Theoretical approach to estimate Molecular Polarizability and Diamagnetic Susceptibility of 6O.CB and 10O.CB Mesogens

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Abstract: **In the present work, phase transition temperatures of hexyloxy and decyloxy cyanobiphenyl liquid crystal compounds are recorded by using Differential Scanning Calorimeter. These temperatures are needed in determining molecular polarizabilities by theoretical approaches viz, Lippincott δ function and Molecular vibration techniques. The molecular polarizabilities attained by the above two approaches are found to be same. The mean Polarizability and diamagnetic susceptibility depend on the number of free electrons which participate in magnetic and optical interactions. Based on these concepts the diamagnetic susceptibilities are evaluated by Rao's and Pascal's methods. In both these cases the diamagnetic susceptibility is found to be comparable.**

Keywords: **Oxycyanobiphenyl liquid crystals, transition temperature, molecular polarizability and diamagnetic susceptibility.**

I. INTRODUCTION

There are certain organic substances which do not directly pass from crystalline solid to isotropic liquid but accept an intermediate phase which flows like liquid but still possess anisotropic property similar to crystalline solid (de Gennes 1974; Brown 1975). The understanding of the molecular organization in mesogenic materials is very much required for the better understanding of these materials and their applications. The molecular Polarizability is one of the significant properties of liquid crystals, according to several theoretical models the intermolecular energy depends on Polarizability (Vuks 1966; Neugebaur 1950; Fakruddin et al. 2009; Ibrahim and Haase 1981; Subhan et al. 2016; Narasimha Murthy et al. 2016). There are both experimental

and theoretical methods to estimate molecular polarizabilities. In the present study the molecular polarizabilities are estimated by theoretical methods viz.

Lippincott δ function model and the molecular vibration methods. In Lippincott δ function model the bond lengths, atomic delta function and reduced electro negativity values are used to evaluate Polarizability. Where as in molecular vibration method, the vibrational frequencies are used, these vibrational frequencies are recorded by using FTIR. Since there is a correlation between Polarizability and diamagnetic susceptibility (Kirkwood 1932; Vinti 1932; Rao et al. 1979) Rao developed semi empirical relation to estimate diamagnetic susceptibility using Polarizability. The susceptibility estimated by Rao's method is verified by Pascal's semi empirical relation (Pascal 1913). In both the methods the susceptibility values are found to be same. For experimental determination of susceptibility bulk sample is required hence theoretical methods are employed.

II. MATERIALS AND METHODS

The compounds used in the present work possess the molecular formula $C_{19}H_{21}NO$ and $C_{23}H_{29}NO$.Perkin Elmer Diamond Series - 2008 Differential Scanning Calorimeter, is used to obtain the thermo grams during both the cycles of heating and cooling at the rate of $5^{\circ}C$/minute. The thermo grams recorded in case of 6O.CB and 10O.CB liquid crystalline compounds are illustrated in figures 1 and 2. The clearing temperatures are identified from thermo grams and represented in table 1.

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Table 1 Phase Transition Temperatures and Phase Variants observed in DSC

