

PHYSICAL, CHEMICAL, OPTICAL AND INSULATING PROPERTIES OF ALKYL BENZOIC ACID DERIVATIVES LIQUID CRYSTAL DUE TO EXTENSION ALKYL CHAIN (C_NH_{2N+1}) LENGTH: A DFT STUDY

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ABSTRACT. The aim of this paper was to analyze the structure, vibrations and to do global analyses of molecules of p-n-alkyl benzoic acid (nBAC). The energy, IR, and HOMO-LUMO optimised parameters were calculated using a density functional method. The global reactivity descriptors of molecules, including electro-negativity, electron affinity, ionisation potential, global softness, chemical potential, and energy gaps is further shown by band gap value drops. It offers important details on the stability of nBAC molecules (n=4,5,6,7,8,9). It has been demonstrated that the molecular series displays the energy of an isolated molecule as the length of the alkyl chain rises. The molecular series is useful for insulating applications since it also has a high band gap.

Keywords: Raman spectra, liquid crystal, polarizability, nBAC, IR and DFT.

INTRODUCTION

The physical and visual characteristics of both liquids and solids are combined in liquid crystals. Despite having certain optical characteristics of solids, such as birefringence, they flow like liquids. Additionally, they respond reliably to an electric current, allowing for the regulation of light transmission. Liquid crystals are utilised in a variety of products with electronic displays, including watches, calculators, mobile phones, desktop monitors, and televisions. The examination of novel liquid crystalline materials with various molecular chemistry has garnered attention recently in order to assess their viability for technological applications (SINGH, 2000; BATES, 2005; MATSUSHITA and KOSEKI, 2005; JADŻYN and CZECHOWSKI, 2007).

Prior to applying and accounting for new advances for aberrant characteristics in materials, a thorough theoretical grasp of liquid crystalline behaviour is necessary. In theoretical studies on molecular contacts, the potential energy of the interaction between two molecules is regarded as a key need. The sorts of kinetics used in the physical and physicochemical reactions taking place in mesomorphic compounds are also determined by this interaction, as well as the positional and orientational order of the compounds. One or two alkyl chains connect an aromatic core that makes up the majority of mesogenic compounds. Alkyl chains have an impact on liquid crystal parameters such as the nematic isotropic transition temperature and the entropy of the transitions. Based on the Rayleigh-Schrödinger disturbance approach, several researchers have focused their attention on the significance of intermolecular forces in mesomorphic behaviour. These investigations sought to determine the pair potential's anisotropy before determining the minimal energy configuration of two liquid crystalline molecules (HARIHARAN and POPLE, 1973; RYZHOV *et al.*, 2001; YAYLOYAN *et al.*, 2001; MISHRA *et al.*, 2006; AJEETHA and OJHA, 2009a,b).

Although p-n-alkyl benzoic acid (BAC), the system chosen for the current experiment, is not exactly liquid crystal, it appears fascinating since it can be transformed into liquid crystal by selecting the right substituent. Because of this, theoretical research into its highly homologous chain which demonstrates the liquid crystalline nature is more appealing. The examination of p-n alkyl benzoic acid's IR, dipole moment, energy, polarizability, Raman and Homo-Lumo is covered in the current article.

MATERIALS AND METHODS

In physics and chemistry, DFT is a quantum mechanical theory that is used to look into the electronic structure of many different body systems, including atoms, molecules, and condensed phases. It is founded on a modelling approach that uses the generic functional of electron density to represent electrons. In the design of non-linear optical materials, DFT simulations have shown to be useful tools for predicting features including dipole moment, polarisation, and hyperpolarizability. The b3lyp/6-31g(d,p) basis set, a hybrid functional with Gaussian type orbital basis set, has been used to compute single point energies, IR, Raman, dipole moment, and polarizability for nBAC molecules using the computational density functional theory technique (HEHRE *et al.*, 1972a, 1972b; GORDON, 1980; HARIHARAN and POPLE, 1974; SIRAJUDDIN *et al.*, 2019).

