# Study of Refractive Indices, Density and Order Parameters of Two Nematogens and Their Eutectic Mixture

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The compounds 5-pentyl-2-(4′-cyanophenyl) pyrimidine [CM 7035] and 4-*n*-butyl-4′-ethoxytolan [PTP4O2] and mixtures of different mole fractions of them show nematic phase with supercooling effect. From the phase diagram the equimolar mixture is found to be the eutectic mixture. Temperature variation of the density and refractive indices ($n_o, n_e$) of the pure compounds and their eutectic mixture have been reported here. The density and birefringence values of the eutectic mixture are found to be less than that of pure compounds. However the average refractive index values of eutectic mixture almost coincide with those of CM 7035 which are much less than those of PTP4O2. The refractive indices and density values have been analyzed to obtain the orientational order parameters. Experimental order parameter values of the pure compounds and the eutectic mixture are compared with theoretical Maier–Saupe values. The possible reasons for disagreement between theoretical and experimental values for the pure compounds are discussed. The agreement between theoretical and experimental order parameters are fairly good for the eutectic mixture.

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## 1. Introduction

Liquid crystalline material research has double importance: firstly, the development of new materials for device applications and, secondly, the better understanding of the behaviour of different soft condensed matter systems. Liquid crystalline materials are nowadays extensively used in display devices as well as many other applications. A particular application of liquid crystal material requires a particular set of parameters such as viscosity, birefringence, dielectric anisotropy, elastic constants, etc. in required range. No single compound is yet found to fulfil all the necessary criterions for a particular application. So multicomponent mixtures are formulated to adjust various parameters [1]. The study of physical properties of various pure compounds and their mixtures are thereby important to have a better understanding of the mesogenic behaviour of the liquid crystalline mixtures so that newer and more acceptable liquid crystalline materials for device applications emerge.

A considerable number of works have been reported in the literature on systems involving polar–nonpolar mixtures of biphenyls, esters, phenyl cyclohexanes, cyclohexane esters, azoxy, alkenyls, tolan-based fluorinated compounds, etc. In this work we report the refractive indices and density measurements of a new binary system consisting of a pyrimidine and a tolan compound.

4-cyano-4′-pentylbiphenyl (5CB) is a liquid crystalline material of technological importance with moderate optical birefringence ($\Delta n = 0.18$ at 25 °C), high dielectric anisotropy ($\Delta\varepsilon = 11.5$ at 25 °C) and a low elastic constant ratio ($k_{33}/k_{11} = 1.33$ at 25 °C) [2, 3]. Replacing the first benzene ring in 5CB by pyrimidine ring results in CM 7035 without much altering the birefringence, but enhancing the dielectric anisotropy and lowering $k_{33}/k_{11}$ ratio [4]. This enhancement of dielectric anisotropy is due to the dipole moments along the long molecular axis associated with the lone pair of electrons on the nitrogen atoms. A pyrimidine ring can have lower viscosity, too. High dielectric anisotropy, moderate optical birefringence, low viscosity and low $k_{33}/k_{11}$ ratio favours the applicability of CM 7035 as a component for formation of mixtures.

There are many ways to influence $\Delta n$. A very effective means to increase $n_\parallel$ and thereby $\Delta n$ is to employ triple (tolan) bond in the rigid core [5]. Thus tolan compounds may be favourable to be used in mixture. Considerable number of works have been reported by different workers on tolan-based compounds and their mixtures [6–9].

We choose CM 7035 and PTP4O2 as the components of our binary mixture.

## 2. Experimental

### *2.1. Materials*

The compounds CM 7035 and PTP4O2 were kindly donated to us by M/S Hoffmann-La Roche & Co., Basel, Switzerland and Prof. K. Czuprynski, Military University of Technology, Poland, respectively.