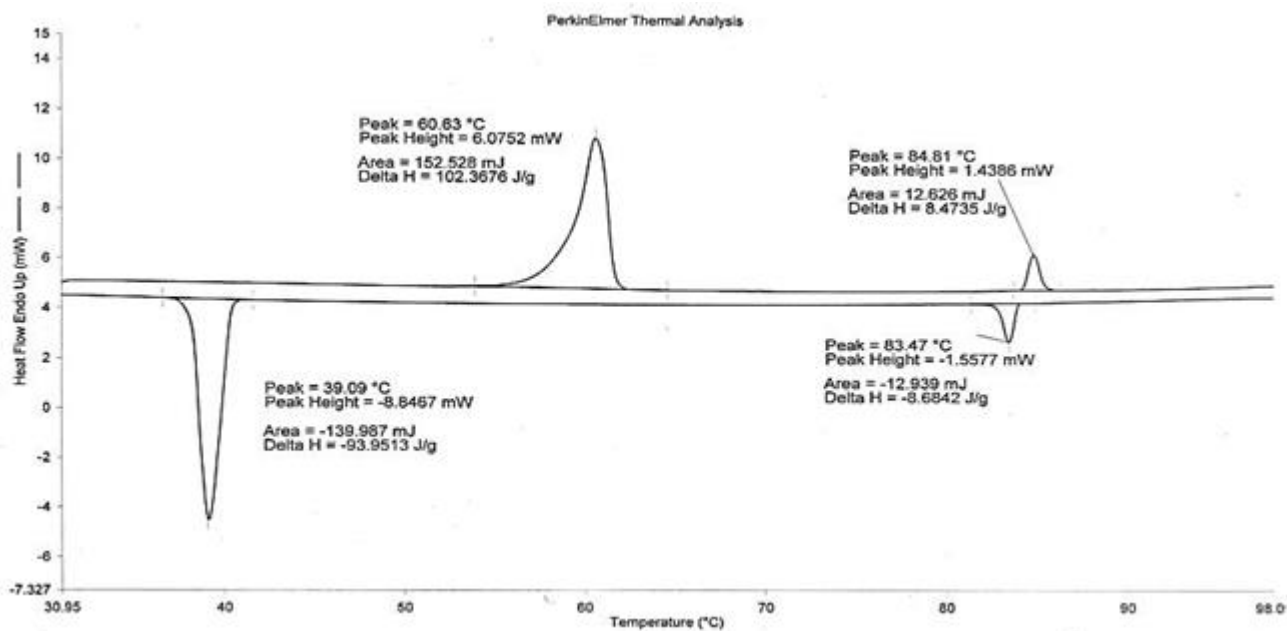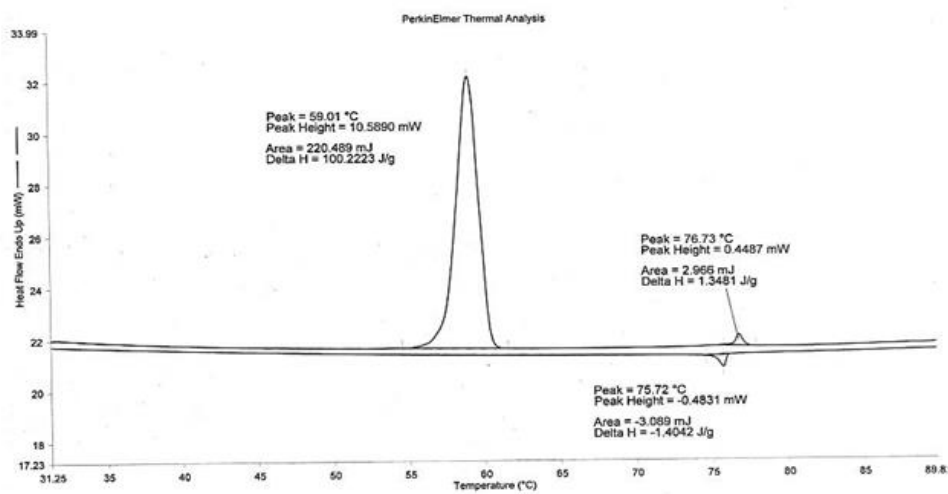| Compound	Transition Temperature in (ºC)				Thermal Range (ºC)	
	I-N	N-Cr	I-SmA	SmA-Cr	ΔN	ΔSmA
6O.CB	76.73	59.01	--	--	17.72	--
10O.CB	--	--	84.81	60.63	--	24.18

Fig. 1 DSC Thermograms of compound 6O.CB

Fig. 2 DSC Thermograms of compound 10O.CB

1 Molecular Polarizability- Lippincott δ Function Potential Model

The detailed description of Lippincott δ - function model is given in references (Lippincott and Dayhoff 1960; Lippincott and Stutmann 1964). This is a quantum mechanical approach. The molecular polarizability value is determined by quantum mechanical δ function potential model recommended by Lippincott and Stutmann. This method consists of

a) Determination of the parallel bond components using the δ-function model

b) Applying rectification to the parallel components contributed from the electrons of non-bond region

c) Estimation of perpendicular bond components by the atomic δ-function polarizabilities.

d) Calculation of mean molecular polarizability.

a) Parallel component:

Using the variational treatment given by (Hylleraas 1930; Hasse 1930), Lippincott and Stutmann arrived at an expression for parallel bond polarizability $\alpha_{\|b}$

$$\alpha_{\|b} = \frac{4nA}{a_0}\left[\frac{R^2}{4} + \frac{1}{2C_R^2}\right] exp\left[-\frac{(X_1-X_2)^2}{4}\right]$$

The application of Lippincott δ - function potential model to determine the mean molecular polarizability value of liquid crystal is performed by (Murthy et al. 1980).

