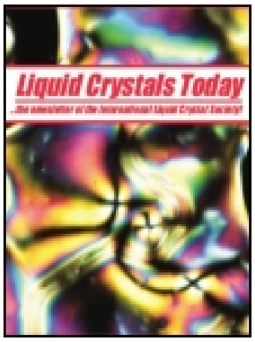

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Crossover temperature (T_{CO}) and temperature gradient of refractive indices and length to breadth ratio of 4O.m mesomorphic compounds – an optical study

V.G.K.M. Pisipati*, D. Madhavi Latha and P.V. Datta Prasad

R&D Centre, SSD Polymers, Machilipatnam, Andhra Pradesh 521 002, India

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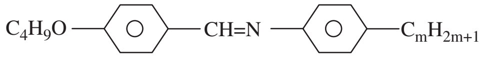
Refractive indices as a function of temperature are measured in a number of liquid crystals which belong to the N-(*p*-*n*-butoxy benzylidene)-*p*-*n* alkyl anilines, 4O.m compounds of the famous Schiff's base *n*O.m liquid crystal compounds with $m = 4$ to 10 and 12. The temperature gradient of refractive indices, dn_e/dT and dn_o/dT, of these compounds are estimated. It is well known that in the case of dn_o/dT, there exists a crossover temperature, T_{CO}, which exhibits an odd–even effect with the alkyl chain length as expected. Further, using the birefringence data, the length to breadth ratio, *k*, for these compounds is estimated, which shows not exactly even–odd effect but irregular change with the chain number. The results are discussed with the body of the data.

Keywords: *n*O.m compounds; crossover temperature; birefringence; order parameter

Introduction

The liquid crystals are one of the important materials which can be used to understand the fundamental laws [1] as well as used in different applications [2]. In order to have technological applications, these materials should possess some interesting physical properties. One of the main properties is that it should possess liquid crystalline nature in and around the room temperature. Further, the birefringence is also an important property in selecting a material for its use in applications and also in the study of the non-linear optics [3,4]. The N-(*p*-*n*-alkoxybenzylidene)-*p*-*n*-alkyl anilines, *n*O.m, form a class of Schiff base compounds, since, they exhibit varying polymorphism with different thermal ranges. The N-(*p*-*n*-butoxybenzylidene)-*p*-*n*-alkyl anilines, 4O.m compounds, exhibit nematic phase with varying thermal ranges (apart from other smectic phases) suitable for the study of birefringence.

In the present article, the temperature gradient of n_e and n_o are obtained from the birefringence data taken from literature. Using this data, both T_{CO} and the length to breadth ratio, *k*, are estimated and studied their variation with the alkyl chain number. The results are discussed with the body of the data available in literature. The chemical structure of the molecules is given below.



where $m = 4$ to 10 and 12

Simple theory involved in the estimation of T_{CO} and k

In order to evaluate the temperature gradients of birefringence and in turn the crossover temperature, T_{CO}, and the length to breadth ratio, *k*, the following parameters such as Δn, β and A are needed from the experimental birefringence. Thus, the expressions employed for evaluating these parameters are given below.

de Gennes and Prost [5] pointed out that the anisotropy of any physical quantity can be a measure of orientational order parameter. In the case of uniaxial liquid crystal, this parameter can be defined as

$$Q = \frac{\delta A}{\Delta A} \tag{1}$$

where δA is the anisotropy of any arbitrary physical quantity $\Delta A = (A_{||} - A_{\perp})$ and ΔA is the hypothetical anisotropy of A in the case of perfect order.

Zywucki and Kuczynski [6] and Kuczynski et al. [7] proposed a simple procedure for the determination of order parameter S from the birefringence measurements δn without considering the local field experienced by the molecule in a liquid crystal phase. The birefringence δn, which is a function of temperature, is fitted to the following equation:

$$\delta n = \Delta n \left(1 - \frac{T}{T^*}\right)^{\beta} \tag{2}$$

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*Corresponding author. Email: venkata_pisipati@hotmail.com
Present affiliation for D. Madhavi Latha is Department of Physics, National Institute of Technology, Warangal-506004, Andhra Pradesh, India

where T is the absolute temperature, T^* and β are constants (T^* is about 1–4 K higher than the clearing temperature, T_C and the exponent β depends on the material but close to 0.20). This procedure enables one to extrapolate δn to the absolute zero temperature.

In practice, the three adjustable parameters T^*, Δn and β were obtained by fitting the experimental data for δn to the following equation written in the logarithmic form

$$\log \delta n = \log \Delta n + \beta \log\left(\frac{T^* - T}{T^*}\right) \tag{3}$$

Thus, Q is given by

$$Q = \frac{\delta n}{\Delta n} \tag{4}$$

Following the procedure of Zywucki and Kuczynski [6] and Kuczynski et al. [7], the authors demonstrated that Q determined in this way describes well the nematic order parameter and is a good approximation of the order parameter S given by equation $S = 1/2 < (3\cos^2\theta - 1) >$, where θ is the angle between the long axis of the molecule and the director 'n'. In general, the order parameter S, defined by Equation (4), must not necessarily be identical with that defined through other tensorial properties and could be different from the order parameter S defined by the above equation. However, one can expect that within a given local field model, there should be a relation between macroscopic and microscopic order parameters and following the procedure of Zywucki and Kuczynski [6] and Kuczynski et al. [7], the authors also demonstrated it using the example of the Vuks isotropic local field model.

