Journal of Atomic, Molecular, Condensate & Nano Physics
Vol. 6, No. 1, pp. 21–32, 2019
ISSN 2349-2716 (online); 2349-6088 (print)
Published by RGN Publications

http://www.rgnpublications.com

DOI: 10.26713/jamcnp.v6i1.1234

Molecular Polarizability Studies on Some Cyano-Biphenyl Series Liquid Crystals by Theoretical and Experimental Approach

Research Article

Rihana Banu[1], C. M. Subhan[2] and K. Fakruddin[3,*]

[1] *Department of Physics, Govt. First Grade College, Davangere 577004, Karnataka, India*
[2] *Department of Physics, Shri Shirdi Sai Institute of Science & Engineering, Vadiyampeta, Anantapur, India*
[3] *Department of Physics, Ghousia College of Engineering, Ramanagram 562159, Karnataka, India*
****Corresponding author:** drfakruddin2008@gmail.com

Abstract. The transition temperatures of Cyano-biphenyl liquid crystalline compounds, (12.CB, 7O.CB and 5O.CB) are recorded by using Differential scanning calorimeter. The transition temperatures are used to estimate molecular polarizability by theoretical approaches, i.e., by Lippincott-delta function technique and molecular vibration technique. The density and refractive indices are measured by using specially designed Pyknometer and indigenously developed spectrometer coupled with small angled prism. The molecular polarizabilities are assessed by Vuks and Neugebauer methods using experimentally obtained refractive indices and density data. The results obtained by the current techniques and their limitations are discussed.

Keywords. Liquid crystals; Phase transition temperatures; Density; Refractive index and molecular polarizability

PACS. 42.70.Df; 31.15.ap; 78.20.Ci

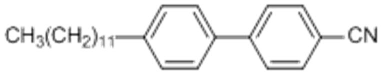
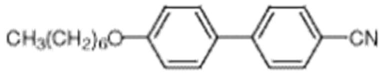
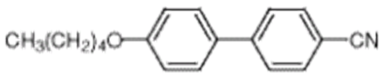
Received: April 24, 2019 **Accepted:** May 5, 2019

Copyright © 2019 Rihana Banu, C. M. Subhan and K. Fakruddin. *This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.*

1. Introduction

The technological applications of liquid crystals are getting larger apart from their well-known uses in display technology and thermography. The distinctive properties of liquid crystalline phases are now being utilized in the production of electronic related devices. The knowledge of molecular arrangement in different LC materials is obviously necessary for the in depth understating of this and other required 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 among prominent material parameters of nematic phase which govern all the anisotropic properties and the relation between macroscopic and microscopic properties [3].

There are dissimilar methods for the exploitation 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 method. 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, 5O.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)**		$C_{25}H_{33}N$	347.53
4-Cyano-4′-heptyloxybiphenyl **(7O.CB)**		$C_{20}H_{23}NO$	293.41
4-Cyano-4′pentyloxybiphenyl **(5O.CB)**		$C_{18}H_{19}NO$	265.36

