanobiphenyl) and 9OCB (4'-nonyloxy-biphenyl-4-carbonitrile) liquid crystal molecules by using density functional theory with basis set 6-31G(d,p). Here due to the C-N group, molecule shows different vibrations at different frequencies. On increasing the terminal chain length, molecule orients itself in the parallel arrangement and this leads to the stacking and hence charge propagation is possible. The different types of spectral studies are performed here like IR (infrared) spectroscopy and RAMAN spectroscopy so that we can get more information regarding molecular analysis.

Keywords: Liquid crystal, DFT, 8OCB, 9OCB, Spectroscopy

Introduction

Besides the three states of matter solid, liquid and gas, one extraordinary intermediate phase exists which resembles to both crystalline solid and isotropic liquid, this is known as mesophase. These have flow property similar to liquids and periodic arrangement of atoms like solids [1-4]. Earlier, these are given the name flowing crystals but today we refer them as liquid crystals.

These are organic compounds having different shapes like rod shaped, disc shaped etc. Due to these different shapes, they exhibit different phases namely nematic, smectic, cholesteric etc. The alkoxy group (OCB) in the terminal chain gives rise to many specular properties. The change in dipole moment of the compound relates to the polarizability of the molecule. For the analysis in the microscopic system of the molecule, its structure plays a very important role. A small change occurred in the molecular structure may lead to the huge change in liquid crystalline properties of the compound [5-10]. The theoretical studies help in analyzing the property of liquid crystals to a greater extent. The increase in alkoxy chain as by increasing the number alkyl groups may lead to the liquid crystal with higher value of melting temperature. The type of interaction on the liquid crystal either sidewise or planar results in increasing the stability of the liquid crystal. For electro-optic applications, the liquid crystals having nematic twist bend transition is suitable. But these are only singular in phase and operate within a narrow range of temperature. On cooling these liquid crystals distort their stability and very few are found operable at room temperature. Due to the delocalization of π electrons, alkoxy group is more favorable than alkyl group. To design the newer liquid crystals, one must know the structure property relationship that leads to specular properties in a desired liquid crystal. As alkoxy group is a polar substituent having strong dipole moment, this can enhance the mesomorphic behavior. On increasing the terminal chain length, molecule orients itself in the parallel arrangement and this leads to the stacking and hence charge propagation is possible. The different types of spectral studies are performed here like IR (infrared) spectroscopy and RAMAN spectroscopy so that we can get more information regarding molecular analysis [10-13].

Computational Methodology

Density functional theory has now become the most significant quantum mechanical technique in providing theoretical insights into the chemical reactivity and selectivity, in terms of popular qualitative Physico-chemical properties. 8OCB and 9OCB liquid crystal molecules have been optimized with Computational Density-Functional Theory (DFT) method using B3LYP basis set which is a hybrid functional for Gaussian type orbitals (GTOs)and 3-21G(d,p) basis set using NWChem software package[14-21].

Results and Discussion

Optimized geometries

The optimized geometries of 8OCB (4-n-octyloxy-4′-cyanobiphenyl) and 9OCB (4'-nonyloxy-biphenyl-4-carbonitrile) liquid crystal molecules are shown in the Figure 1(a) and (b). The magnitude of minimum energies of 8OCB (4-n-octyloxy-4′-cyanobiphenyl) and 9OCB (4'-nonyloxy-biphenyl-4-carbonitrile) liquid crystal molecules are 945.28 a.u. and 984.60 a.u. respectively. In similar manner, The dipole moment 5.7D for 8OCB and 6.97D for 9OCB respectively.