Table 1. Parameters for (4O.m compounds) the best fit through linear regression for the equation $\log \delta n = \log \Delta n + \beta\ \log(T^* - T/T^*)$.

		δn			
Compound	T_C (K)	T^* (K)	β	Δn	Reg. Coeff.
4O.4	347.40	347.70	0.150	0.390	0.9833
4O.5	354.50	354.51	0.120	0.346	0.9880
4O.6	349.00	349.30	0.130	0.320	0.9575
4O.7	355.80	356.10	0.172	0.362	0.9973
4O.8	351.20	351.50	0.173	0.386	0.9913
4O.9	353.20	353.50	0.142	0.295	0.9962
4O.10	349.70	350.60	0.182	0.310	0.9920
4O.12	350.50	351.90	0.184	0.300	0.9797

The regression analysis is employed to get the best fit for the three parameters, T_C, Δn and β and the values are given in Table 1 for the all compounds studied. The log–log plot to obtain the Δn value is shown in Figure 1 for the compound 4O.7 as a representative case.

Vuks has modified the Lorentz–Lorenz equation for his isotropic model to explain the nematic LC molecule and the following equation expresses the molecular polarisabilities in terms of the experimental refractive indices [8].

$$(n^2_{e,o} - 1)/(<n2> + 2) = (4\pi/3)N\alpha_{eo} \tag{5}$$

where $<n^2> = (n^2e + 2n^2o)/3$. N is the number of molecules per unit volume. α_e and α_o are the molecular polarisabilities. Based on Vuks isotropic model,

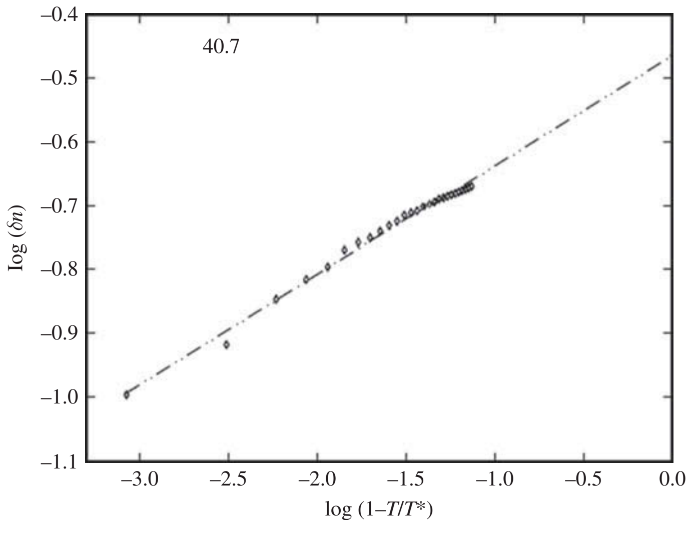

Figure 1. The log–log plot of birefringence δn versus reduced temperature for the 4O.7 compound.

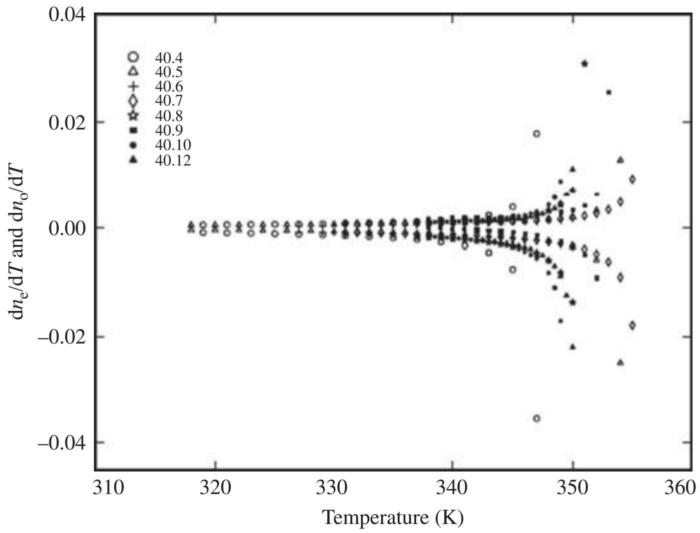

Figure 2. Temperature gradient of refractive indices of 4O.m compounds.