The distance between the lowest vacant molecular orbital and the highest occupied molecular orbital is known as the energy gap. This characteristic is crucial since it enables us to understand the molecules' stability and reactivity. We have calculated the E_{HOMO} , E_{LUMO} , and other characteristics, including the electron affinity (E.A.) and ionisation potential (I.P.). All of these parameters may be calculated using Koopman's theorem (TSUNEDA *et al.*, 2010; PAL *et al.*, 2022).

$$\begin{aligned}
 IP &= -E_{HOMO} \quad \text{and} \quad EA = -E_{LUMO} \\
 \text{Electronegativity}(\chi) &= -\frac{1}{2}(E_{LUMO} + E_{HOMO}) = -\mu \\
 \text{Chemical potential} (\mu) &= \frac{1}{2}(E_{LUMO} + E_{HOMO}) \\
 \text{Global hardness} (\eta) &= \frac{1}{2}(E_{LUMO} - E_{HOMO}) \\
 \text{Softness} (\zeta) &= \frac{1}{\eta}
 \end{aligned}$$

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

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

RESULTS AND DISCUSSION

The optimized geometries for nBAC (n=4,5,6,7,8,9) obtained using b3lyp/6-31g(d,p) have been shown in Fig. 1. The magnitude of minimum energy obtained -578.106 a.u., -617.423 a.u., -656.739 a.u., -696.056 a.u., -735.3727 a.u. and -774.689 a.u. for 4BAC, 5BAC, 6BAC, 7BAC, 8BAC and 9BAC respectively. The dipole moments of these molecules are 2.436 Debye, 2.439 Debye, 2.474 Debye, 2.464 Debye, 2.491 Debye and 2.479 Debye respectively. The optimized geometry gives information about molecules at macroscopic and microscopic levels. The isotropic polarizability of nBAC molecules are 122.64 Bohr³, 134.32 Bohr³, 157.29 Bohr³, 168.67 Bohr³ and 180.10 Bohr³ respectively (KUMAR *et al.*, 2020a, 2020b).