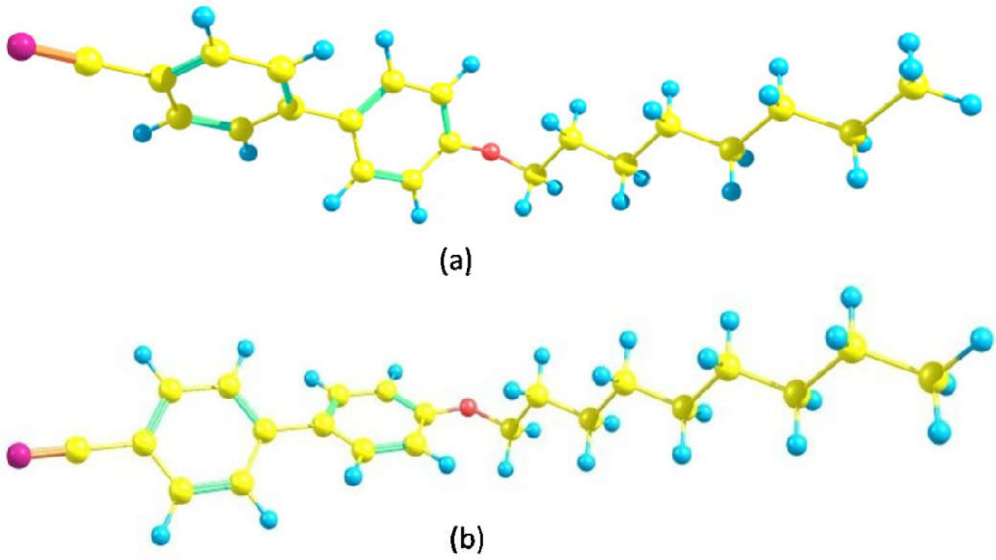

Figure1:- Optimized geometries of 8OCB and 9OCB liquid crystal molecules

Vibrational spectrum analysis

Density functional theory calculations of vibrational frequencies are useful for reliable assignment of the fundamental vibrations. The computed IR intensities amd Raman activities of both molecules for corresponding wave numbers by DFT/B3LYP/6-31G(d,p) have been reported in Table 1. The calculated IR and Raman activity of 8OCB and 9OCB liquid crystal molecules have presented in Figure 2 and 3.