2. DSC Thermograms

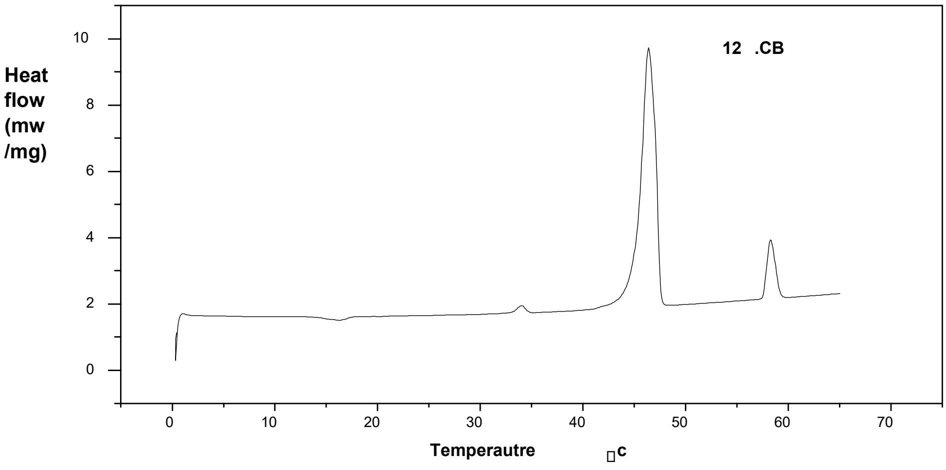


Figure 1. DSC thermograms of 12.CB

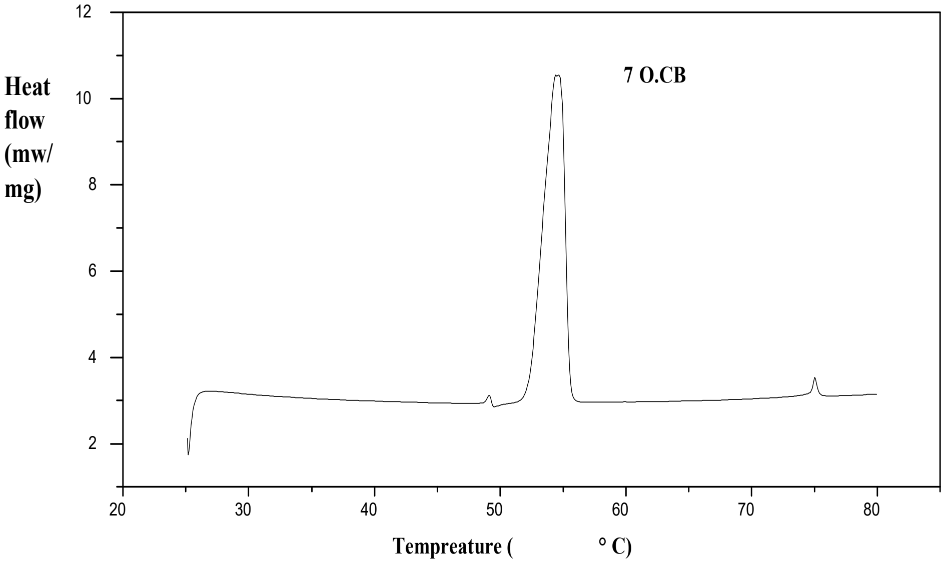


Figure 2. DSC thermograms of 7O.CB

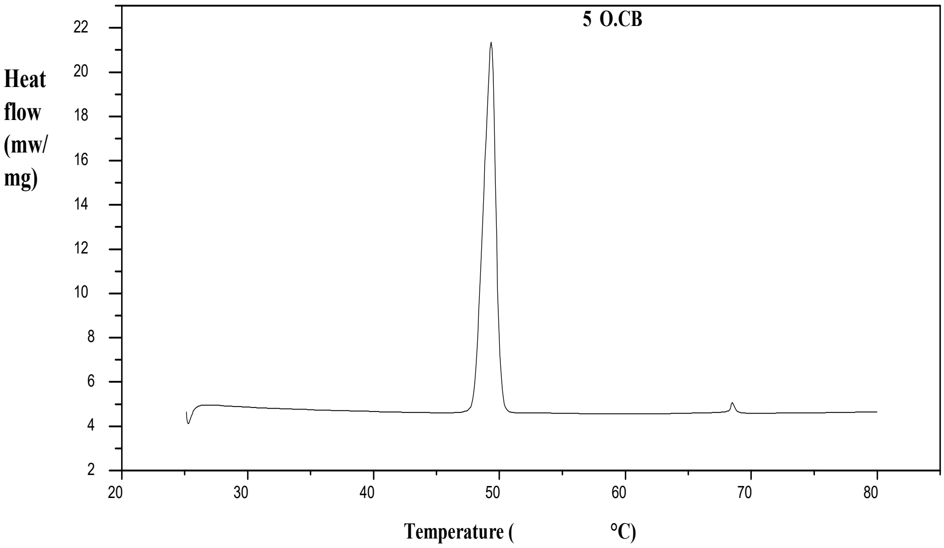


Figure 3. DSC thermograms of 5.CB

Table 1. Transition temperatures of the sample

Sl. No.	Compound	Scan rate	Technique	Transition temperature (° C)		
				Crystal to Nematic	Nematic to Isotropic	Thermal range
1	12.CB	5 °C/min	DSC	46.48	58.25	11.77
2	7O.CB	5 °C/min	DSC	54.34	74.95	20.61
3	5O.CB	5 °C/min	DSC	49.25	68.28	19.03

