

Theoretical Investigation of Electronic and Spectroscopic Properties of MHPBC and MHPOBC Molecules and Their Dimers Using Density Functional Theory (DFT)

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Abstract

In this work, we investigated the IR, RAMAN spectra, Mulliken atomic charge, and chemical reactivity parameters of considered molecules and their dimers using density functional theory calculations via the B3LYP/6-31G level of theory. The simulation results revealed that the values of the energy gap, chemical potential, and hardness are decreased due to the interaction of monomers (dimers). And the values of softness and electrophilicity index are increased.

Keywords: MHPBC, MHPOBC, liquid crystal, IR, Raman, DFT

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I. Introduction

Liquid crystal dimers represent a captivating class of molecules that have gained significant attention in the field of liquid crystal research. These dimers are characterized by their unique molecular structure, typically composed of two mesogenic units linked together. The mesogenic units are responsible for the liquid crystalline properties, making liquid crystal dimers a subject of great interest due to their potential applications in various technologies, including displays, sensors, and photonic devices [1-4].

The study of liquid crystal dimers encompasses their synthesis, structural characterization, and investigations into their phase behavior and electro-optical properties. Researchers are particularly interested in understanding how the dimeric structure influences the liquid crystal properties and phase transitions, which can be crucial for optimizing their performance in practical applications [4-6].

The exploration of electro-optical properties in liquid crystal dimers, facilitated by the application of Density Functional Theory (DFT), represents a fascinating and multidisciplinary research domain at the intersection of chemistry, physics, and materials science. Liquid crystal dimers, consisting of two mesogenic units connected by a flexible linker, exhibit unique behavior under the influence of external electric fields, making them indispensable in various technological applications. DFT, a powerful computational approach rooted in quantum mechanics, offers a precise and insightful means to unravel the intricate electro-optical phenomena that govern the behavior of these molecules [7-10].

The electro-optical properties of liquid crystal dimers hold immense significance in the development of cutting-edge technologies, including liquid crystal displays (LCDs), optical switches, and photonic devices. Understanding and manipulating these properties are key to enhancing the performance and functionality of these devices. Through DFT simulations and calculations, researchers can delve deeply into the electro-optical characteristics of liquid crystal dimers, including their response to electric fields, optical anisotropy, polarizabilities, and alignment behavior [11,12].

Liquid crystal dimers have garnered significant attention due to their potential in various applications, including liquid crystal displays, optical switches, and photonic devices. The ability to finely tune their physical properties, such as phase transition temperatures and optical characteristics, makes them valuable in designing novel materials for emerging technologies [12-14].

The LC molecules used in this work are [1,1'-biphenyl]-4-carboxylic acid, 4'-octyl-, 4-[[[1-methylheptyl]oxy]carbonyl]phenyl ester (MHPBC) and [1,1'-biphenyl]-4-carboxylic acid, 4'-(octyloxy)-, 4-[[[1-methylheptyl]oxy]carbonyl]phenyl ester (MHPOBC) for the investigation of electro-optical, electronic properties.

1.2 Methodology

Using the B3LYP functional and Pople's split valence basis sets [15,16] 6-31G, we carried out DFT calculations on the MHPBC, MHPOBC, and its dimer molecules. These calculations included polarization and diffuse functions on the major group elements, as implemented in the Gaussian 09 software [17]. The starting geometries, optimized geometries, and molecular orbitals of the compounds under study were all shown using Gauss View 5.0 [18]. For many substances, the computations at the B3LYP/6-31G and 6-311G levels produced accurate predictions. By using full structural optimization in the gas phase, the molecular and electronic structures of the molecules under consideration as well as their dimers were investigated. The terms polar and freq= raman were used, respectively, to calculate the energy, dipole moment, and chemical reactivity parameters in the optimized geometries.

1.3 Results and Discussion

Density functional theory (DFT) turns the calculation of multielectron issues into the total electron density and employs electron density as the fundamental quantity of inquiry instead of the wave function. DFT is the most used approach for calculating electronic structures in various domains since it streamlines the calculation model and reduces computation time. Through DFT, topological properties are obtained from the nuclei's and electrons' opposing contributions. The optimized structures of considered molecules and their dimers are shown in Figures 1 and 2. The energy of MHPBC, MHPOBC, and its dimer are -1700.957789, -1776.187281, -3401.915728, and -3552.378138 a.u. respectively. The dipole moment of considered molecules and their dimer are 4.796D, 4.955D, 9.531D, and 9.478D.

