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Phase Transition and Molecular Polarizability Studies in Liquid Crystalline Mixtures

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***Abstract*—**In this work, two mixtures with equal concentrations of 1) 4'-(6-(4-(pentylamino) methyl)-3-hydroxyphenoxy) hexyloxy) biphenyl-4-carbonitrile+-4-((4-(hexyloxy) benzylidene) amino) phenyl 4-butoxy benzoate and 2) 4' - (6-(4-(hexylamino) methyl)-3-hydroxyphenoxy) hexyloxy) biphenyl-4-carbonitrile+-4-((4-(octyloxy) benzylidene) amino) phenyl 4-butoxy benzoate, have been prepared. The transition temperature and optical texture are observed by using thermal microscopy. Density and birefringence studies are carried out on the above liquid crystalline mixtures. Using density and refractive indices data, the molecular polarizabilities are evaluated by using well-known Vuks and Neugebauer models. The molecular polarizability is also evaluated theoretically by Lippincott δ function model. The results reveal that the polarizability values are same in both experimental and theoretical methods.

***Keywords*—**Liquid crystals, optical textures, transition temperature, birefringence, polarizability.

I. Introduction

THE nematic liquid crystals and their mixtures are found to be useful in electro optical devices due to their exquisite optical, physical and electrical properties [1]-[8]. By mixing two nematogens, one can often obtain a lower melting point. Usually, two nematogens exhibit the property of continuous miscibility without crossing any line (First order or second order transition line) [2]. Binary mixtures offer the advantage of frequently exhibiting eutectic behaviors in their solid-mesophase transition and in mesophase-isotropic transition, the temperature varies linearly with composition. Further, for technological use of liquid crystals, the liquid crystalline materials of specific molecular design and synthesis are viable but expensive to influence the properties of mesophases. The needed properties can rather be reached by mixing compounds with various molecular shapes and properties rather than by looking for pure compounds [9], [10]. Miscibility studies are still in their infancy [11]-[15]. Following this reason, we have studied the mixtures of some novel liquid crystals.

The oxy benzylidene aminophenyl butoxy benzoates and amino methylhydroxyl phenoxyhexyloxybiphenyl carbonitrile liquid crystals are new and exciting class of liquid crystals with different chemical structures. The mixtures of the compounds in equal concentrations have been prepared subsequently carried out thermal microscopy, birefringence and dilatometric studies. The dilatometric investigations on phase transitions of liquid crystals play a vital role. The density results [16]-[18] are complementary to the optical studies [19], [20], thermal studies [21] and provide information regarding the nature of phase transition. The important parameter of the liquid crystals which governs most of the physical properties is its polarizability. There are different methods to evaluate the polarizability. Using experimental density and birefringence data, the mean molecular polarizability is estimated by well-known internal field models such as Vuks and Neugebauer methods. The polarizability is also evaluated theoretically by Lippincott δ function models. The polarizability obtained by experimental and theoretical methods are nearly same.

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II. Experimental

Liquid crystalline compounds are birefringent and exhibit optical textures for different phases under crossed polars. A polarizing microscope (SDTECHS-SDVPM2727) with the hot stage is used to identify the different phases and to determine the phase transition temperatures.

A U-shaped bi-capillary Pyknometer in conjunction with the cathetometer was used for the density measurements. The absolute difference in the measurements of density is $\pm 10^{-4}$ g/cm^{-3}. The cooling rate during the measurement was 0.5 K/h.

The refractive indices of the liquid crystal were measured with wedge shaped glass cell with a modified spectrometer. A wedges shaped glass cell was formed with two optically flat rectangular glass plated (50 mm x 25 mm) sandwiched with glass plate (0.4 mm) which acts as a wedge spacer. The optical flats are uniformly rubbed along the short edge the alignment of the LC molecule. The cell is filled with the LC material. The LC in the cell acts as a uniaxial crystal with its optic axis parallel to the edge of the spacer glass plate. The temperature accuracy of the heating block was ±0.1 °C. The accuracy in the measured refractive indices was ±0.0005.

III. Results and Discussions

The optical textures observed across different phases and respective transition temperature are measured by using thermal microscope and illustrated in Fig. 2 and Table I.

