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Physical properties of 4-n-pentyl-4′-cyanobiphenyl (n=9,10,11,12) under the effect of external field: A DFT study

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Abstract
In the present work, molecular structure and thermodynamical properties of 4-n-pentyl-4'-cyanobiphenyl (nCB) have been investigated under the effect of electric field. Molecular geometries of nCB (n=9,10,11,12) have been optimised by DFT method with 6-311G(d,p) basis set. The isotropic polarizability of nCB molecules are also computed under the effect of applied electric field using B3LYP method with6-311G(d,p) basis set.
Keywords:- *DFT, Thermodynamical properties, 4-n-alkyl-4-cyanobiphenyl (nCB)*

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I. Introduction:

In the 19th century, Reinitzer and Lehmann made the discovery of liquid crystals (LCs). The fascinating materials known as LCs exist in a phase that is in-between the liquid and crystalline phases [1]. The LC possesses crystalline properties similar to solids and a liquid-like flow characteristic. Liquid crystals come in a variety of forms with various optical properties, including thermotropic, lyotropic, and metallotropic liquid crystals. The majority of liquid crystals are employed to investigate the electro-optical properties.The rigid rod-like nCB molecules have cylindrical symmetry along their axis of greatest polarizability. Due to high polarity, the cyanobiphenyl (nCB) LCs have extremely good thermal and electrochemical stability. These LCs have extensive uses in passive matrix LCDs and a wide range of photonic applications. The structure of nCB molecule is given below [2,3]:

Figure1: Structure of nCB(n=1,2,3,4,5,6) molecule.

Gray et al. created the nCB LC family for the first time specifically for the electro-optical application of display technology [4].Lalanne et al. described the odd-even effect of nCB LC when increased the alkyl chain length and also told about that the optical polarizability shows the even-odd effect on increasing alkyl chain length [5].

Praveen et. al. studied have been done on the commercially and practically relevant electronic transitions of 4-n-alkyl-4-cyanobiphenyl (nCB) with propyl, pentyl, and heptyl groups in the uv-visible region. The time dependent Becke3-Lee-Yang-Parr hybrid functional 6-31+G(d,p) approach has been used to simulate the uv-visible and circular dichroism spectra of nCB (n = 3,5,7) molecules [6]. Popov et. al. examined the insertion of nCB (4-Cyano-4-n-biphenyl) molecules with n = 0,1,6 into a bent-core liquid crystal monolayer, which was recently discovered to give good vertical alignment for liquid crystals. Vertical alignment is the most common configuration for modern liquid crystal panels (LCD) [7]. Sharmaet.al. investigated the structure-property relationship, the nematic or smectic phase in the liquid crystal series is produced by the number of carbon atoms in the alkyl chain of 4-n-alkyl-4'- cyanobiphenyl. The 4-n-alkyl-4'-cyanobiphenyl (nCB) homologous series, which is well known for its electro-optical characteristics, includes the 4-n-heptyl-4'-cyanobiphenyl (7CB) [8].

In this paper, emphasize the electro-optics properties viz. of the nCB (where n=9,10,11,12) and calculation has been done through density functional theory with basis set 6-311G(d) and using GAUSSIAN09 software.

II. Computational Methodology

Quantum chemical calculations have been performed using gradient corrected density functional theory (DFT) with Li, Yang and cross correlation functional theory as well as hybrid functional Bake3 parameter for the exchange part. It is supplemented with the standard 6-311G(d,p) basis set in the Gaussian 09 program for the calculation of molecular structure, bond length, bond angle. The 6-311G(d,p) split valence-shell basis set augmented by 'd' polarization function on heavy atoms and 'p' polarization function on hydrogen atoms have been used [9-13].