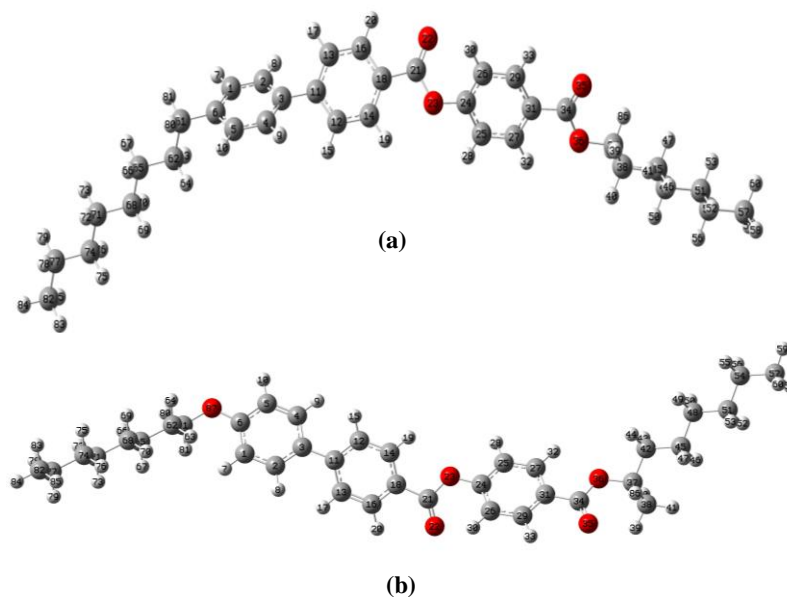


Figure 1: Optimised geometries of MHPBC and MHPOBC molecules

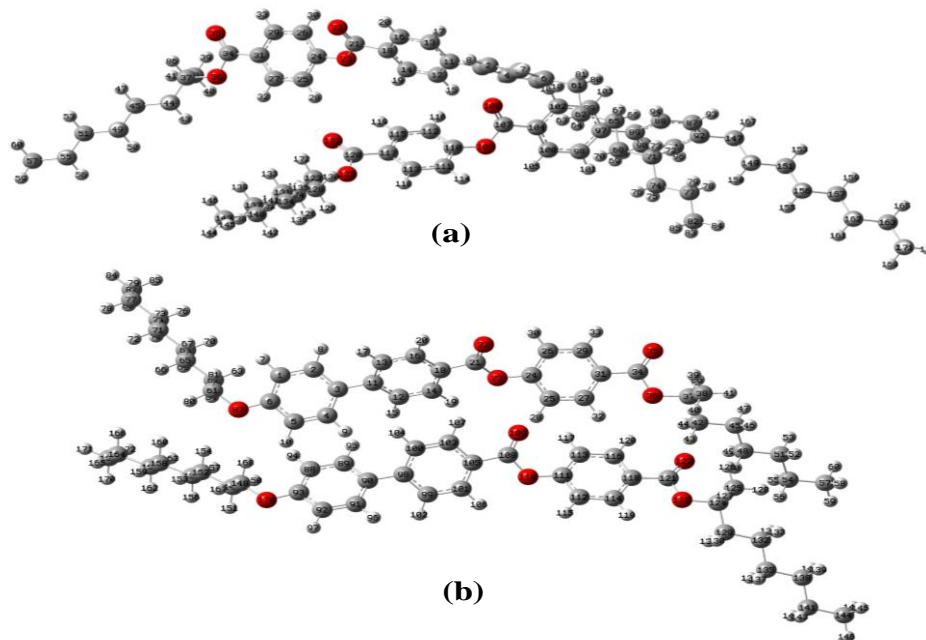
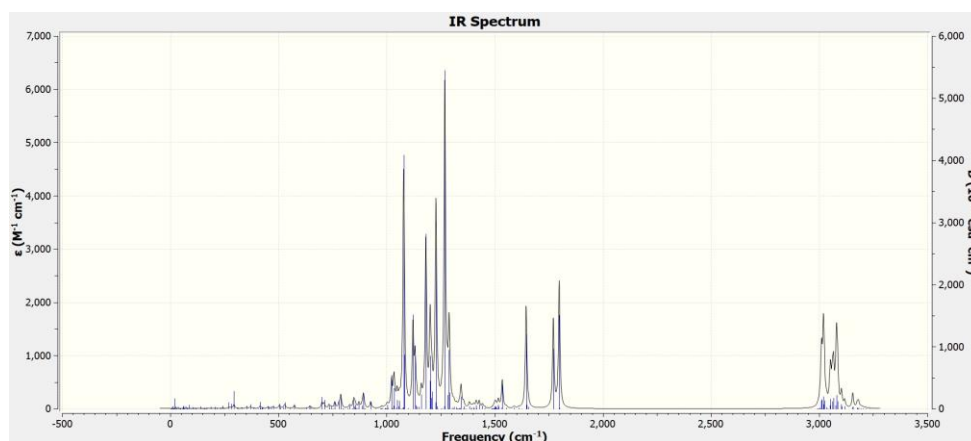
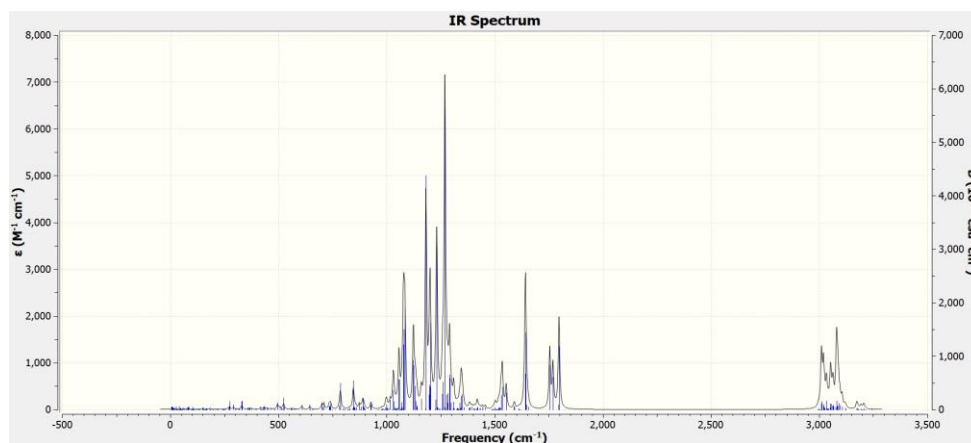


