Molecular Polarizability Studies on 12. CB, 7O. CB Cyano-biphenyl Liquid Crystal by Theoretical and Experimental Approach

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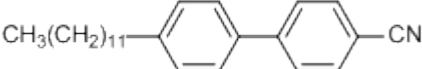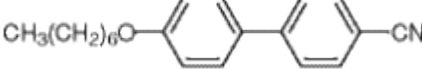Corresponding author E-mail: *rihanabanu786[at]gmail.com*

Abstract: *The transition temperatures of Cyano-biphenyl liquid crystalline compounds, (12.CB, 7O.CB) are recoded by using Differential scanning calorimeter. The transition temperatures are used to estimate molecular polarizability by theoretical approaches. I.e. by quantum dynamical- δ function model and molecular vibration method. The density and refractive indices are measured by using specially designed Pyknometer and indegeneously developed spectrometer coupled with small angled prism the molecular polarizabilities are evaluated by Vuks and Neugebauer methods using experimentally obtained refractive indices and density data. The results obtained from these methods are compared from one another and the limitations of this methods are discussed.*

Keywords: Liquid crystals, Phase transition temperatures, density, refractive indices, and molecular polarizabilities

1. Introduction

The technological applications of liquid crystals are growing steadily apart from theirwell-known uses in display technology and thermography. The unique properties of liquid crystalline phases are now being utilized in the production of electronic related devices. The knowledge of molecular organization in different liquid crystalline materials is evidently necessary for the deeper understating of this and other possible applications. Molecular spectroscopic studies have been much interest in recent years to study the structural and physical properties of liquid crystals [1-2] these studies are quite helpful in getting the understating of molecular and structural characteristic of the material. The polarizability is one of the most important material parameters of nematic phases which determines all the anisotropic properties and the relation between macroscopic and microscopic properties [3]

There are different methods for the evaluation of mean molecular polarizabilities among them the refractivity method, the magneto optic method of Faraday, the modified Lippincott $-\delta$ function and molecular vibration methods are few. The first two methods are purely experimental and the last two are theatrical. The refractivity method is used for experimental studies. The vibrational frequencies of above compounds are recorded by FTIR and these vibrational frequencies are used in estimating the polarizabilities by molecular vibration methods. The bond lengths, atomic delta function and reduced electro negativities are used in evaluating polarizability by Lippincott delta function potential model. In the present work the molecular polarizability and polarizability anisotropy are evaluated on 12.CB, 7O.CB, liquid crystalline compounds. The compounds used have the following molecular structure.

Name of the sample	Structure of the sample	Molecular formula	Atomic weight
4-Cyano-4'-dodecylbiphenyl (12.CB)	$CH_3(CH_2)_{11}$—[biphenyl]—CN	$C_{25}H_{33}N$	347.536
4-Cyano-4'-heptyloxybiphenyl (7O.CB)	$CH_3(CH_2)_6O$—[biphenyl]—CN	$C_{20}H_{23}NO$	293.41

2. DSC Thermograms
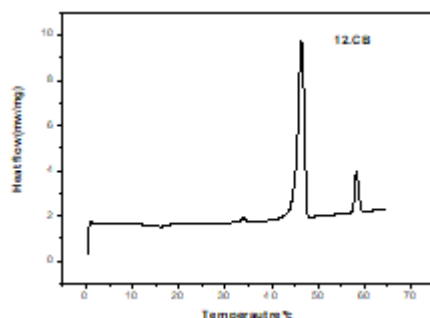
Figure 1: DSC thermograms of 12. CB
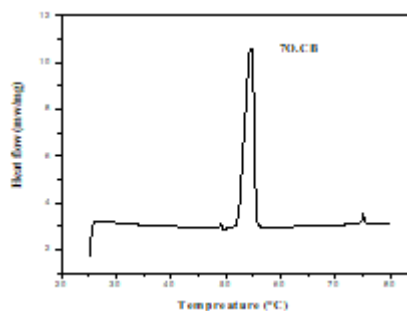
Figure 2: DSC thermograms of 7O. CB

Table 1: Transition temperatures of the sample

Sl. No.	compound	Scan rate	technique	Transition temperature		
				Crystal	Nematic To Isotropic	Thermal range
01.	12.CB	5℃/min	DSC	46.48	58.25	11.77
02.	7O.CB	5℃/min	DSC	54.34	74.95	20.61