3. Theoretical Studies

3.1 Determination of the mean polarizability from Modified Lippincott-delta function method

The modified Lippincott δ-function model is found to be effective [4–7] for different types of liquid crystals. The detail description is given in references [8, 9]. In this method the mean polarizability is evaluated in terms of parallel bond constituent ($\Sigma\ \alpha\ \|_p$), the perpendicular bond constituent ($\Sigma\ 2\ \alpha\ \perp$) and the non-bond region electron contribution ($\Sigma\ \alpha\ \|_n$). The expression for the mean polarizability is

$$\alpha_M = \frac{1}{3}(\Sigma\ \alpha\ \|_p + \Sigma\ \alpha\ \|_n \Sigma\ 2\ \alpha\ \perp) \tag{3.1}$$

where the parallel bond component is given as

$$\Sigma\ \alpha\ \|_p = \frac{4nA[\exp(T - T_c)/T_c]}{a_0}\left[\frac{R^2}{4} + \frac{1}{2C_{R^2}}\right]\exp\left[-\frac{(x_A - x_B)^2}{4}\right]. \tag{3.2}$$

where n is the bond order 'A' is 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 (3.1), we have

$$\Sigma\ \alpha\ \|_n = \Sigma_i f_j \alpha_j, \tag{3.3}$$

where 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

$$\Sigma\ 2\ \alpha\ \perp = n_{df}\frac{\Sigma x_j^2 \alpha_j}{\Sigma x_j^2} \tag{3.4}$$

where n_{df} is 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.

3.2 Estimation of mean polarizability from Molecular Vibration method

The mean molecular polarizability α_M is calculated by the expression

$$\alpha_M = \Sigma_i n_i \frac{(b_L + 2b_T)_i}{3} \tag{3.5}$$

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

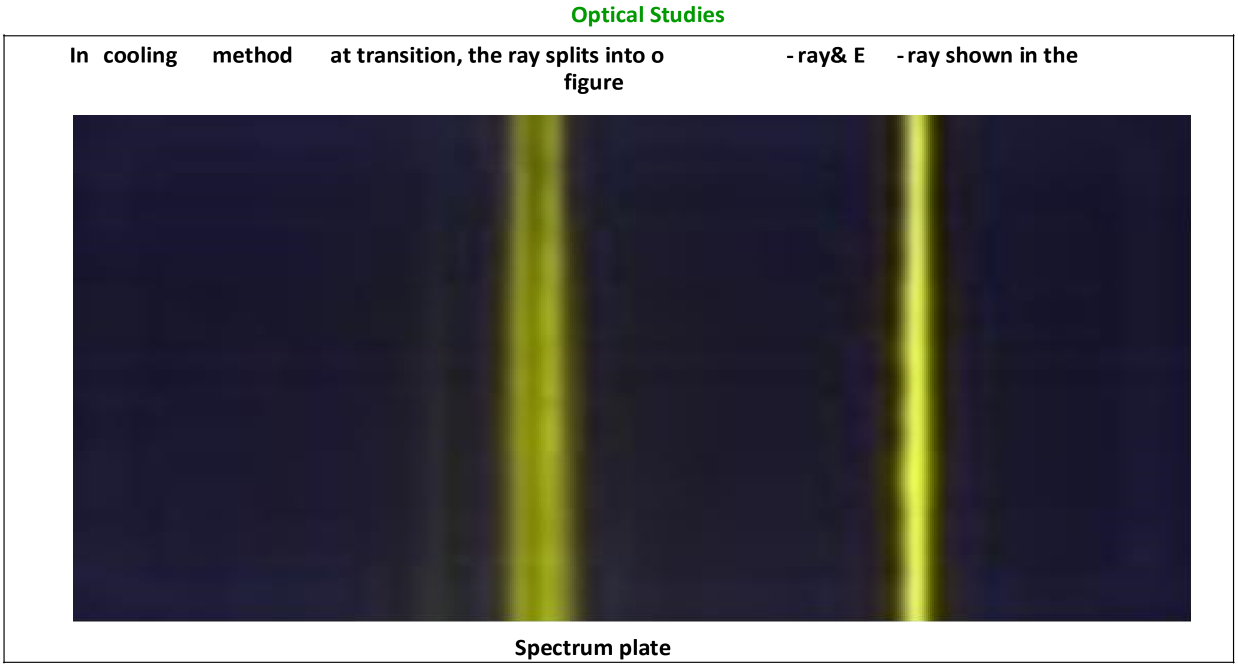
$$b_L - b_T = A\left[(x_1 x_2)^{S/2}\left(\frac{aN}{k-b}\right)^{2S/3}\right] \tag{3.6}$$