III. Results and Discussions

The equilibrium geometries of nCB (n=9,10,11,12) LC molecules obtained using DFT with B3LYP/6-311G(d,p) method are shown in figure 2. The total electronic energy of 12CB is large in comparison to 9CB molecule and hence 12CB is more stable than 5CB. The total electronic energy of nCB (n=9,10,11,12) molecules are -909.397, -948.711, -988.027 and -1027.343 a.u. respectively. The dipole moments of molecules are 5.99, 6.04, 6.01 and 6.04 respectively. It is clear from above energies and dipole moments that additional methyl group in 10CB, 11CB and 12CB LC molecules significantly increases the dipole moment, polarisability, anisotropy in polarisability and and energy of the system.

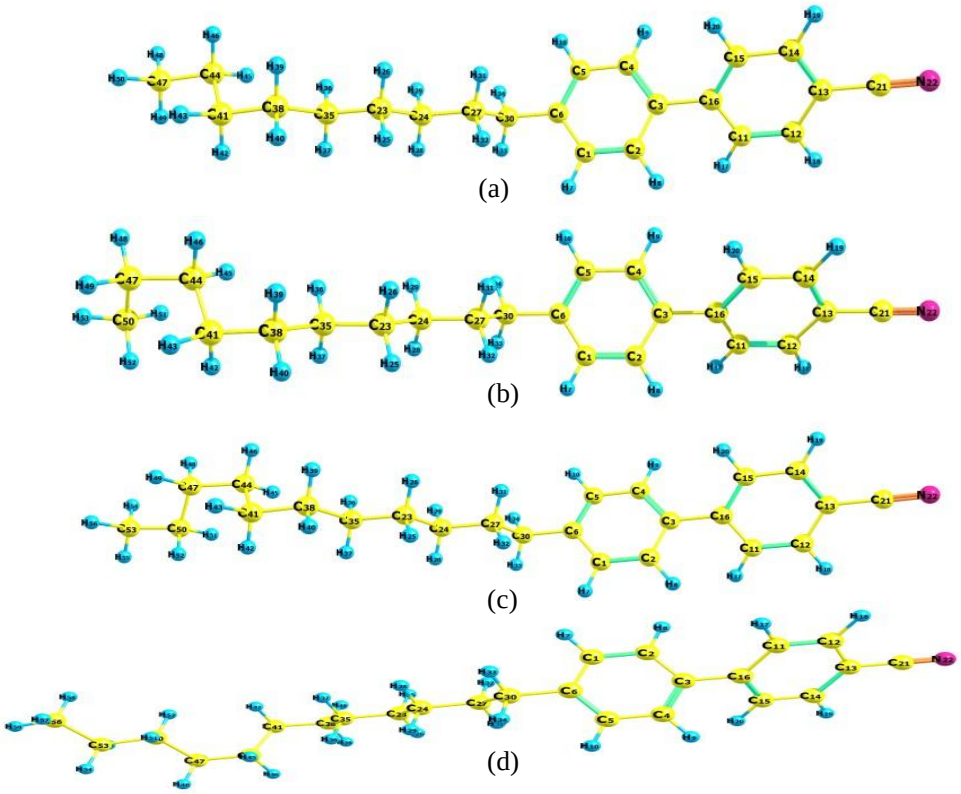
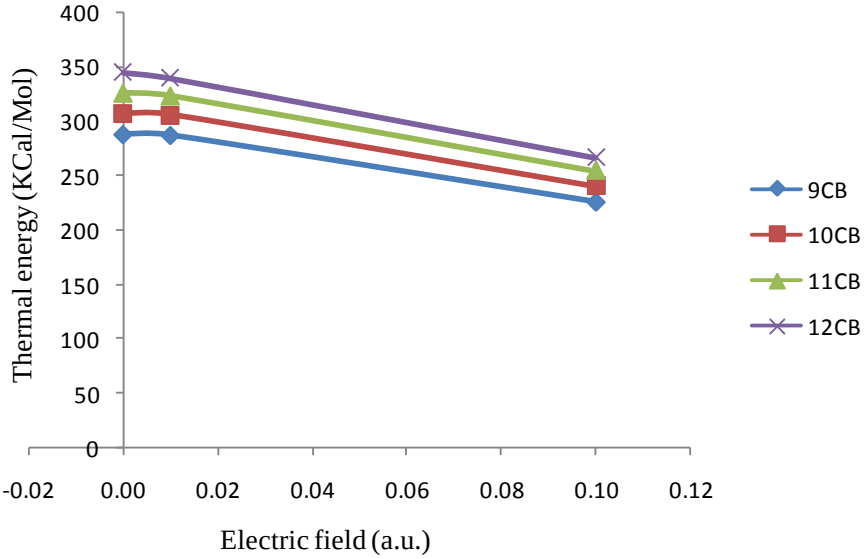