TABLE I
Transition Temperatures of the Compounds

Sl.No	Compound	Transition temperature
1	C1 = 50%A1 + 50%B1	C_r 143 °C -- 165.1 °C-Sm A
2	C2 =50%A2 + 50%B2	C_r 111 °C -- 158.6 °C-Sm A- 160 °C N - 167.7 °C ISO

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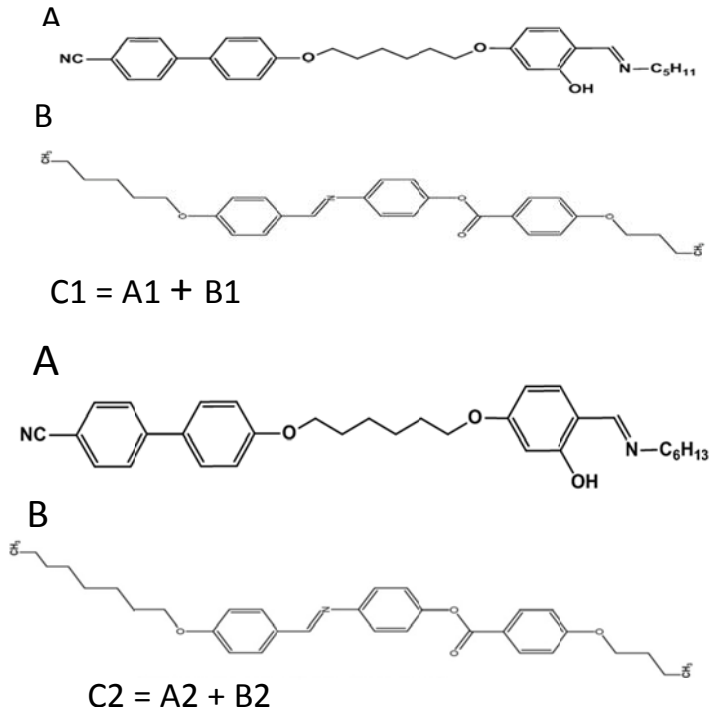
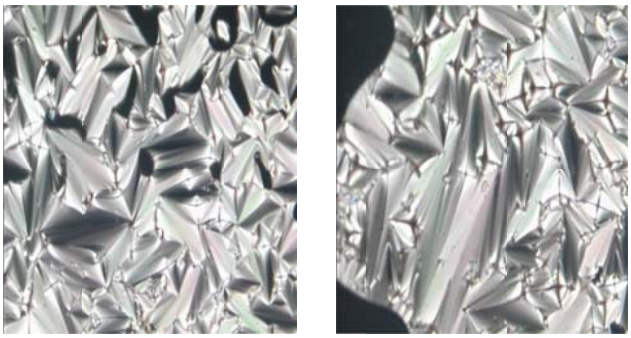
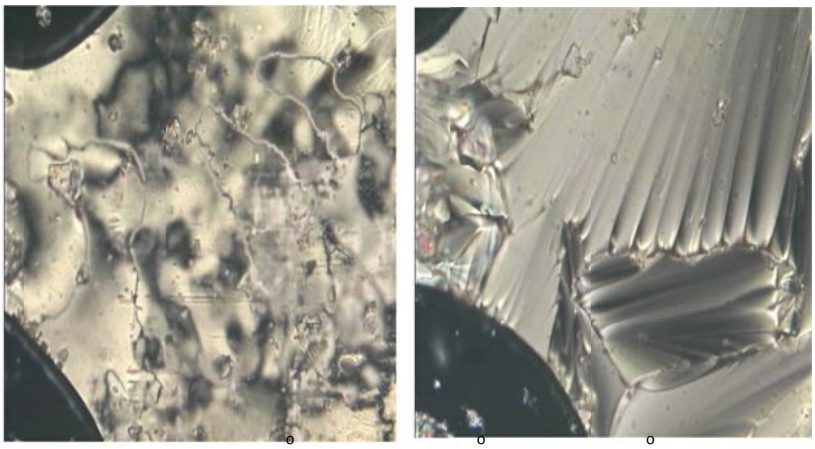


Fig. 1 Chemical Structures of the Studied Compounds



C1-143C-SmAC2-160C-SmA C1-143C-SmA

C1: Iso - SmA-165.1 °C



C2: Iso - N- 167.7 °C N-SmA – 158.6 °C Cryst ~ 111 °C

Fig. 2 Optical Textures of the compounds

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IV. Dilatometric Studies

The temperature variation of density is measured by using dilatometer, and the density decreases with the increase of temperature in the above liquid crystalline mixtures. However, it shows a steep increase in the vicinity of phase transition. The temperature variations of density, ρ(T) and thermal expansion coefficient, α(T) = 1/ρ(dρ/ρ) for the above mixtures are shown in Figs. 3 and 4.