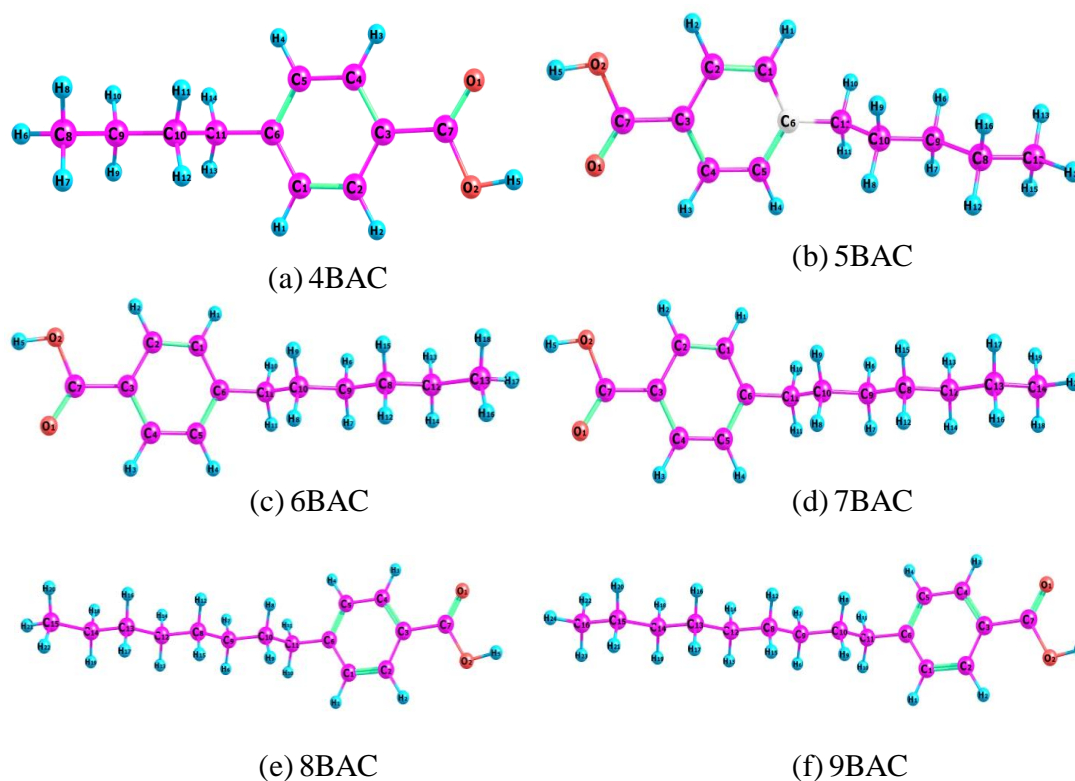


Figure 1. Optimized geometries of nBAC (n=4,5,6,7,8,9) molecules.

Harmonic vibrational frequencies were calculated for 4BAC, 5BAC, 6BAC, 7BAC, 8BAC, and 9BAC molecules at the B3LYP level using a double zeta basis set, 6-31G (d,p) with no Diffuse functions.

The out-of-plane bending in the aromatic ring continually increases in the 4BAC, 5BAC, 6BAC and 9BAC however it is decreasing in the 7BAC and 8BAC. The 6BAC represents the maximum out-of-plane bending in the aromatic ring as shown in Table 3. The In-plane bending in the aromatic ring is maximum enhances in the 7BAC as shown in Table 4. The scissoring in the aromatic ring increases with an increment of alkyl chain length in the BAC liquid crystal series. The 5BAC represents the maximum stretching of C-O bonds as shown in

Table 2. The 5BAC also indicated the maximum symmetric stretching in the benzene ring as shown in Table 2. At the frequency of 1816.86, the 5BAC expresses the maximum C=O bonds stretching as a comparison with all the series of BAC. The symmetric stretching in the terminal only decreased in the 5BAC however symmetric stretching increased in all the series. The asymmetric stretching in the alkyl chain maximum enhances in the 7BAC as shown in Table 4. The 5BAC indicated the maximum O-H bond stretching as shown in Table 2. The C=O stretching is responsible for the maximum IR absorbance or transmittance as shown in Figures 2 (b) and 2(c). The 6BAC and 9BAC express the maximum in plane bending and twisting. The stretching of the C-O bond only decreases in the 7BAC however it will remain constant in the whole series as shown in Figure 2 (d).