$$b_L = 2b_T = [Cp(j)^{n\gamma}\sigma^{1/2}]. \tag{3.7}$$

Utilizing the expressions (3.5), (3.6) and (3.7) the bond polarizability coefficients b_L and b_T and mean molecular polarizability α_M are evaluated.

4. Experimental

Figure 4. Modified spectrometer



Optical Studies

In cooling method at transition, the ray splits into o - ray& E - ray shown in the figure

Spectrum plate

The refractive indices of the LC samples were measured with wedge shaped glass cell similar to the one used to obtain birefringence by Haller et al. [10] and modified spectrometer. A wedge shaped glass cell was prepared with two optical flat rectangular glass plates (50 mm × 25 mm) 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 U shaped bi-capillary pyknometer in conjunction with cathetometer was used for the density measurements at various temperatures. The cooling rate during measurement was 0.5k/hour.

4.1 Estimation of molecular polarizabilities by experimental methods

For the estimation of the molecular polarizabilities of liquid crystalline molecules, the author has chosen 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 technique

The Vuks technique was first implemented to liquid crystalline molecules by Chandrasekhar et al. [11] assuming the internal field is isotropic even in anisotropic crystal. These assumptions lead to the following equations.

$$\alpha_e = \left[\frac{3}{4\pi N}\right]\left[\frac{n_e^2-1}{\bar{n}^2-1}\right], \qquad \alpha_o = \left[\frac{3}{4\pi N}\right]\left[\frac{n_o^2-1}{\bar{n}^2-1}\right] \tag{4.1}$$

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 $N = N_A\alpha/M$ where N_A is the Avogadro number, 'α' is the density and 'M' is the molecular weight.

4.2 Neugebauer technique

Saupe and Maier and Subramanyam et al. [12] applied this method to LC molecule. According to this technique the molecular polarizabilities are

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

$$\alpha_o = \left(AB+3\pm\sqrt{(AB+3)^2-16AB}\right)/4A \tag{4.2}$$

where

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

$$B = \left(\alpha_{\parallel}+2\alpha_{\perp}\right) = (\alpha_e+2\alpha_o) = 3\alpha = 9(\bar{n}^2-1)\left[(4\pi N_i)(\bar{n}^2+2)\right]$$

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

5. Results and Discussion

The bond lengths, atomic delta function and reduced electro negativity values are used to evaluate the molecular polarizabilities of 12.CB, 7O.CB and 5O.CB of liquid crystals by modified Lippincott delta function model. In crystalline state there will be only crystalline field acting on the condensed system whereas in liquid phase pure Brownian field alone will act on the system. But in liquid crystalline phase these two fields will be acting the resultant effect due to these two fields is to decrease the potential on the electron hence contributing more to polarization.

This behavior is expressed by e^{T-Tc}/T. The Polarizability values obtained by this method are represented in Table 2.

Table 2. Parallel, Perpendicular constituent Non bond and mean Polarizability of the Cyanobiphenyl Compounds (10^{-24} cm^3)

Compounds	Lippincott δ function method			
	$\alpha_{\parallel}$	$2\alpha_{\perp}$	α_n	$\alpha_m \times 10^{-24}$
12.CB	71.09	46.03	1.337	39.48
7O.CB	65.95	35.61	1.337	34.29
5O.CB	57.97	29.23	1.337	29.51

The polarizability of a molecule is associated with its vibration and force constant by using force constant and vibrational frequencies of different bonds in a molecule the molecular polarizability is estimated for the above liquid crystalline compounds and represented in Table 3.