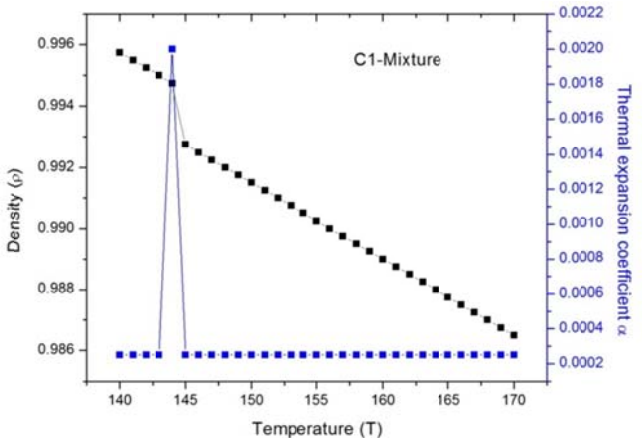


Fig. 3 Variation of Density and Thermal expansion coefficient with Temperature in C1-Mixture

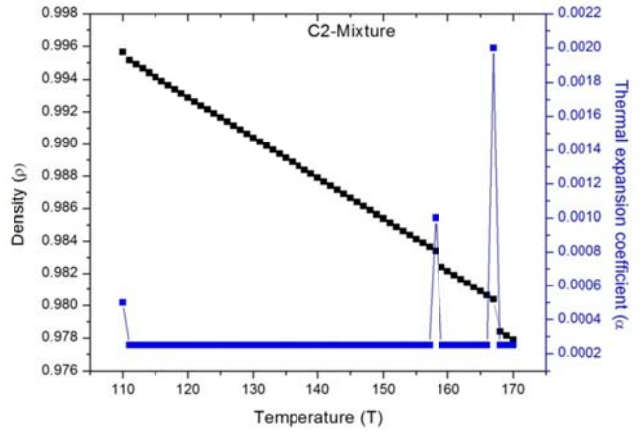


Fig. 4 Variation of Density and Thermal expansion coefficient with Temperature in C2-Mixture

The density jump, (Δρ/ρ) is calculated as the vertical distance between the density values (ρ1 and ρ2) obtained by the linear extrapolation from either sides of the transitions, (which are in fact the average value of the above two extrapolated density values i.e., [{(ρ1-ρ2)}/{(ρ1+ρ2)/2}]. The observed percentages of density jumps in both cases at the IN interphase are 0.2013 and 0.2042, respectively, and the values are consistent within the range reported for other compounds in the some homologous series as well as other LC compounds which exhibit IN transition. The observed density jumps and the thermal expansion coefficient maxima observed at the IN transition suggest that the transition is first order as expected.

V. Birefringence Studies

The refractive indices of the above liquid crystalline mixtures are measured using the modified spectrometer and wedged shaped cell. The refractive indices n_e and n_o are measured at wavelength 589.3 nm. The refractive index practically shows no change in the isotropic phase. At the IN phase transformation, the isotropic value splits into two; one value lower and another higher than isotropic value corresponding to extraordinary (n_e) and ordinary refractive indices (n_o), respectively. This is clearly observed in the telescope of the modified spectrometer at the angle of minimum deviation. In the nematic region, the n_e increases, while n_o decreases with the decrease of temperature, and both the values attain saturation deep in the nematic region. The variation of refractive indices with temperature is illustrated in Figs. 5 and 6.