3. Theoretical Studies

3.1 Estimation of mean polarizability from Modified Lippincott δ-function method.

The modified Lippincott δ- fuction model is found to be effective [4-5] for different types of liquid crystals. The detail description is given in references [6-7]. In this method the mean polarizability is evaluated in terms of parallel bond component($\sum \alpha \parallel_p$),the perpendicular bond component ($\sum 2 \alpha \perp$)and the non-bond region electron contribution($\sum \alpha \parallel_n$). The expression for the mean polarizability is

$$\alpha_M = \frac{1}{3}(\sum \alpha \parallel_p + \sum \alpha \parallel_n + \sum 2 \alpha \perp) \qquad (1)$$

Where the parallel bond component is given as

$$\sum \alpha \parallel_p = \frac{4nA\left[exp(T-T_c)/T_c\right]}{a_0}\left[\frac{R^2}{4} + \frac{1}{2C_{R2}}\right] exp\left[-\frac{(x_A - x_B)^2}{4}\right] \quad (2)$$

Here n is the bond order Ais the δ – function strength, R is the bond length, X_A and X_B are the Pauling's electro negativities of atoms A and B in the bond AB, a_o is the radius of the first Bohr orbit of the atomic hydrogen, and C_R is the geometric mean molecular δ –function strength. For the second term on the right hand side of the equation (1) we have

$$\sum \alpha \parallel_n = \sum_j f_j \, \alpha_j \qquad (3)$$

Here f_j is the fraction of the non-bonded electrons of the jth atom and α_j is its atomic polarizability.

For the third term in the equation

$$\sum 2 \alpha \perp = n_{df} \frac{\sum x^2_j \alpha_j}{\sum x^2_j} \qquad (4)$$

Here ndfis the number of degrees of freedom given by the equation $n_{df} = (3N-2n_b)$ where N is the number of atoms and n_b is the number of bonds in the molecule.

Estimation of mean polarizability from Molecular Vibration method.

The mean molecular polarizability α_M is calculated by the expression

$$\alpha_M = \sum_i n_i \frac{(b_L + 2b_T)_i}{3} \qquad (5)$$

Where n_i is the number of bonds of type i, b_L and b_T are the longitudinal and transverse polarizabilities of the bonds.

The equations connected to the above parameters reads as

$$b_L - b_T = A\left[(x_1 x_2)^{S/2}\left(\frac{aN}{k-b}\right)^{2S/3}\right]$$
$$\qquad (6)$$
$$b_L + 2b_T = \left[Cp^j(j)^{n\,\gamma}\sigma^{1/2}\right] \qquad (7)$$

Utilizing the expressions (5), (6) & (7) the bond polarizability coefficients b_L and b_T and mean molecular polarizability α_M are evaluated.

Table 2: Parallel, Perpendicular components Non bond and mean Polarizability of the Cyano-biphenyl Compounds (10^{-24} cm^3)

| Compounds		Lippincott δ function method		
		$\alpha_\parallel$	$2\alpha_\perp$	α_n	α_mx10^{-24}
4-Cyano-4'-dodecylbiphenyl		71.09	46.03	1.337	39.48
4-Cyano-4'-heptyloxybiphenyl		65.95	35.61	1.337	34.29

Table 3: Mean Polarizabilities of the Cyano-biphenyl Compounds (10^{-24} cm^3) by Molecular vibrational method

Compound	Bond in molecule	Number of bonds	$(b_{L+}2b_T)/3$ 10^{-24}	Mean Polarizability 10^{-24}
12.CB	C-H	33	22.39	44.33
	C-C	20	16.89	
	C=C	06	4.321	
	C≡N	01	0.739	
7O.CB	C-H	23	15.09	33.78
	C-C	15	12.67	
	C=C	06	4.321	
	C≡N	01	0.739	
	C-O	01	0.9619	