Table 3. Mean Polarizabilities of the cyano-biphenyl compounds (10^{-24} cm^3) by Molecular vibrational method

Compounds	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	0.962	
5O.CB	C−H	19	12.89	28.89
	C−C	11	9.98	
	C=C	06	4.320	
	C≡N	01	0.739	
	C−O	01	0.962	

The liquid crystals are birefringent in nature the ordinary and extra-ordinary refractive indices of the above series of liquid crystals are measured in nematic phase and represented in Figure 5-7. The temperature variation of density of these compounds is represented in Figure 8-10. Using refractive indices and density data the ordinary and extra ordinary polarizabilities are estimated by well known Vuks and Neugebauer techniques. The polarizability anisotropy and mean molecular polarizabilities are evaluated and represented in Tables 4-6.

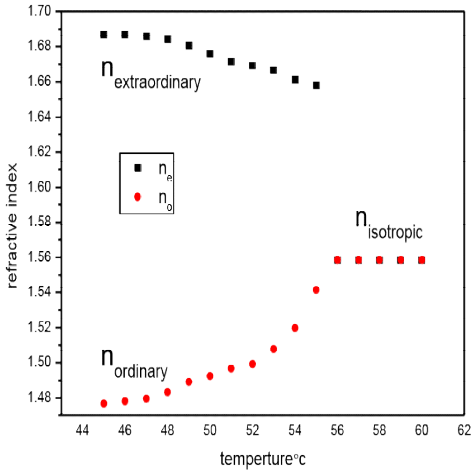


Figure 5. Variation of temperature with refractive index 12.CB

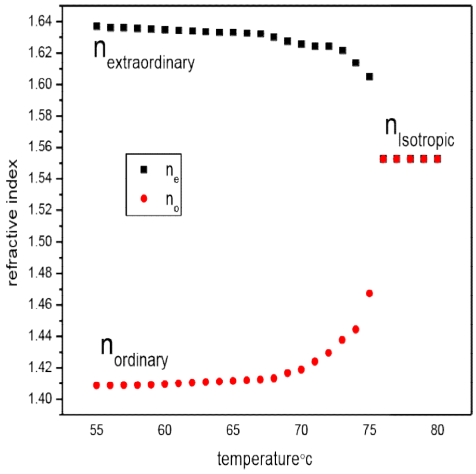


Figure 6. Variation of temperature with refractive index in 7O.CB

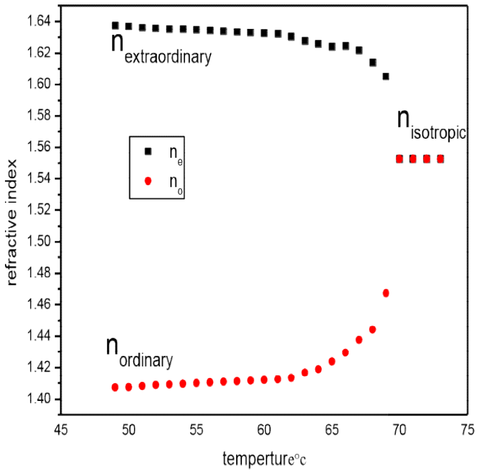


Figure 7. Variation of temperature with refractive index 5O.CB

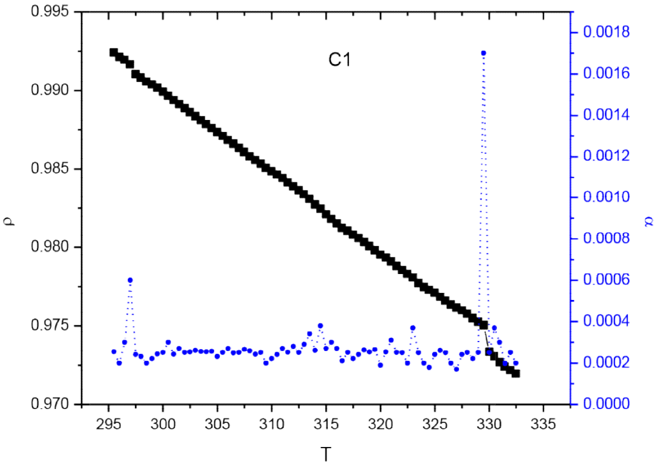


Figure 8. Variation of density and Thermal expansion Co-efficient of 12.CB

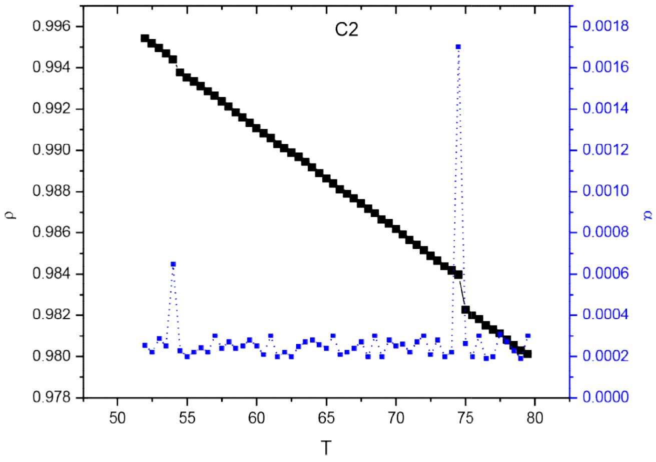


Figure 9. Variation of density and thermal expansion Coefficient of 7O.CB