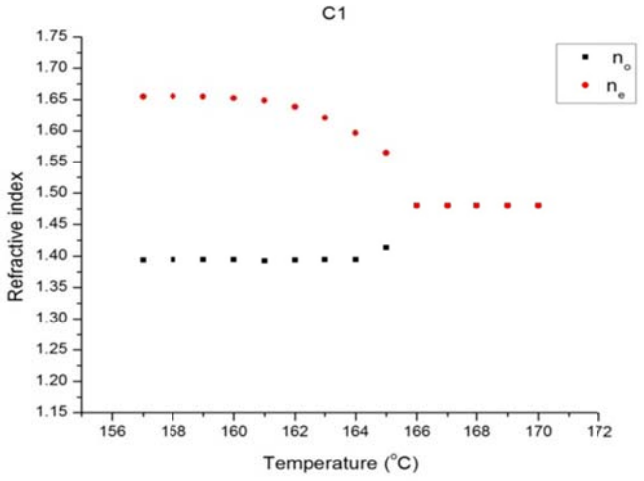


Fig. 5 Temperature variation of Refractive index in C1

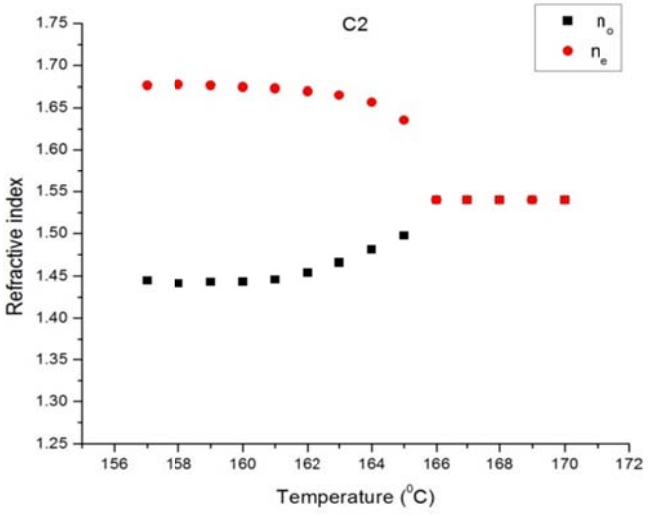


Fig. 6 Temperature variation of Refractive index in C2

A. Estimation of Molecular Polarizabilities - Experimental

For the estimation of the molecular polarizabilities of LC molecules, the author has considered Vuks model which

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assumes that the local field of the molecule is isotropic and Neugebauer model which assumes that the local field is anisotropic. The relevant equations of the two models for the calculation of molecular polarizabilities are given below.

1. Vuks Method

This model was first applied to LC molecules by Chandrasekhar et al. [25] assuming the internal field is isotropic even in anisotropic crystal. These assumptions lead to:

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

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

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.

2. Neugebauer Method

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,

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

$$B = \left(\alpha_{\|} + 2\alpha_{\perp}\right) = \left(\alpha_e + 2\alpha_o\right)$$

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

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

B. Estimation of Molecular Polarizabilities- Theoretical

The modified Lippincott δ function model is used for the evaluation of mean molecular polarizability. The detailed description is given in references [22], [23]. However, a brief description is given below.

Lippincott et al. [23] calculated molecular polarizabilities for a number of diatomic and polyatomic molecules and in brief the principle and the formulae involved are given below:

- Evaluating the parallel bond components from the δ-function model.
- Corrections are to be made to the parallel component from the nonbonding regions.
- Obtaining the perpendicular bond components from the δ-function strengths.
- Finally evaluating the mean polarizabilities from the parallel and perpendicular components.

The non-bond-region electron contribution $\alpha_{\|n}$ is calculated from the fraction of the atom not involved in bonding and its atomic polarizability; and the basis for such calculation is the Lewis-Langmuir Octet rule modified by Linnett [24] as the double quartet of electrons.

$$\alpha_{\|n} = \Sigma f_j \alpha_j \quad (1)$$

It is well known that the δ- function model is one dimensional. Hence, the perpendicular component of polarizability of diatomic molecule can be obtained from this method. The relevant equation used here is

$$\Sigma 2\alpha_{\perp} = n_{df}\left[\frac{\sum_j x_j^2\,\alpha_j}{\sum_j x_j^2}\right] \quad (2)$$