Figure 2: Optimised geometries of MHPBC and MHPOBC dimer molecules



(a)



(b)

Figure 3: IR spectra of MHPBC and MHPOBC dimer molecules

Infrared (IR) and Raman spectroscopy are two powerful techniques used in chemistry and materials science to analyze the vibrational modes of molecules. They provide valuable information about the chemical composition, structure, and bonding of substances. The IR and RAMAN of considered molecule and their dimers are shown in figure 3 and figure 4.

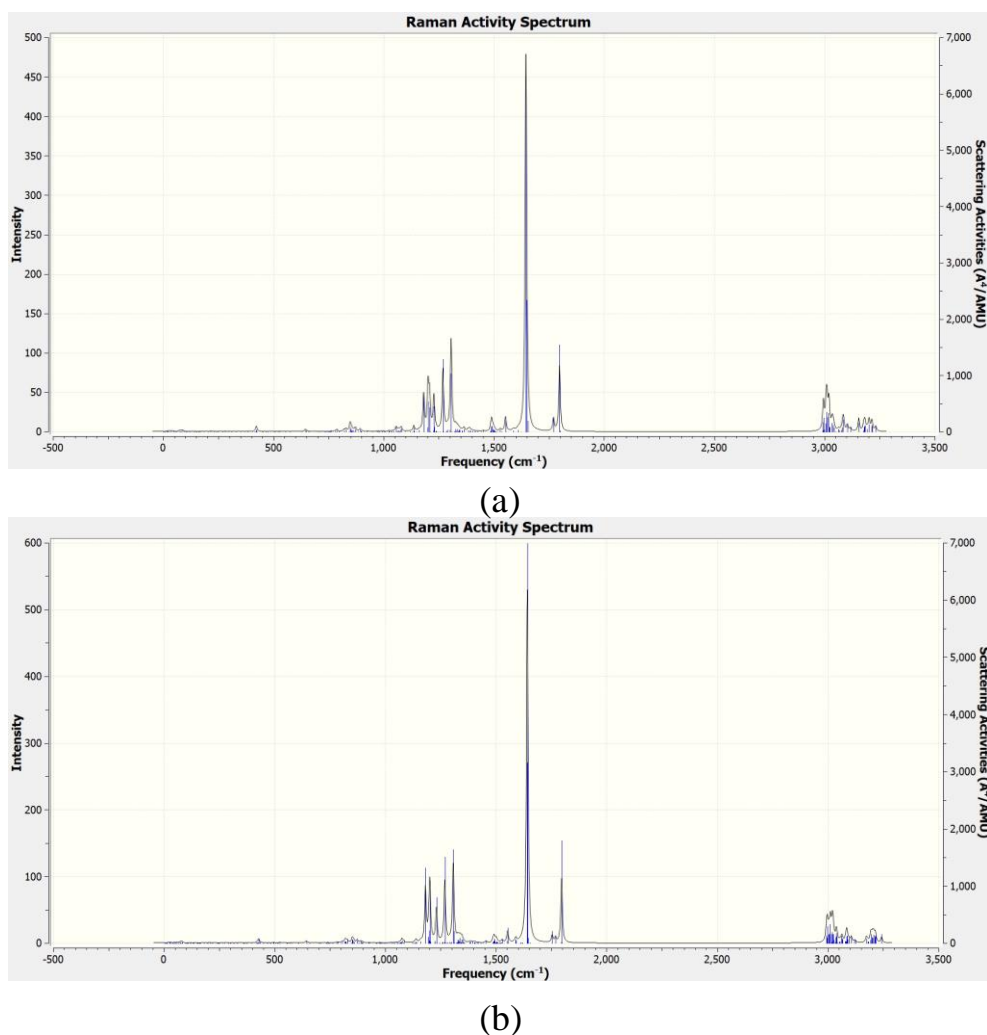


Figure 4: Raman spectra of MHPBC and MHPOBC dimer molecules

Mulliken atomic charges are a useful tool in computational chemistry for assessing the distribution of electron density within molecules and gaining insights into their chemical reactivity. Researchers often use these charges