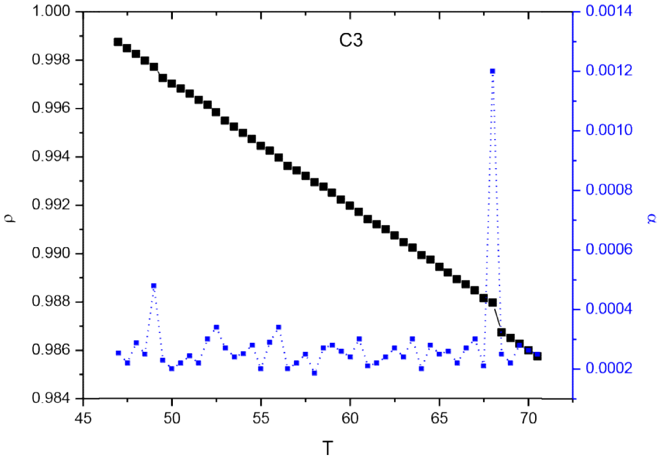


Figure 10. Variation of density and thermal expansion Coefficient of 5O.CB

Table 4. Molecular polarizabilities of Ordinary and extraordinary polarizabilities anisotropies of sample 12.CB

T (℃)	Vuks				Neugebauer			
	αe	αo	αe-αo	α mean	αe	αo	αe-αo	α mean
58	55.03657	43.27688	11.75969	47.19678	53.18955	44.2004	8.98915	47.19678
57	56.2837	41.49188	14.79649	46.42404	54.17377	42.54918	11.62459	46.42404
56	56.5032	40.48049	16.02271	45.82139	54.28845	41.58786	12.70059	45.82139
55	56.94079	39.77325	17.16754	45.49576	54.62115	40.93307	13.68808	45.49576
54	57.18385	39.53539	17.64846	45.41821	54.81584	40.71939	14.09645	45.41821
53	57.68212	39.14669	18.53543	45.32517	55.22216	40.37667	14.84549	45.32517
52	58.15309	38.81608	19.33701	45.26175	55.60807	40.08859	15.51948	45.26175
51	58.62161	38.30578	20.31583	45.07772	55.98045	39.62636	16.35409	45.07772
50	58.83931	37.98347	20.85584	44.93542	56.14701	39.32962	16.81000	44.93542
49	58.9366	37.85291	21.08369	44.88081	56.22186	39.21028	17.01158	44.88081
48	58.95582	37.72563	21.30319	44.80236	56.22901	39.08903	17.13998	44.80236
47	58.97684	37.67378	21.30306	44.7748	56.24273	39.04083	17.2019	44.7748
46	58.99339	37.61913	21.37426	44.74388	56.2522	38.98973	17.26247	44.74388

Table 5. Molecular polarizabilities of Ordinary and extraordinary polarizabilities anisotropies of Sample 7O.CB