In crystalline state, there will be only the crystalline field acting on the system whereas in liquid phase, pure Brownian field only acts on the system. However, in liquid crystalline state, both these fields will be acting as this state will have the flow property like a liquid and anisotropic property like pure crystal. The resultant effect is to increase the potential on the electron (system). In other words, the shielding on the electrons will be less thus contributing to more polarization. This behaviour can be expressed empirically as

$$A_{LC} = A \exp\left[T - T_C\right] / T_C \quad (3)$$

where T is the temperature pertinent to the study of the liquid crystal property, and T_C is the liquid crystalline transition temperature (clearing temperature). A and A_{LC} are the reduced electro negativities (REN) values in isotropic and LC phases.

$$\Sigma \alpha_{\|P} = \frac{4nA\left[\exp\left(T - T_C\right) / T_C\right]}{a_0}\left[\frac{R^2}{4} - \frac{1}{2C_R^2}\right]\exp\left[\frac{\left(x_1 - x_2\right)^2}{4}\right] \quad (4)$$

Using (1), (2) and (4) $\Sigma\alpha_{\|P}$, $\Sigma\alpha_{\|}n$ and $\Sigma 2\alpha_{\perp}$ can be calculated. Now the mean polarizability:

$$\alpha = \left[\frac{\sum \alpha_{\|P} + \sum \alpha_{\|n} + \sum 2\alpha_{\perp}}{3} \right] \quad (5)$$

The mean molecular polarizabilities of Liquid crystalline mixtures can be estimated by.

$$\alpha_{Mix} = \alpha_1 x + \alpha_2 (1 - x) \quad (6)$$

where α_1 and α_2 are the polarizabilities of 1st and 2nd compounds and x, (1-x) are the mole fractions of the 1st and 2nd compounds, respectively.

The polarizabilities estimated by this method is illustrated in Table II, and the polarizabilities obtained by experimental and theoretical methods are shown in Table III.

TABLE II
MEAN MOLECULAR POLARIZABILITIES OF INDIVIDUAL COMPOUNDS AND MIXTURES A_M (10^{-24} CM^3)

Sl.No.	Individual Compounds				Mixtures
	A-series	α_M (10^{-24} cm^3)	B-series	α_M (10^{-24} cm^3)	α_M (10^{-24} cm^3)
1	A1	61.24	B1	49.67	58.84
2	A2	68.73	B2	52.87	60.72

TABLE III
COMPARISON OF MEAN MOLECULAR POLARIZABILITIES BOTH THEORETICAL AND EXPERIMENTAL A_M (10^{-24} CM^3)

Sl. No.	Compounds	Theoretical Method	Experimental Methods	
		Lippincott δ Function method 10^{-24} cm^3	Neugebaur Method (10^{-24}) cm^3	Vuk's Method (10^{-24}) cm^3
1	C1	58.847	59.223	59.297
2	C2	60.720	61.644	62.036

The salient features from dilatometric and birefringence studies are:

- The liquid crystalline mixtures selected for the present research work, exhibits nematic and smectic phases.
- The density measurement is useful in finding the order of phase transition. It is found that density decreases with increase of temperature except in the vicinity of phase transition, where it shows steep increase.
- The distinct density jumps, thermal expansion coefficient suggest that I-N, N-smecticA transition are first order. The density slope in smectic phase is higher compare to I-N phases which suggest that there is closer packing of molecules in this phase.
- The observations on benzoate and carbonitrile LC mixtures reveals that the compounds with oxygen atom on both sides of rigid core will have higher clearing temperature compare to the compounds which possess oxygen atom on any one side of the rigid core. Further it is reported that the removal of oxygen atom from the molecular moiety the LC properties can brought to ambient temperature and even in some cases below room temperature.
- The manifestation of nematic phase is more in compounds with oxygen atom in its moiety. If there is less no. of oxygen atoms there will be more LC phases like smectic A, B, C in addition to nematic phase.
- In the present A series of mixtures only two oxygen atoms are present whereas in B series three oxygen atoms is present, hence the transition temperature of B series is more than A series. In case of mixtures, the transition temperatures lie in between the transition temperatures of A&B.
- The refractive indices of the mixture are measured by using modified spectrometer at wavelength 589.3 nm and shown in above graphs.
- The R.I in isotropic phase is normal. At I-N phase changes the isotropic ray split in ordinary and extra-ordinary rays, which shows the onset of birefringence.
- The birefringence observed in all the mixtures is in between 0.25-0.30.
- The transition temperatures observed in birefringence are in good agreement with those observed in density measurements.
- Using refractive indices and density data the polarizability is calculated by well-known Vuks and Neugebauer method. These polarizabilities obtained by these methods are same as in Lippincott method.