In crystalline state, it is the crystalline field which would be acting on the condensed system. In the liquid phase, only the Brownian field which will be acting on the system and, in the liquid crystalline state, both of these would be acting. The resultant effect of these forces decreases the potential on the electron (system). Thus, shielding on the electron will be reduced and the contribution to the polarization will be more. This is represented by the equation $A_{LC} = A\, exp\left(\frac{T-T_C}{T_C}\right)$

Where T represents the temperature at which mesogenic property is investigated and T_c is the transition temperature. A_{LC} and A represents the reduced electro negative values (REN) of liquid crystalline and isotropic phases.

$$\sum \alpha_{\|P} = \frac{4nA\left[\exp\frac{(T-T_C)}{T_C}\right]}{a_0}\left[\frac{R^2}{4} - \frac{1}{2C_R^2}\right] exp\left[\frac{(X_1-X_2)^2}{4}\right]$$

b) Non-bond region electron contribution:

The contribution from electrons of non bound region to $\alpha_\|$ is determined by the valence

electrons of an atom, which are free from any bonding and atomic polarizability. (Linnett 1961) model is employed to consider the same.

$$\alpha_{\|n} = \sum_j f_j\alpha_j$$

c) Perpendicular component:

Every atom possesses three degrees of freedom and their contribution to polarizability is equal in all directions. A degree of freedom contributed from each atom will be lost during the formation of the bond in a molecule. For a polyatomic molecule, the two perpendicular components of polarizability is

$$\sum_i 2\alpha_{\perp i} = (3N - 2n_b)\frac{\sum x_j^2\alpha_j}{\sum x_j^2}$$

d) Mean molecular polarizability:

Mean value of molecular polarizability is determined from

$$\alpha_M = \frac{1}{3}\left(\sum \alpha_{\|p} + \sum \alpha_{\|n} + \sum 2\alpha_\perp\right)$$

2 Molecular Vibration Method:

The polarizability of any molecule is found to be related to its normal vibration, (Rao and Murthy 1979) suggested that the mean amplitudes of vibration ($\sigma^{1/2}$) and the bond polarizabilities (b_L and b_T) are found to be reliant on the bond strength variations with the internuclear distance. The suggested relation is of the form

$$b_L + 2b_T = Cp^{jB}J_B^{ny}\sigma^{\frac{1}{2}}$$

Here C = 5.24 x 10^{-15} (constant),' p' characterises the electronegative atom present in the bond and will be equal to 1, 1.2, 1.3, 1.4 and 1.5 depending on the 2nd to 6th rows of the periodic table. 'n' will be +1 for non-hydride and -1 for hydride. 'γ' represents the saturation factor which represents the valence electrons present in more electronegative atom participating during the bond formation.

After evaluating the values of b_L and b_T associated with all the bonds of the molecule, the mean molecular polarizability value of the molecule is estimated by

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

Here 'n_i' denotes the bonds of type i (Murthy et al.1997; Ranga Reddy et al. 1994). This method is used to determine mean molecular polarizability of liquid crystalline compounds.

3 Diamagnetic Susceptibility by Polarizability Method:

Diamagnetic susceptibility depends on the operative number of free electrons which participate in the magnetic and the optical interactions. Considering this fact, the relation was proposed based on semi-empirical grounds.

$$\chi_M = -(\gamma m\,\sigma^1)\alpha_M$$

Here, $\gamma = (0.9)^n$ discloses the saturation state of a molecule, with 'n' denoting the bonds which are unsaturated and the rings present in the molecule. σ^1 represents the amount of covalence of the representative group evaluated by the equation.

$$\sigma^1 = \left(\sigma_1^{1/n1}, \sigma_1^{1/n2}, \sigma_3^{1/n3} \dots \dots \dots \sigma_p^{1/np}\right)$$

Where, σ_1, σ_2 ……. σ_p denotes the Pauling's percent covalence characters associated with the bonds of the representative group, 'm' signifies the characteristic constant whose value is 0.72×10^{19}.