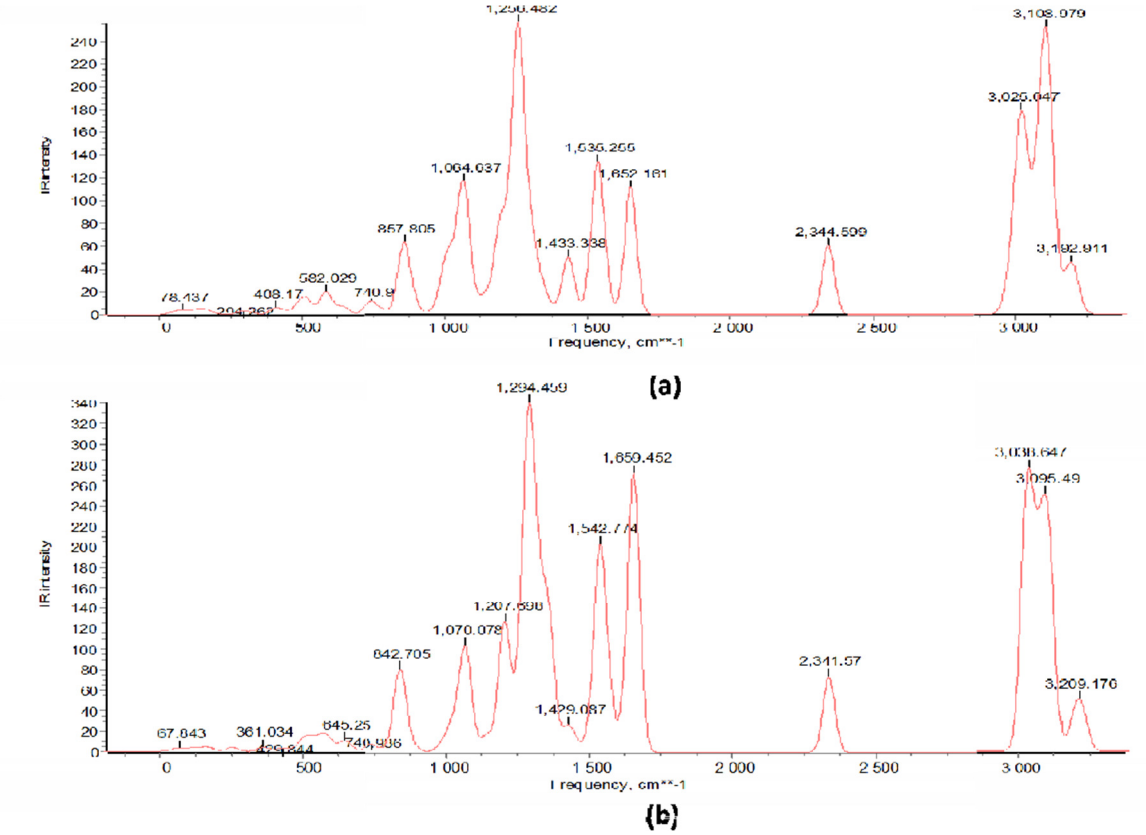

Figure2:- IR spectrum of 8OCB and 9OCB liquid crystal molecules

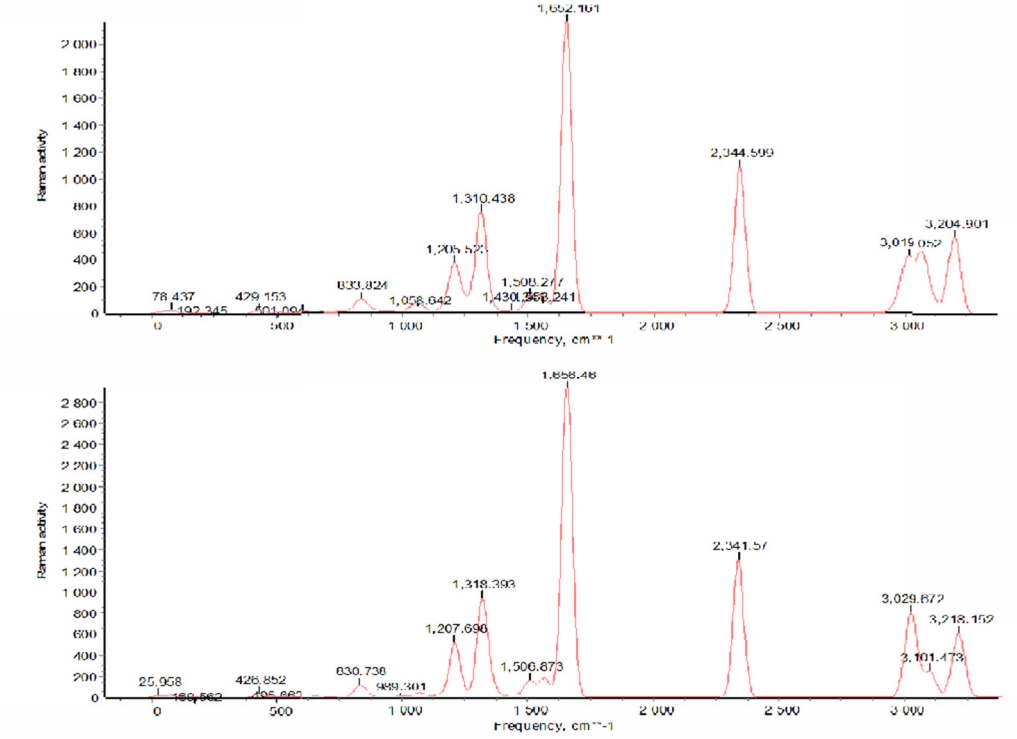

Figure 3: Raman activity of 8OCB and 9OCB liquid crystal molecules

Table 1: Molecular vibrations of 8OCB and 9OCB liquid crystal molecule

S.No.	Frequency (cm^{-1})	Modes of Vibration
1.	**857**	Wagging of hydrogen in aromatic ring (8OCB)
2.	**1061**	Stretching of O-C bond (8OCB)
3.	**1535**	Rocking of H-atom in aromatic ring (8OCB)
4.	**1652**	Symmetric stretching between C-C in benzene ring (8OCB)
5.	**2344**	Stretching of C-N bond (8OCB)
6.	**3108**	Asymmetrical stretching between C-H bond in terminal group (8OCB)
7.	**842**	Wagging of hydrogen in aromatic ring (9OCB)
8.	**1070**	Stretching of O-C bond
9.	**1542**	Rocking of H-atom in aromatic ring and also show twisting of C-N bond
10.	**1659**	Symmetric stretching between C-C in benzene ring (9OCB)
11.	**2341**	Stretching of C-N bond
12.	**3038**	Symmetric stretching of C-H bond in terminal group (9OCB)

Conclusion

The stretching of C-N bond at frequency 2344 cm^{-1} in 8OCB but in 9OCB it is at 2341 cm^{-1}. Stretching of C-O bond at frequency 1061 found in 8OCB liquid crystal molecule. But this stretching found in 9OCB at frequency 1070 cm^{-1}. The cyano-substituent exhibits great thermal and chemical stability thus contributes to many applications.

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