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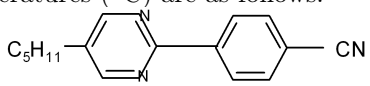
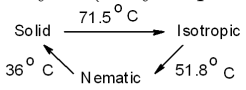
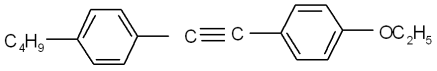
Their structural formula, chemical names and transition temperatures (°C) are as follows:

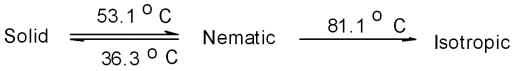



CM 7035: 5-pentyl-2-(4′-cyanophenyl)pyrimidine




PTP4O2: 4-*n*-butyl-4′-ethoxytolan




### *2.2. Preparation of the mixtures*

Five mixtures with mole fractions of CM 7035 equal to 0.034, 0.087, 0.250, 0.500 and 0.733 were prepared. To obtain a homogeneous mixture at a particular concentration, weighed amount of components are mixed thoroughly and then kept at a temperature slightly higher than its nematic–isotropic transition temperature for several hours.

### *2.3. Texture studies*

Routine texture studies were carried out to confirm the nature of the mesophases and the phase-transition temperatures. The texture studies were conducted by using a Leica Make DMLP polarizing microscope equipped with a Linkam hot stage LTSE-350 with TMS 94 temperature programmer. The samples were heated at a rate of 1 °C/min. Representative texture photographs for both the pure compounds and all the five mixtures were taken and phase-transition temperatures are noted.

### *2.4. Density studies*

The temperature variation of the densities of pure compound and their eutectic mixture were measured by putting weighed samples inside a dilatometer of the capillary type which was placed in a water bath heated electrically and controlled manually. The length of the sample column was measured by a traveling microscope. The densities were calculated by correcting for the expansion of the glass capillary. Experimental uncertainty in density measurements is 0.1%.

### *2.5. Refractive index studies*

The ordinary and extraordinary refractive indices $(n_o, n_e)$ of the pure compounds and their eutectic mixture were measured by using the thin prism method [10]. We prepared hollow glass prism with refracting angle less than 2°. We used the surface treatment (with 1% polyvinyl alcohol) to produce a homogeneous nematic specimen with the optic axis parallel to the refracting edge of the prism. The prism was placed inside an electrically heated brass thermostat which is controlled manually to ±0.5 °C. The refractive indices $(n_o, n_e)$ of the samples for wavelength $\lambda = 589$ nm are measured with a precision spectrometer within ±0.001.

## 3. Results and discussion

### *3.1. Texture studies*

The phase diagram of polar–nonpolar binary system (PTP4O2 + CM 7035) which is reported earlier [11] is shown in Fig. 1.

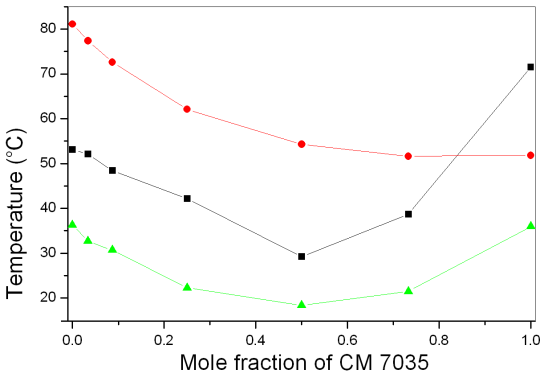



Fig. 1. Phase diagram of binary mixture (CM 7035 + PTP4O2). • indicates nematic–isotropic transition temperature, ■ — melting temperature, ▲ — supercooling temperature.

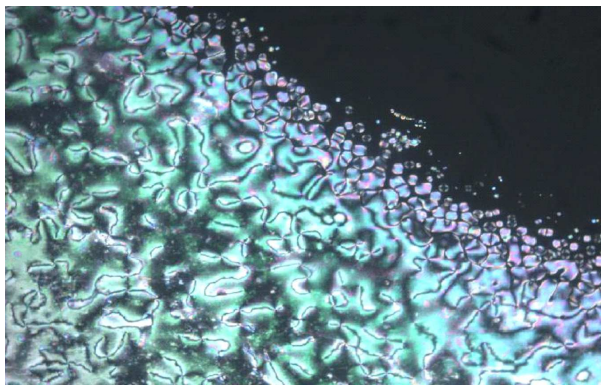


Fig. 2. Nematic texture of CM 7035 at 51.5 °C during cooling.