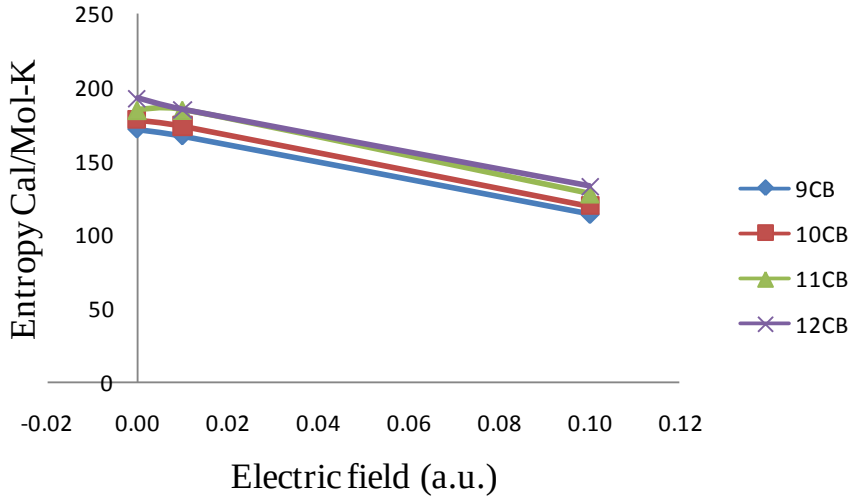
Figure2: Optimised geometries of nCB (n=9,10,11,12) molecules

Table1: Effect of electric field on thermodynamical properties of nCB (n=9,10,11,12) molecules

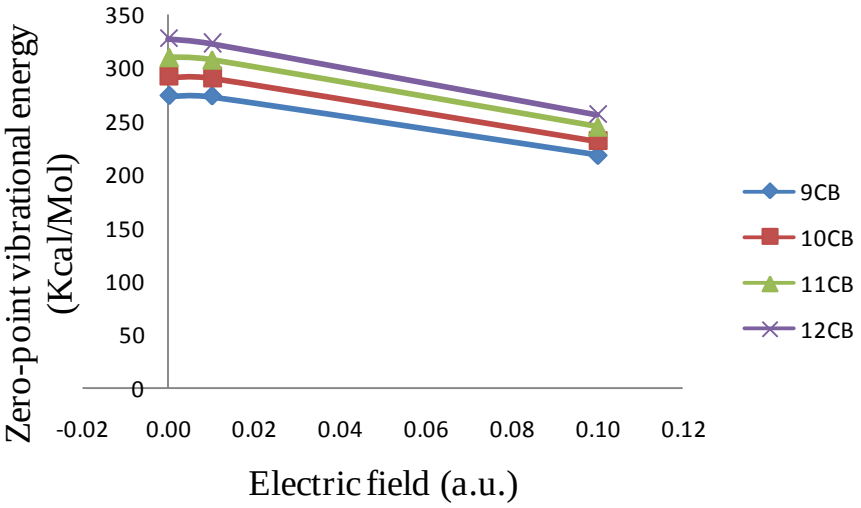
Molecules		Thermal energy (KCal/Mol)	Specific heat constant at constant volume (Cal/Mol-K)	Entropy Cal/Mol-K	Zero-point vibrational energy (Kcal/Mol)
9CB	0.00 a.u.	288.335	87.056	171.624	273.719
	0.01 a.u.	287.518	85.260	167.053	273.384
	0.10 a.u.	226.114	59.771	113.726	217.793
10CB	0.00 a.u.	307.136	91.793	177.762	291.754
	0.01 a.u.	306.215	90.053	173.679	291.292
	0.10 a.u.	241.049	64.516	119.619	231.959
11CB	0.00 a.u.	325.897	96.632	184.914	309.665
	0.01 a.u.	323.319	95.980	185.021	307.388
	0.10 a.u.	254.817	69.037	128.336	244.760
12CB	0.00 a.u.	344.638	101.467	192.608	327.568
	0.01 a.u.	339.473	98.534	184.849	323.228
	0.10 a.u.	267.388	72.122	132.950	256.868