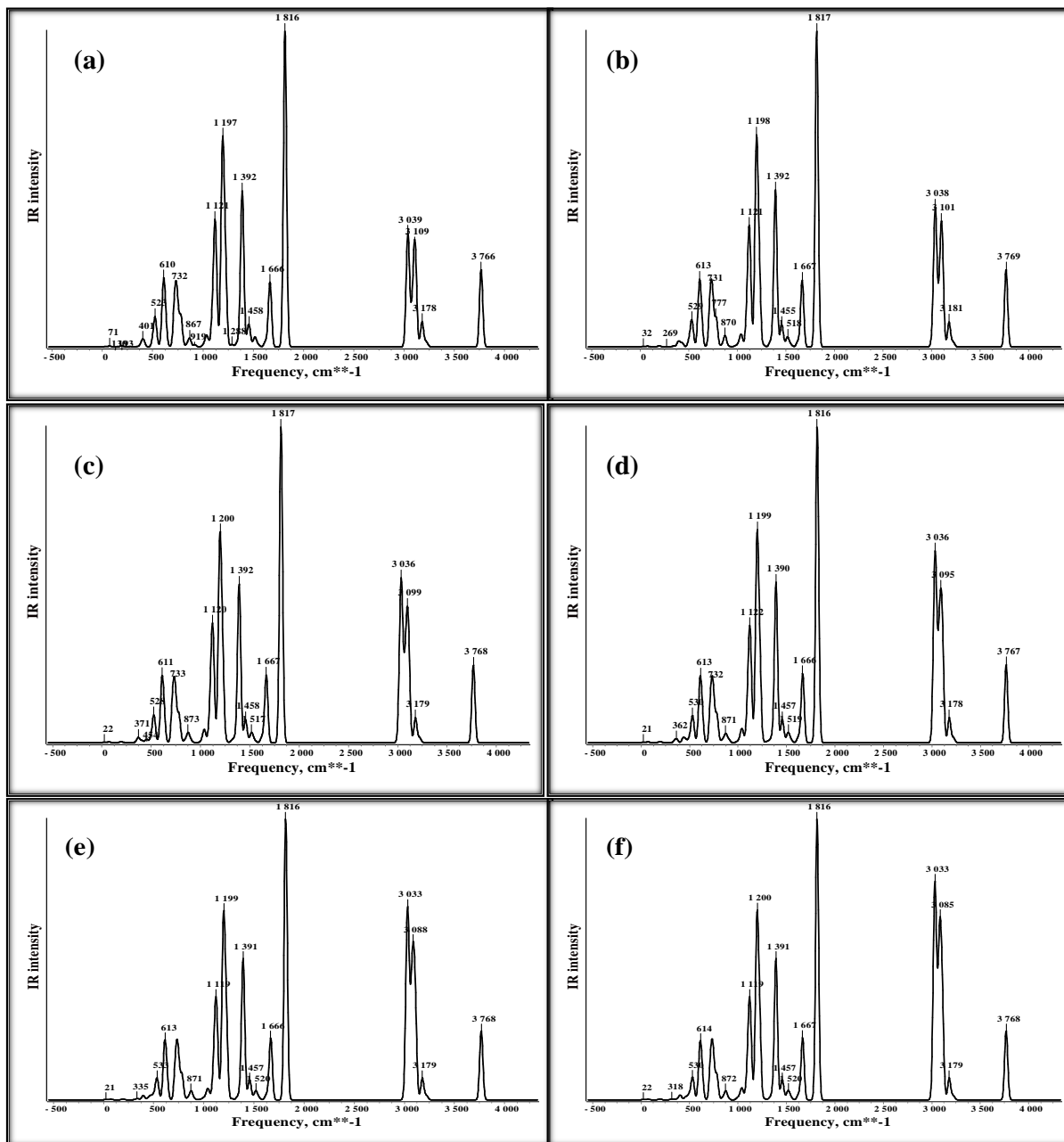


Figure 2. IR activity of (a) 4BAC, (b) 5BAC, (c) 6BAC, (d) 7BAC, (e) 8BAC and (f) 9BAC molecules.

Table 1. Molecular vibrations of 4BAC molecule.

S. No.	Frequency (cm ⁻¹)	Vibrations
1.	609.90	Out of plane bending in aromatic ring
2.	1120.79	In plane bending in aromatic ring
3.	1200.72	Scissoring in aromatic ring
4.	1391.87	Stretching of C-O bond
5.	1666.43	Symmetric stretching in benzene ring
6.	1815.87	Stretching in C=O bond
7.	3042.69	Symmetric stretching in C-H bond in terminal group
8.	3101.77	Asymmetric stretching
9.	3765.58	Stretching of O-H bond

Table 2. Molecular vibrations of 5BAC molecule.

S. No.	Frequency (cm ⁻¹)	Vibrations
1.	612.99	Out of plane bending in aromatic ring
2.	1120.98	In plane bending in aromatic ring
3.	1201.01	Scissoring in aromatic ring
4.	1392.37	Stretching of C-O bond
5.	1667.24	Symmetric stretching in benzene ring
6.	1816.86	Stretching in C=O bond
7.	3041.60	Symmetric stretching in terminal group
8.	3097.27	Asymmetric stretching in terminal group
9.	3768.79	Stretching of O-H bond

Table 3. Molecular vibrations of 6BAC molecule.

S. No.	Frequency (cm ⁻¹)	Vibrations
1.	614.67	Out of plane bending in aromatic ring
2.	1119.91	In plane bending in aromatic ring
3.	1200.04	In plane bending and twisting
4.	1391.69	Stretching of C-O bond
5.	1666.95	Symmetric stretching in benzene ring
6.	1816.78	Stretching in C=O bond
7.	3043.27	Asymmetric stretching in terminal group
8.	3768.02	Stretching of O-H bond

Table 4. Molecular vibrations of 7BAC molecule.