Generally induced, smectic phases are formed in nematogenic binary mixtures of compounds, one having polar terminal and another nonpolar one. In our polar–nonpolar mixture, there is no induction of smectic phase throughout the whole concentration range. This may be favourable for device applications.

From the phase diagram it is clear that the mixture with concentration $x = 0.500$ is the eutectic mixture.

Representative texture photographs of the pure compounds and their eutectic mixture are shown in Figs. 2–4.

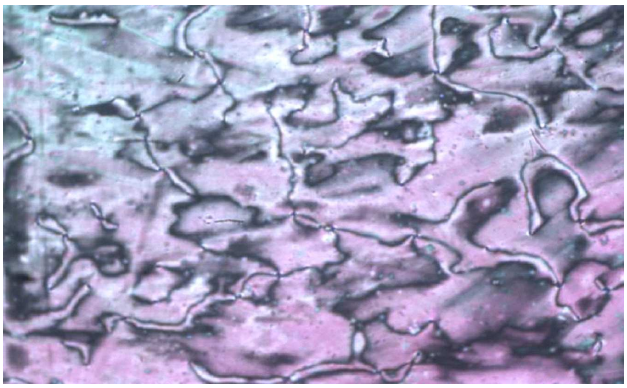


Fig. 3. Nematic texture of PTP4O2 at 59.3 °C during cooling.

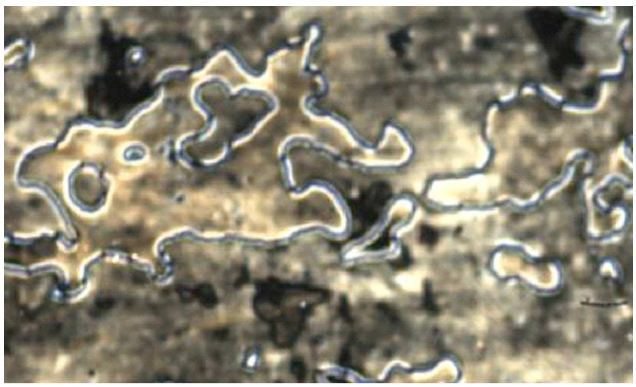


Fig. 4. Nematic texture of eutectic mixture at 44.3 °C during cooling.

### *3.2. Density studies*

The density variation of pure compounds and their eutectic mixture with reduced temperature ($T^* = T/T_{\mathrm{NI}}$) is shown in Fig. 5.

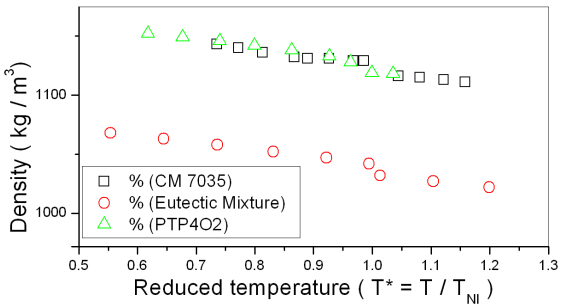



Fig. 5. Temperature variation of density of CM 7035, PTP4O2 and their eutectic mixture.

A small jump in density values near $T_{\mathrm{NI}}$ suggests a weakly first order N–I transition. It is observed that $\rho_{\text{eutectic mixture}} < \rho_{\mathrm{CM7035}} < \rho_{\mathrm{PTP4O2}}$. So in the mixture the unlike molecules, though present in equal numbers, are less densely packed than in the pure compounds. The existence of short range antiferroelectric ordering in pure cyano compound CM 7035 may be partly destroyed by the inclusion of PTP4O2 in the eutectic mixture. This may result in larger intermolecular distance in the eutectic mixture compared to the pure compounds and hence a lower density is observed in the eutectic mixture.

### *3.3. Refractive index measurements*

The temperature variation of the ordinary, extraordinary and average refractive indices ($n_{\mathrm{o}}, n_{\mathrm{e}}, \langle n \rangle$) of the pure compounds and their eutectic mixture at wavelength $\lambda = 589$ nm are shown in Figs. 6 and 7. Average refractive indices ($\langle n \rangle$) are obtained from the equation $\langle n \rangle = (n_{\mathrm{e}} + 2n_{\mathrm{o}})/3$.