in conjunction with other methods to understand and predict chemical behavior and interactions in various applications, including drug discovery, materials science, and organic synthesis.

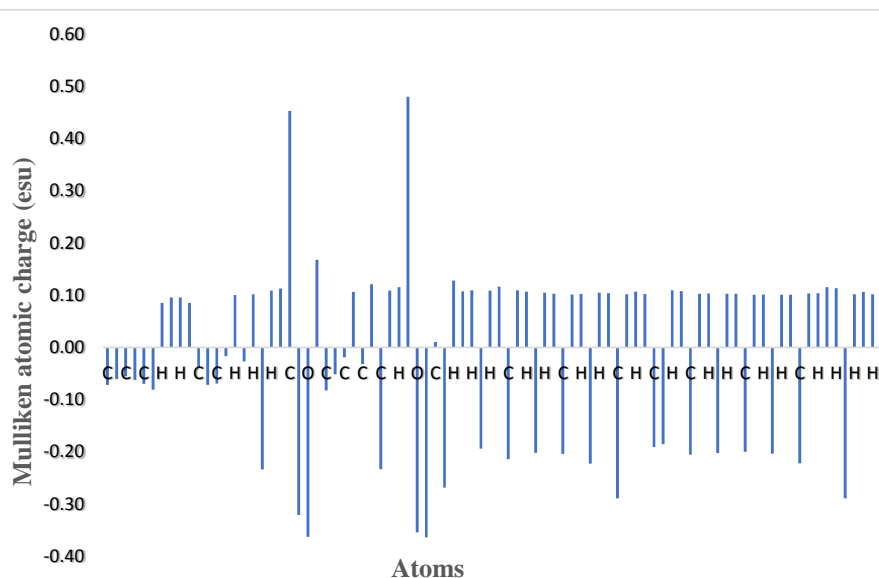


Figure 4: Mulliken charges on atoms in MHPBC molecule

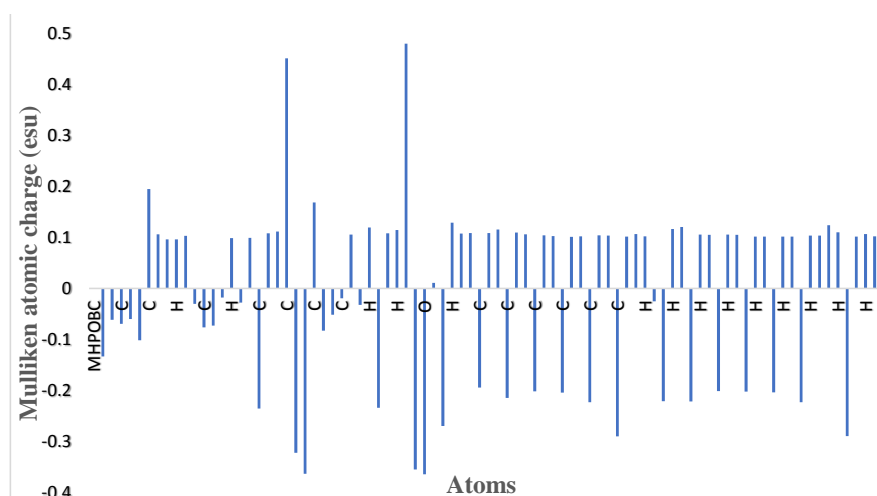


Figure 5: Mulliken charges on atoms in MHPOBC molecule

Mulliken atomic charges can be used to understand the reactivity of atoms in a molecule. For example, atoms with large negative charges may be prone to nucleophilic attacks, while those with large positive charges may act as electrophiles. However, it's important to note that other charge schemes, such as the Hirshfeld charges or natural population analysis (NPA), provide alternative ways to analyze electron distribution.