4. Experimental

Figure 3: Modified Spectrometer
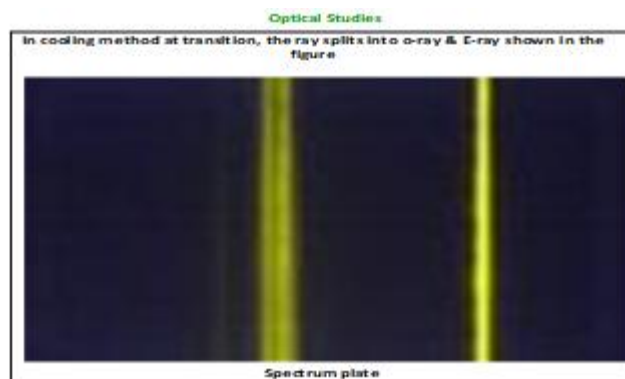
The refractive indices of the liquid crystalline compounds were measured with wedge shaped glass cell similar to the one used to obtain birefringence by Haller et. al.7] and modified spectrometer. A wedge shaped glass cell was prepared with two optical flat rectangular glass plates (50mm x 25mm) sandwiched with glass slide of 0.05mm thick which acts as a wedge spacer. The cell is filled with the liquid crystal material. The liquid crystal material in the cell acts as a uniaxial crystal with its optic axis parallel to the edge of the spacer glass plate. The refractive indices are measured by using modified spectrometer at wavelength of 589.3 nm. The refractive index practically shows no change in isotropic phase. At the isotropic nematic transformation the isotropic ray is splitted into two, one is lower than isotropic value called ordinary ray and another higher than isotropic value called extra-ordinary these are clearly observed in the telescope of modified spectrometer at angle of minimum deviation. In nematic region the n_e increases while n_o decreases with the decrease of temperature. The refractive indices variation with temperature is illustrated in Figure.4 and 5.

The U shaped bi-capillary pycnometer in conjunction with cathetometer was used for the density measurements at various temperatures. The cooling rate during measurement was 0.5k/hour.
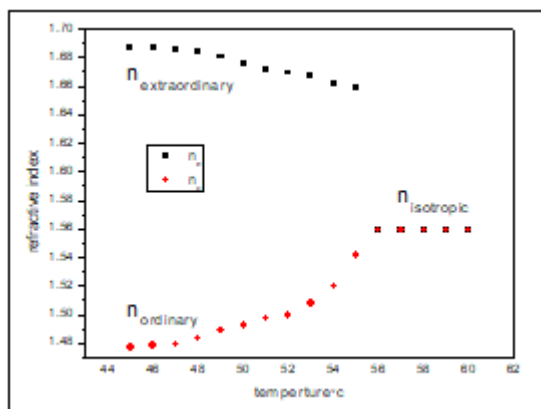

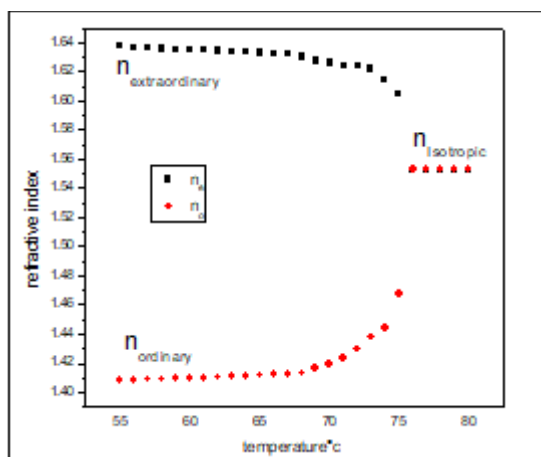**Figure 4:** Variation of temperature with refractive index 12. CB

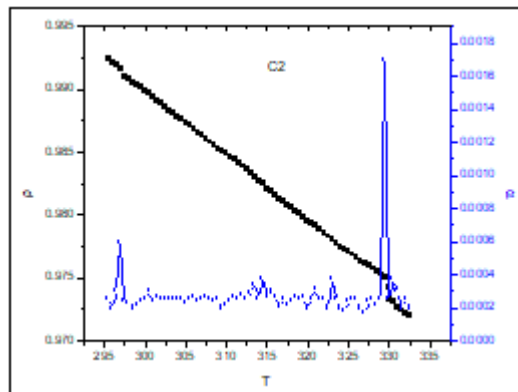**Figure 5:** Variation of temperature with refractive index in 7O. CB