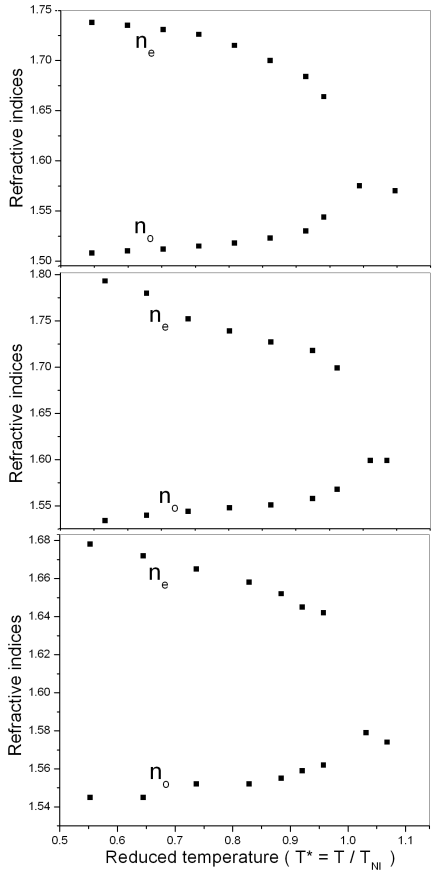



Fig. 6. (a) Temperature variation of refractive indices of CM 7035, (b) PTP4O2, (c) eutectic mixture of CM 7035 and PTP4O2.

As evident from Fig. 6, optical birefringence $\Delta n$ of eutectic mixture is smaller than of the both pure compounds. However, as evident from Fig. 7, the average refractive index values of eutectic mixture almost coincide with those of CM 7035 which are much less than those of PTP4O2.

The refractive index and density data have been analyzed to determine the orientational order parameter $\langle P_2 \rangle$ which is a quantitative measure for the parallel arrangement of the molecules in the liquid crystalline phases.

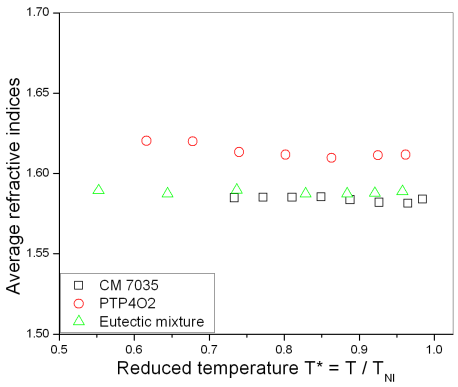



Fig. 7. Average refractive indices of CM 7035, PTP4O2 and their eutectic mixture as a function of reduced temperature.

The order parameter is given by the relation

$$\langle P_2 \rangle = \langle 3\cos^2\theta - 1 \rangle / 2\,. \tag{1}$$

The mean value of the direction of the molecular long axes is called the director, $\theta$ is the angle between the long molecular axis and the director, brackets indicate the average.

We can measure $\langle P_2 \rangle$ from density and refractive index data by using the relation

$$\langle P_2 \rangle = (\alpha_e - \alpha_o)/\Delta\alpha\,, \tag{2}$$

where $\alpha_e$ and $\alpha_o$ are the effective polarizabilities for extraordinary and ordinary rays which were calculated from the measured values of refractive indices using the Vuks formulae [12]:

$$(n_o^2 - 1)/(n^2 + 2) = 4\pi N\alpha_o/3 \tag{3a}$$

and

$$(n_e^2 - 1)/(n^2 + 2) = 4\pi N\alpha_e/3\,. \tag{3b}$$

Here $n^2 = (2n_o^2 + n_e^2)/3$, and $N$ is the number of molecules per c.c. $\Delta\alpha = \alpha_\parallel - \alpha_\perp$, where $\alpha_\parallel$ and $\alpha_\perp$ are the polarizabilities parallel and perpendicular to the long axis of the molecule in the solid state. The polarizability anisotropy in the perfectly ordered state ($\Delta\alpha$) has been estimated by applying the well-known Haller extrapolation procedure [13].