S. No.	Frequency (cm ⁻¹)	Vibrations
1.	613.17	Out of plane bending in aromatic ring
2.	1122.04	In plane bending in aromatic ring
3.	1202.21	Scissoring in aromatic ring
4.	1390.42	Stretching of C-O bond
5.	1665.77	Symmetric stretching in benzene ring
6.	1815.64	Stretching in C=O
7.	3042.49	Symmetric stretching
8.	3174.94	Asymmetric stretching
9.	3767.46	Stretching of O-H bond

Table 5. Molecular vibrations of 8BAC molecule.

S. No.	Frequency (cm ⁻¹)	Vibrations
1.	613.49	Out of plane bending in aromatic ring
2.	871.44	Wagging in aromatic ring
3.	1118.92	C-O bond stretching and rocking in C-H bond
4.	1202.58	Symmetric stretching in benzene ring
5.	1390.80	Stretching in C-O bond
6.	1666.17	Symmetric stretching in terminal group
7.	1816.06	Stretching in C=O bond
8.	3043.02	Stretching of C-H bond in terminal group
9.	3768.04	Stretching of O-H bond

Table 6. Molecular vibrations of 9BAC molecule.

S. No.	Frequency (cm ⁻¹)	Vibrations
1.	614.12	Out of plane bending in aromatic ring
2.	1119.45	Rocking and stretching in C-h bond
3.	1203.09	Scissoring in aromatic ring
4.	1391.28	Stretching in C-O bond
5.	1666.60	Symmetric stretching in terminal group
6.	1816.46	Stretching in C=O bond
7.	3043.19	Asymmetric stretching
8.	3768.08	Stretching of O-H bond

The chemical potential, global hardness, softness, energy gap, electronegativity and electrophilicity index are presented in Table 7. The higher value of ionization potential shows greater stability of the molecule while a small value of ionization potential indicates high reactivity of the molecules. The Ionization potential indicates the amount of energy required to remove an electron from a molecule. The electro-negativity of the molecules measure ability to attract electrons. The value of electron affinity refers to the amount of energy emitted when an electron is added to a neutral molecule. Chemical hardness is the resistance to any change or deformation. Softness and chemical hardness are important concepts to understand the behavior of chemical systems (PAL *et al.*, 2022).

Table 7. Global reactivity of nBAC (n=4,5,6,7,8,9) molecules.

MOLECULE	4BAC	5BAC	6BAC	7BAC	8BAC	9BAC
HOMO(eV)	-6.793	-6.788	-6.784	-6.782	-6.781	-6.780
LUMO(eV)	-1.200	-1.198	-1.196	-1.196	-1.195	-1.195
IP	6.793	6.788	6.784	6.782	6.781	6.780
EA	1.200	1.198	1.196	1.196	1.195	1.195
χ	3.997	3.993	3.990	3.989	3.988	3.987
μ	-3.997	-3.993	-3.990	-3.989	-3.988	-3.987
η	2.797	2.795	2.794	2.793	2.793	2.793
SOFTNESS	0.179	0.179	0.179	0.179	0.179	0.179
ω	2.856	2.852	2.850	2.848	2.847	2.846
ΔE_g (eV)	5.593	5.590	5.588	5.587	5.585	5.585

CONCLUSION

In the present work, it has been found that the lengthening of the alkyl chain initially causes the dipole moment of nBAC molecules to grow, however, at n=7 and n=9 the value of the dipole moment decreases. While the length of the alkyl chain grows, the molecules' isotropic polarizability linearly rises. The length of the alkyl chain causes a reduction in the molecules' energy band gap. Because of the length of the alkyl chain, electron affinities, electronegativity, and global hardness are similarly reduced. The C=O bond stretching is responsible for maximum IR absorbance or transmittance. The 5BAC liquid crystal expresses the maximum O-H bond stretching. This molecular series' have most suitable for absorbance or transmittance application devices. At room temperature, this molecular series is also excellent for insulating application devices.

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