The expression for diamagnetic susceptibility,

For saturated compounds

$$\chi_M = -0.72 \times 10^{19}\,(\sigma^1)(\alpha_M)$$

For unsaturated compounds

$$\chi_M = -0.72 \times 10^{19}\,(0.9)^n(\sigma^1)(\alpha_M)$$

σ^1, the degree of covalency for different types of compounds, is calculated using the respective formulae.

4 Evaluation of Diamagnetic Susceptibility - Pascal's Method:

Pascal from his exhaustive study on large number of compounds established magnetic susceptibility expression.

$$\chi_M = \sum n_A \chi_A + \lambda^i$$

Where, n_A denotes the number of atoms with susceptibility χ_A in a molecule and λ^i represents constitutive correction dependent on the nature of the bonds existing between the atoms.

III. RESULTS AND DISCUSSION

- According to Lippincott and Stutman the molecular polarizability comprises of parallel bond component, perpendicular bond component and non-bond region component.
- In crystalline state, the only field acting on the system is crystalline field, pure brownian field will be acting on the liquid system. In mesogenic phase both of these fields will be acting and the net effect of these forces decreases the shielding on the electrons contributing more to the polarization. This behavior is expressed as $\exp\left(\frac{T-T_C}{T_C}\right)$. This modification is included in Lippincott relation.
- Using the valence electrons present in the atom, the non-bond region electron share is considered for polarizability.
- During the molecule formation from atoms, a degree of freedom contributed from each atom will be lost due to the bond formation, thus only two perpendicular components contributing to polarizability are considered.
- The mean amplitude of vibration and bond polarizabilities are found to be reliant on the bond strength variation with respect to internuclear distances. The longitudinal and transverse polarizabilities for the bonds present in a molecule are estimated as per semi empirical relation proposed by Rao and Murthy and are represented in table 3.
- The mean molecular polarizability by Lippincott δ function model and the molecular vibration methods are nearly same which is illustrated in table 4.
- The diamagnetic susceptibility is dependent on polarizability and the degree of Pauling's covalence

character, based on this analogy diamagnetic susceptibility is estimated by Rao's method. The diamagnetic susceptibility obtained by Rao's method is verified by Pascal's constant method. In both of these cases, the diamagnetic susceptibility is found to be the same. The polarizability and diamagnetic susceptibility increase with the chain length in the compounds.

Table 2 Parallel, Non Bond Region, Perpendicular and the Mean polarizability values of the mesogens calculated by Lippincott δ function method

Compound	Parallel Bond Component of Polarizability $\alpha_{\parallel}$ $(10^{-24}cm^3)$	Perpendicular Bond Component of Polarizability $2\alpha_{\perp}$ $(10^{-24}cm^3)$	Polarizability of Non Bond Region Electrons α_n $(10^{-24}cm^3)$	Mean Polarizability α_{Mean} $(10^{-24}cm^3)$
6O.CB	79.8566	31.796	1.337	37.6632
10O.CB	90.9183	40.877	1.337	44.294

Table 3 Mean Polarizabilities of the compounds by Molecular Vibrational method

Compound	Bond in molecule	Number of Bonds	$(b_{L}+2b_{T})/3$ 10^{-24} (cm^3)	Mean Polarizability 10^{-24} (cm^3)
6O.CB	C–H	21	15.69	35.1438
	C–C	13	12.17	
	C=C	6	4.621	
	C–O	2	1.9238	
	C≡N	1	0.739	
10O.CB	C–H	29	21.026	44.8948
	C–C	17	16.885	
	C=C	6	4.321	
	C–O	2	1.9238	
	C≡N	1	0.739	

Table 4 Comparison of polarizability values

Compound	Lippincott δ function method $(10^{-24}cm^3)$	Molecular vibration method $(10^{-24}cm^3)$
6O.CB	37.6632	35.1438
10O.CB	44.294	44.8948

Table 5 Comparison of diamagnetic susceptibilities evaluated by theoretical methods

Compound	Rao's method in CGS units	Pascal's method in CGS units
6O.CB	19.89×10^{-6}	18.08×10^{-6}
10O.CB	25.41×10^{-6}	22.83×10^{-6}

IV. CONCLUSION

The polarizabilities obtained by Lippincott δ function model and the molecular vibration method are almost same. Hence the both of these methods are applicable for liquid crystalline compounds. Among these two methods, the molecular vibration method has an upper hand than Lippincott δ function model, because even a small variation in the intermolecular forces arising due to the fluctuations in any chemical environment is found to be registered in force constant and vibrational frequencies. The bond lengths and the reduced electro negativities employed in Lippincott method are less profound than the conformational variations in vibrational frequencies. The polarizability can also be estimated experimentally by refractivity method, sometimes the splitting does not occur in smectic phases and hence refractivity method cannot be used, then the theoretical approaches are useful. Estimation of diamagnetic susceptibility by experimental method demands large quantity of the sample, which is difficult in liquid crystal research, hence theoretical approaches are more relevant in such environments.