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REFERENCES

[1] T. Chandrakumar, E.E. Burnell, Molecular Physics., 90, 3(1997).
[2] P.G. de Gennes and J. Prost, The Physics of Liquid Crystals, (Clarendon Press, Oxford), (1998).
[3] M.M. Naoum, G.R. Saad, R.I. Nessim, T.A.A. Aziz, Liquid Crystals.,25, 2 (1998).
[4] M.C. Chang, H.W. Chiu, X.Y. Wang, T. Kyu, N. Leroux, S. Champbell, L.C. Chien, Liquid Crystals., 25, 6 (1999).
[5] M.M. Naoum, R.I. Nessim, T.Y. Labeeb, Liquid Crystals.,27, 7 (2000).
[6] N.V.S. Rao, D.M. Potukuchi, VGKM Pisipati, Mol. Cryst. Liq. Cryst., 196, 71 (1991).
[7] A.P. Divya, K. Narayanamurthy, M.S. Madhava, D. Revannasiddaiah and R. Somashekar, Mol. Cryst. Liq. Cryst., 304, 9 (1997).
[8] S.R Kumaraswamy, D. Krishnegowda, R. Somashekar and D. Revannasiddaiah, Ind.J.Phys.,66A(5), 683 (1992).
[9] Obadovic D.Z, Stojanovic .M, Jovanovic-Santa .S, Cvetinov .M, Lazar .D, Vajda .A, Eber .N and Ristic .I, 2011 Molecular Cryst. Liq. Cryst. 547, 1736.
[10] Eren .S.S, Okutan .M, Koysal .O and Yerli .Y 2008 Chin. Phys. Lett. 25, 212.
[11] Sathyanarayana .P, Sadashiva .B.K and Dhara .D 2011 Soft Matter 7, 8556.
[12] Salamon .P, Eber .N, Buka .A, Gleeson .J.T, Sprunt .S and Jakli .A 2010 Phys, Rev. E 81, 031711.
[13] Cventinov .M, obadovic .D, Stajanovic .M, Lazar .D, vajda .A, Eber .N, Fodor-Csorba .K and Ristic .I 2013 liquid Crystals 40, 1512.

Open Science Index, Chemical and Molecular Engineering Vol:10, No:7, 2016 publications.waset.org/10004994/pdf

[14] Hong .S.H, Verduzco .R, Gleeson .J.T, Sprunt .S and Jakli .A 2011 Phys. Rev. E 83, 061702.
[15] Kundu .B, Roy .A, Pratibha .R and Madhusudana .N 2009 Appl. Phys. Lett. 95, 081902.
[16] Burmistrov, V.A., Zavyaloy, A.V., Novikoy, .I.V., Kuvshinova, S. A., and Aleksandriskii, V.V. (2005). Russ. J. Phys. Chem., 79, 130.
[17] Gogoi, B., Ghosh, T.K., and Alapati, P.R. (2005). Cryst. Res. Tech., 40, 709.
[18] Ajeetha, n., Ramakrishna NancharaRao, M., Datta Prasad, P.V., &Pisipati, V.G.K.M. (2005). Z. Naturforsch, 60(a), 746.
[19] George, N.A., Vallabhan, C.P.G., Nampoori, V.P.N., George, A.K., and Radhakrishnan, P. (2000). J. Phys., 33, 3228.
[20] Rajasree, K., Vidyalal, V., Radhakrishnan, P., Nampoori, V.P.N., Vallabhan, C.P.G., and George, A.K. (1998). Mater, Lett.,36, 76.
[21] Rananavare, S.B., Pisipati, V.G.K.M., and Freed, J.H. (1998). Liq. Cryst., 3, 957.
[22] Lippicott, E.R. &Dayhoff, M.O. (1960). Spectrochim. Acta, 16, 807.
[23] Lippicott, E.R. &Stutman, J.M. (1964). J. Phys. Chem., 68, 2926.
[24] J.W. Linnett, J. Am. Chem. Soc83, 2643 (1961).
[25] S. Chandrasekhar and N. V. Madhusudhana, *J.Phy.*(Paris) Colloq.C-4 Supp. 11-20, C4-24(1969).

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