Figure 6: Variation of density and Thermal Expansion Co-efficient of12. CB
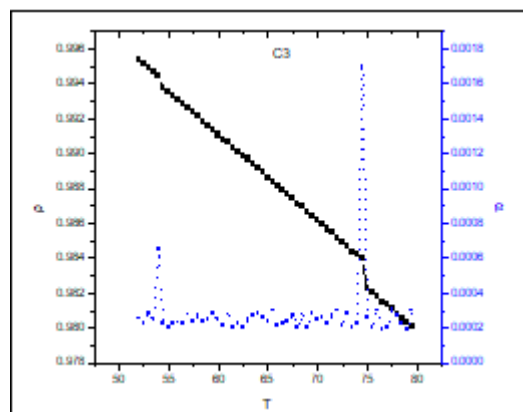

Figure 7: Variation of density and thermal expansion Co-efficient of 7O. CB

Estimation of molecular polarizabilities from refractive indices and density

In uniaxial LC the extraordinary (α_e) and ordinary (α_o) polarizabilities corresponding to the electric vector parallel and perpendicular to the optic axis are given as

$$\alpha_e = \bar{\alpha} + 2\left(\alpha_\parallel - \alpha_\perp\right)S/3$$
$$\alpha_o = \bar{\alpha} - \left(\alpha_\parallel - \alpha_\perp\right)S/3 \qquad (8)$$

Where S is the order parameter $\alpha_\parallel$ and $\alpha_\perp$ is polarizabilities of the molecule parallel and perpendicular to the long molecular axis of the LC molecule. The average molecular polarizability $\bar{\alpha}$ is given as

$$\bar{\alpha} = \left(\alpha_e + 2\alpha_o\right)/3 = \left(\alpha_\parallel + 2\alpha_\perp\right)/3 \quad (9)$$

Combining the above two equations S, the order parameter is

$$S = \left(\alpha_e - \alpha_o\right)/\left(\alpha_\parallel - \alpha_\perp\right) \qquad (10)$$

For the estimation of the molecular polarizabilities of LC molecules, the author has considered Vuks model which considers the local field of the molecule is isotropic and Neugebauer model which considers the local field as anisotropic. The relevant equations of the two models for the calculation of molecular polarizabilities are given below.

Vuks method

This model was first applied to LC molecules by Chandrasekhar et. al [8] assuming the internal field is isotropic even in anisotropic crystal. These assumptions lead to the following equations.

$$\alpha_e = \left[\frac{3}{4\pi N}\right]\left[\frac{n_e^2 - 1}{\bar{n}^2 - 1}\right]$$

$$\alpha_o = \left[\frac{3}{4\pi N}\right]\left[\frac{n_o^2 - 1}{\bar{n}^2 - 1}\right] \quad (11)$$

Where N is the number of molecules per unit volume, n_e and n_o are the extraordinary and ordinary refractive indices of the LC molecule.

$$\bar{n}^2 = \left[\frac{n_e^2 + 2n_o^2}{3}\right]$$

And $N = N_A\rho/M$ where N_A is the Avogadro number, ρ is the density and M is the molecular weight.

Neugebauer method

Saupe and Maierand Subramanyam et. al [9] applied this method to LC molecule. According to this method the molecular polarizabilities are

$$\alpha_e = \left(AB - 3 \pm \sqrt{(AB-3)^2 - 4AB}\right)/2A$$

$$\alpha_o = \left(AB + 3 \pm \sqrt{(AB+3)^2 - 16AB}\right)/4A$$

Where

$$A = \frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3}\left[\frac{n_e^2 + 2}{n_e^2 - 1}\right] + \left[\frac{2(n_o^2 + 2)}{n_o^2 - 1}\right]$$

$$B = \left(\alpha_\parallel + 2\alpha_\perp\right) = \left(\alpha_e + 2\alpha_o\right) =$$

$$3\alpha = 9\left(\bar{n}^2 - 1\right)/\left[\left(4\pi N_i\right)\left(\bar{n}^2 + 2\right)\right] \quad (12)$$

N_i is the number of molecules per unit volume in the isotropic phase.

Table 4: Molecular Polarizability by different methods comparative table

Compounds	Molecular Polarizability by Theoretical methods		Molecular Polarizability by Experimental methods	
	Lippincott δ	Molecular vibration	Vuk's	Neugebauer
12.CB	39.48	43.33	44.84	44.82
7O.CB	34.29	33.44	34.84	35.08

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