Global reactivity parameters in the context of molecules are important descriptors used in the field of computational chemistry, particularly within the framework of Density Functional Theory (DFT). DFT is a quantum mechanical method used to calculate the electronic structure and properties of molecules, and global reactivity parameters provide valuable insights into the chemical reactivity and stability of molecules. Here are some key global reactivity parameters frequently employed in DFT calculations:

The chemical potential, often denoted as μ , represents the change in energy of a system as the number of electrons is varied while keeping the number of particles constant. It is a fundamental global reactivity parameter in DFT, reflecting the electron density of a molecule. The chemical potential is closely related to electronegativity and is used to predict whether a molecule will act as an electron donor (electrophilic) or an electron acceptor (nucleophilic).

Hardness, denoted as η , is a measure of the resistance of a molecule to changes in electron density when it interacts with other molecules or ions. It is calculated as the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) divided by two: High hardness values indicate that a molecule is relatively unreactive, while low hardness values suggest high reactivity.

Softness, denoted as S , is the reciprocal of hardness and provides a measure of the overall reactivity of a molecule. It is calculated as the inverse of hardness: $S = 1 / \eta$. Molecules with high softness are more prone to electron transfer and chemical reactions.

Electrophilicity Index (ω) The electrophilicity index, denoted as ω , is a global reactivity parameter that quantifies the ability of a molecule to act as an electrophile, i.e., as a species that seeks to accept electrons in a chemical reaction. It is related to the chemical potential and hardness: High electrophilicity values indicate a strong tendency to accept electrons and participate in chemical reactions.

Nucleophilicity Index (N): Nucleophilicity, often denoted as N , is a global reactivity parameter that characterizes the tendency of a molecule to donate electrons in a chemical reaction. It is related to the electrophilicity index and is useful in predicting nucleophilic reactions. High nucleophilicity values suggest a molecule's strong tendency to donate electrons.

Global reactivity parameters in DFT calculations are valuable tools for understanding the chemical reactivity, stability, and behavior of molecules. They aid in predicting how molecules will interact with other species, participate in chemical reactions, and provide a quantitative basis for designing and understanding chemical processes at the molecular level. These parameters are particularly useful in the fields of organic chemistry, catalysis, and materials science.

The ionization potential and electron affinity values were correlated with the frontier orbitals using Koopman's theorem [19].

$$IP = -E_{HOMO} \quad \text{and} \quad EA = -E_{LUMO} \quad 1$$

$$\text{Electronegativity}(\chi) = -\frac{1}{2}(E_{LUMO} + E_{HOMO}) = -\mu \quad 2$$

$$\text{Chemical potential} (\mu) = \frac{1}{2}(E_{LUMO} + E_{HOMO}) \quad 3$$

$$\text{Chemical hardness} (\eta) = \frac{1}{2}(E_{LUMO} - E_{HOMO}) \quad 4$$

$$\text{Softness} (\varsigma) = \frac{1}{\eta} \quad 5$$

$$\text{Energy gap} (E_g) = E_{LUMO} - E_{HOMO} \quad 6$$

$$\text{Electrophilicity index} (\omega) = \frac{\mu^2}{2\eta} \quad 7$$

Table 1: Chemical reactivity parameters of MHPBC, MHPOBC, MHPBC dimer and MHPOBC dimer

Molecules	MHPBC	MHPOBC	MHPBC dimer	MHPOBC dimer
HOMO (eV)	-6.4528	-6.0271	-6.3616	-5.9778
LUMO (eV)	-1.9271	-1.8498	-2.0164	-1.8561
E_g (eV)	4.5257	4.1773	4.3453	4.1217
μ (eV)	-4.1900	-3.9385	-4.1890	-3.9170
η (eV)	2.2629	2.0886	2.1726	2.0609
S (eV) ⁻¹	0.2210	0.2394	0.2301	0.2426
ω (eV)	3.8791	3.7133	4.0383	3.7224
ΔN_{max}	1.8516	1.8857	1.9281	1.9006

II. Conclusion

In this article, we investigated the IR, RAMAN spectra, Mulliken atomic charge, and chemical reactivity parameters of considered molecules and their dimers using density functional theory calculations via the B3LYP/6-31G level of theory. The simulation results revealed that the values of the energy gap, chemical potential, and hardness are decreased due to the interaction of monomers (dimers). And the values of softness and electrophilicity index are increased.

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