T (℃)	Vuks				Neugebauer			
	αe	αo	αe-αo	α mean	αe	αo	αe-αo	α mean
75	43.43177	31.77798	11.65379	35.66258	41.90956	32.53909	9.37047	35.66258
74	44.50937	30.11259	14.39678	34.91152	42.75752	30.98852	11.769	34.91152
73	45.22377	29.60439	15.61938	34.81085	43.35554	30.5385	12.81704	34.81085
72	45.57453	29.02452	16.55001	34.54119	43.63003	29.99678	13.63325	34.5412
71	45.65582	28.63033	17.02549	34.30549	43.67896	29.61876	14.0602	34.30549
70	45.86252	28.2763	17.58622	34.13837	43.84075	29.28718	14.55357	34.13837
69	46.01355	28.109	17.90455	34.07718	43.96373	29.13391	14.82982	34.07718
68	46.28097	27.84606	18.43491	33.99103	44.18416	28.89447	15.28969	33.99103
67	46.4269	27.76271	18.66419	33.98411	44.30699	28.82266	15.48433	33.9841
66	46.44662	27.7212	18.72542	33.96301	44.3213	28.78386	15.53744	33.96301
65	46.46112	27.67663	18.78449	33.93813	44.33063	28.74187	15.58876	33.93812
64	46.47575	27.63219	18.84356	33.91338	44.34011	28.70001	15.6401	33.91338
63	46.49132	27.58836	18.90296	33.88935	44.35048	28.65878	15.6917	33.88935
62	46.51149	27.5473	18.96419	33.8687	44.36524	28.62042	15.79664	33.8669
61	46.52789	27.50406	19.02383	33.84534	44.37643	28.57979	15.84906	33.84534
60	46.54617	27.46197	19.0842	33.82337	44.38941	28.54035	15.84906	33.82337
59	46.56106	27.41794	10.14312	33.79898	44.39916	28.49888	15.90028	33.79897
58	46.66613	27.42696	19.23917	33.84002	44.49491	28.51256	15.98235	33.84001
57	46.59787	27.30989	19.28798	33.73922	44.42395	28.39684	16.02711	33.73921
56	46.60686	27.22377	19.38309	33.6848	44.42675	28.31383	16.11292	33.6848
55	46.75074	27.08213	19.66861	33.63833	44.54544	28.18477	16.36067	33.63833
54	46.80409	26.92787	19.87622	33.55328	44.5832	28.03831	1654489	33.55327

Table 6. Molecular polarizabilities of Ordinary and extraordinary polarizabilities anisotropies of Sample 5O.CB

T (°C)	Vuks				Neugebauer			
	αe	αo	αe-αo	α mean	αe	αo	αe-αo	α mean
69	39.110	28.616	10.494	32.114	37.739	29.301	8.438	32.114
68	40.115	27.139	12.975	31.464	38.536	27.929	10.607	31.464
67	40.742	26.671	14.071	31.361	39.059	27.512	11.547	31.361
66	41.059	26.149	14.910	31.119	39.308	27.025	12.282	31.119
65	41.132	25.793	15.338	30.906	39.351	26.684	12.667	30.906
64	41.319	25.475	15.844	30.757	39.498	26.386	13.112	30.757
63	41.453	25.323	16.130	30.700	39.606	26.246	13.360	30.700
62	41.694	25.086	16.607	30.622	39.805	26.030	13.774	30.622
61	41.829	25.013	16.815	30.618	39.919	25.968	13.950	30.618
60	41.842	24.973	16.869	30.596	39.927	25.930	13.997	30.596
59	41.855	24.933	16.922	30.573	39.936	25.892	14.043	30.573
58	41.872	24.895	16.977	30.554	39.948	25.857	14.090	30.554
57	41.888	24.856	17.031	30.534	39.959	25.821	14.138	30.534
56	41.901	24.817	17.084	30.511	39.968	25.783	14.184	30.511
55	41.916	24.778	17.138	30.491	39.978	25.747	14.231	30.491
54	41.930	24.738	17.191	30.469	39.987	25.710	14.277	30.469
53	41.944	24.699	17.245	30.448	39.997	25.673	14.323	30.448
52	41.953	24.657	17.296	30.422	40.001	25.633	14.368	30.422
51	41.975	24.601	17.374	30.392	40.017	25.580	14.437	30.392
50	42.026	24.549	17.476	30.375	40.058	25.533	14.524	30.375
49	42.014	24.519	17.495	30.350	40.045	25.503	14.541	30.350

The molecular polarizabilities obtained by above techniques are found to be same, there is a small deviation in polarizability values from one technique to another technique but this deviation is within experimental error. The polarizabilities obtained by different methods are illustrated in Table 7.