REFERENCES

Brown, G.H. (1975). Advances in Liquid Crystals. Academic Press, New York.

de Gennes, P.G. (1974). The Physics of Liquid Crystals. Clarendon Press, Oxford.

de Jeu, W.H., & Bordewijk, P. (1978). Physical studies of nematic azoxybenzenes. II. Refractive indices and the internal field. *J. Chem. Phy.* 68(1), 109-115.

Fakruddin. K., Jeevan Kumar, R., Datta Prasad P.V. & Pisipati, V.G.K.M. (2009). Phase Transition and Molecular Polarizability Studies in Lower Homologues of Alkoxybenzylidene Alkoxyanilies. *Mol. Cryst. Liq. Cryst.* 511, 146-157.

Hasse, H.R. (1930). *Proc. Cambridge. Phil. Soc.,* 26, 542.

Hylleras, E. (1930). About the basic term of the two-electron problems of H⁻, He, Li, Be, etc. Z. Physik. 65, 209-225.

Ibrahim, I.H. & Haase, W. (1981). On the Molecular Polarizability of Nematic Liquid Crystals. *Mol. Cryst. Liq. Cryst* 66, 189-198.

Kirkwood, J.G. (1932). *Phys. ZS*, 33:57.

Linnet, J.W. (1961). A Modification of the Lewis-Langmuir Octet Rule. *J. Am. Chem. Soc.* 83, 2643-2653.

Rao, B.P., Murthy, V.R., Subbaiah, D.V. & Naidu, S.V. (1979). *Acta Sciencia Indica* 5, 124.

Subhan, C.M, Jeevan Kumar, R. Pandu Ranga, P., Jayashree, B., & Fakruddin, K. (2016). An Optical Study to Estimate Orientational Order Parameter on Some Benzylidene aminophenyl benzoate Liquid Crystals. *Acta Physica Polonica A* 129, 284-288.

Vinti, J.P. (1932). A Relation between the Electric and Diamagnetic Susceptibilities of Monatomic Gases. *Phys. Rev.* 41, 813-817.

Vuks, M.F. (1966). *Opt. Spectroscope,* 20, 361.

Lippincott, E.R., & Dayhoff, M.O. (1960). *Spectrochim, Acta* 16, 807.

Lippincott, E.R., & Stutman, J.M. (1964). Polarizabilities from δ-Function Potentials. *J. Phys. Chem.* 68, 2926-2940.

Murthy, V.R., Naidu, S.V., & Ranga Reddy, R.N.V. (1980). Polarizabilities of few nematic liquid crystals. *Mol. Cryst. Liq. Cryst.* 59, 27-32.

Murthy, Y.N., Murthy, V.R., & Ranga Reddy, R.N.V. (1997). Molecular Vibration Approach to Polarizabilities of Methyl Cinnamate Liquid Crystal Compounds. *Acta Physica Polonica A*. 91, 1069-1079.

Narasimha Murthy, G.K., Subhan, C.M., Seema Agarwal, Rangappa, S., Yalamaggad, C.V., & Fakruddin, K. (2016). Orientational order parameter of some CBOnO.m liquid crystalline compounds—an optical study. *Mol. Cryst. Liq. Cryst* 641, 25-36.

Neugebaur, H.E.J. (1950). *Can. J. Phy*., 18, 292.

Pascal, P. (1913). *Ann.Chim.et Phys.* 29, 218.

Rao, B.P., & Murthy, V. R. (1979). *Ind. Chem. J*. 13, 17.

Ranga Reddy, R.N.V., Reddy, K.C., & Rama Murthy, V. (1994). Physical Studies of Binary Mesophase Mixtures Containing N-(p-Propoxy Benzylidene)-p-Pentylaniline. Acta Physica Polonica A. 86, 385-391.

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