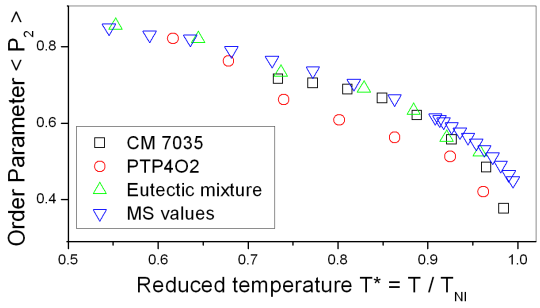



Fig. 8. Variation of order parameters with reduced temperature for CM 7035, PTP4O2 and their eutectic mixture.

Variation of order parameter for pure compounds and their eutectic mixture with reduced temperature is shown in Fig. 8. Theoretical Maier–Saupe [14] values are also plotted in the same figure for comparison. In case of PTP4O2, at lower temperature experimental $\langle P_2 \rangle$ values more or less agree with the Maier–Saupe values, but at higher temperature experimental values fall quicker than those predicted by Maier and Saupe. This lowering of experimental order parameter may be due to the thermal fluctuation of the chain part at higher temperatures which was not considered in theoretical calculations.

In case of CM 7035, only at moderate temperature the agreement between theoretical and experimental values is good, both at lower and higher temperatures experimental values fall below the theoretical values. Dimer formation and fluctuation of chain part may be responsible for this disagreement. The agreement between experimental order parameters of the eutectic mixture and the Maier–Saupe theoretical values is fairly good.

## 4. Conclusion

Here we obtain the eutectic mixture of a monotropic nematogenic polar and an enantiotropic nematogenic nonpolar liquid crystalline compound which is enantiotropic nematogenic in nature having a moderate temperature range (29.2 °C–54.3 °C) with supercooling temperature 18.4 °C and moderate birefringence ($\Delta n = 0.133$ at 30 °C). The high value as well as smooth temperature variation of the orientational order parameter $\langle P_2 \rangle$ of the eutectic mixture may make it suitable to be used as a component in multicomponent mixtures for practical applications. The absence of any induced smectic phase in this mixture may also be a favourable condition for practical applications.

## Acknowledgments

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## References

[1] R. Dabrowski, K. Czuprynski, in: *Induced Smectic and Nematic Phases and Reentrant Nematic Phenomena, Modern Topics in Liquid Crystals from Neutron Scattering to Ferroelectricity*, Ed. A. Buka, World Sci., London 1993, p. 126.

[2] P.G. Cummins, D.A. Dunmur, D.A. Laidler, *Mol. Cryst. Liq. Cryst.* **30**, 109 (1975).

[3] V.F. Petrov, *Liquid Cryst.* **29**, 805 (2002).

[4] B. Bahadur, *Liquid Crystals: Applications and Uses*, Vol. 1, World Sci., Singapore 1990, p. 119.

[5] S. Singh, D.A. Dunmur, *Liquid Crystals: Fundamentals*, World Sci., Singapore 2002, p. 87.

[6] Yoichitakanishi, M. Yoshimoto, K. Ishikawa, H. Takezoe, *Mol. Cryst. Liq. Cryst.* **331**, 619 (1999).

[7] J. Li, S. Gauza, S.-T. Wu, *Opt. Exp.* **12**, 2002 (2004).

[8] S. Gauza, H. Wang, C.-H. Wen, S.-T. Wu, A.J. Seed, R. Dabrowski, *Jpn. J. Appl. Phys.* **42**, 3463 (2003).

[9] S. Gauza, S.-T. Wu, A. Spadlo, R. Dabrowski, *J. Display Technol.* **2**, 247 (2006).

[10] A.K. Zeminder, S. Paul, R. Paul, *Mol. Cryst. Liq. Cryst.* **61**, 191 (1980).

[11] S. Datta Sarkar, B. Choudhury, *Asian J. Phys.* **18**, 3 (2010) (accepted).

[12] M.F. Vuks, *Opt. Spectrosc.* **20**, 361 (1966).

[13] I. Haller, H.A. Higgin, H.R. Lilienthal, T.R. Mcguire, *J. Phys. Chem.* **77**, 950 (1973).

[14] W. Maier, A. Saupe, *Z. Naturforsch. A* **15**, 287 (1960).