Table 7. Molecular Polarizability by different methods comparative table (10^{-24} cm^3)

Compound	Molecular Polarizability by Theoretical methods		Molecular Polarizability by Experimental methods	
	Lippincott δfunction	Molecular vibration	Vuk's	Neugebauer
12.CB	44.48	44.33	45.39	45.82
7O.CB	34.29	33.44	34.84	35.08
5O.CB	29.51	30.54	30.73	30.93

The polarizabilities obtained by Lippincott-delta function model and Molecular vibration techniques are matching with experimental values hence the theoretical approaches exploited in the present investigation are said to be applicable to liquid crystalline compounds.

6. Conclusion

In molecular vibration method a small deviation in inter molecular forces due to changes in chemical environment will truly registered in their force constant and vibrational frequencies whereas the bond lengths, reduced electro-negativity values used in Lippincott delta function model are less sensitive than the conformational changes in vibrational frequencies. Hence molecular vibration method is superior to delta function method. The refractive indices method is ideal and authentic method to estimate the polarizabilities hence the theatrical methods can be compared with refractive indices method.

Acknowledgement

Authors express their gratitude to the Department of Physics, GCE, Ramanagara, Karnataka, India for providing laboratory facilities. The author Rihanabanu is thankful to UGC for deputating her to carry out research work under the FIP.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

References

[1] J. P. Stephen, J. D. Theo, A. M. Louis, F. Oriano and T. S. Edwart, *Liq. Cryst.* **39**(1), 19 – 23 (2012), DOI: 10.1080/02678292.2011.631593.

[2] R. D. Mallikarjuna and S. Varghese, *Liq. Cryst.* **39**(1), 63 – 70 (2012), DOI: 10.1080/02678292.2011.611899.

[3] P. G. de Gennes and J. Frost, *The Physics of Liquid Crystals*, University Press, New York (1993).

[4] K. Fakruddin, R. Jeevan Kumar, P. V. Datta Prasad and V. G. K. M. Pisipati, *Mol. Cryst. Liq. Cryst.* **511**(1), 146 – 157 (2009), DOI: 10.1080/15421400903053693.

[5] V. R. Murthy, S. V. Naidu and R. N. V. Ranga Reddy, *Mol. Cryst. Liq. Cryst.* **59**(1-2), 27 – 32 (1980), DOI: 10.1080/00268948008073496.

[6] C. M. Subhan, R. Jeevan Kumar, P. PanduRanga, B. Jayashree and K. Fakruddin, *Acta Physica Polonica A* **129**, 284 – 288 (2016), DOI: 10.12693/AphysPolA.129.284.

[7] G. K. Narasimhamurthy, C. M. Subhan, S. Agarwal, S. Rangappa, C. V. Yellamaggadd and K. Fakruddin, *Mol. Cryst. Liq. Cryst.* **641**, 25 – 36 (2016), DOI: 10.1080/15421406.2016.1235928.

[8] E. R. Lippincott and M. O. Dayhoff, *Spectrochim Acta* **16**, 807 (1960).

[9] E. R. Lippincott and J. M. Stuttman, *J. Phys. Chem.* **68**(10), 2926 – 2940 (1964), DOI: 10.1021/j100792a033.

[10] I. Haller, H. A. Huggins and M. J. Freisner, *Mol. Cryst. Liq. Cryst.* **16**, 53 (1972).

[11] S. Chandrasekhar and N. V. Madhusudhana, *J. Phy. (Paris)* Colloq. C-4 Supp. 11-20, C4-24 (1969).

[12] H. S. Subramhanyam and D. Krishnamurti, *Mol. Cryst. Liq. Cryst.* **22**, 239 – 248 (1973), DOI: 10.1080/15421407308083347.