(a)



(b)



(c)

Figure3: Effect of electric on thermal energy, entropy and zero-point vibrational energy

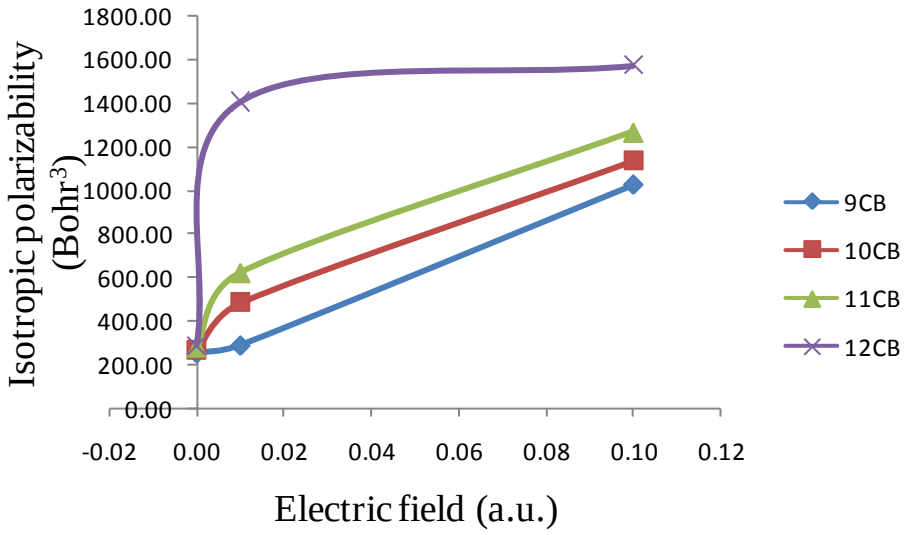


Figure4: Effect of field on isotropic polarizability of nCB (n=9,10,11,12) molecules

The thermodynamical parameters like thermal energy, entropy, specific heat at constant volume and zero point vibrational energy are computed by DFT method are listed in table1. At higher field application the thermal energy, entropy and zero point vibrational energy of the molecules are reduced. All these parameter of 12CB molecule in zero external field are larger than other molecules which means that the randomness of the 12CB molecules is higher than that of other molecules. That is, the entropy, vibrational energy and thermal energy of the 12CB molecule are more than that of the 9CB, 10CB and 11CB molecules.

IV. Conclusion

All molecules of nCB (n=9,10,11,12) are optimized using Gaussian 09 and obtain stable geometry. Optimized geometries of nCBs are used for the calculation of molecular structure and thermodynamic properties. After energy calculation we applied electric field and calculated the effect of electric field on molecular structure and thermodynamic parameter of nCB molecules. We have observed that thermal energy, vibrational energy, specific heat at constant volume and entropy of nCB molecules decrease in the higher region. The isotropic polarizability of the nCB molecules are computed using DFT method under the effect of electric field and observed value of isotropic polarizability is increases due to increase in the value of electric field.

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