the temperature dependent refractive indices can be written in terms of average refractive index <*n*> and the birefringence $\delta n = (n_e - n_o)$ [8]. The refractive indices n_e and n_o can be written as

$$n_e = <n^2>1/2 + (2/3)(\delta n) \tag{6}$$

and

$$n_o = <n^2>1/2 - (1/3)(\delta n) \tag{7}$$

The temperature derivatives of the refractive indices are shown in the following equations:

$$\mathrm{d}n_e/\mathrm{d}T = (\mathrm{d}<n>)/\mathrm{d}T) + (2/3)(\mathrm{d}\delta n/\mathrm{d}T) \tag{8}$$

$$\mathrm{d}n_o/\mathrm{d}T = (\mathrm{d}<n>)/\mathrm{d}T) + (1/3)(\mathrm{d}\delta n/\mathrm{d}T) \tag{9}$$

Figure 2 shows the variation of dn_e/dT and dn_o/dT with temperature in all the compounds of 4O.m series. In Equation (8), on the right hand side, both the terms are negative and independent of temperature, which implies that n_e decreases as the temperature increases. However, Equation (9) consists of a negative first term and a positive second term, which is temperature dependent. At low temperatures ($T << T^*$), the second term is less than the first term resulting in a negative dn_o/dT. With an increase in temperature, the positive term also increases. When $T \cong T^*$, dn_o/dT jumps to a large positive value. However, in the intermediate stage, there exists a crossover temperature, T_{CO}, where dn_o/dT = 0. Further, it is a known fact experimentally [9] that <*n*> decreases linearly with the temperature and can be expressed linearly by Equation (10).

From birefringence data, the square of the average refractive index is $<n^2> = (1/3)(n^2{}_e + 2n^2{}_o)$ and from this we obtain the following:

$$<n> \; = \; A - BT \tag{10}$$

The crossover temperature is given by the following equation:

$$T_{CO} = T^*\left[1 - \{3BT^*/(\beta \Delta \mathrm{n})\}^{1/\beta - 1}\right] \tag{11}$$

The refractive index data is taken from literature [10]. Using the above equations, the T_{CO} in these compounds can be obtained and the values are listed in Table 2 and the variation of T_{CO} with the alkyl chain number is shown in Figure 3.

In the estimation of the length to breadth ratio, *k*, the procedure adopted by Roushdy [11] and the equations of Palffy-Muhoray and Balzarini [12] are used.

Table 2. The intercept and slope values *A* and *B*, respectively, of 4O.m compounds.

Compound	*A*	*B*	T_{CO} (°C)
4O.4	1.7691	−0.000158	−28.4
4O.5	1.6157	−0.0003	46.6
4O.6	1.5558	−0.000127	−15.8
4O.7	1.5296	–0.000293	32.1
4O.8	1.9627	−0.0002204	0.4
4O.9	1.9502	−0.00022	32.4
4O.10	1.7063	−0.000225	15.9
4O.12	1.6221	−0.00017	–5.5

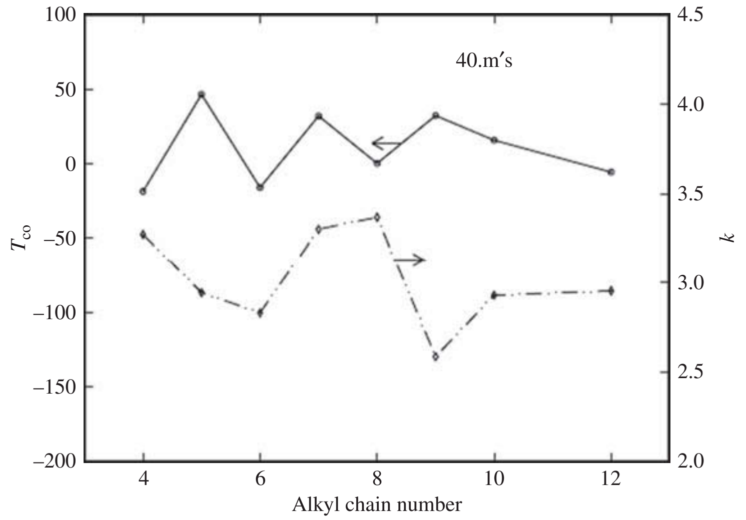

Figure 3. Variation of the crossover temperature, T_{CO}, and length to breadth ratio, *k*, with alkyl chain number.

Palffy-Muhoray and Balzarini [12] have given that the local field η_{zz} for LC molecules is nearly proportional to the order parameter and the slope of that plot is equal to $[-4(k-1)]/[5(k+2)]$. η_{zz} is given as follows:

$$\eta_{zz} = (1/3)\left[\left\{\left(n^2+2\right)/\left(n^2-1\right)(1+2dS)\right\} - \left(n_e{}^2+2\right)/\left(n_e{}^2-1\right)\right] \quad (12)$$

Using the relation given in the text, *k*-value is estimated and the values are shown in Figure 3 along with the T_{CO} value for 4O.m compounds.

Conclusions

The crossover temperature, T_{CO}, and the length to breadth ratio, *k*, for 4O.m compounds are estimated using the respective equations given in the text. As expected, the T_{CO} has exhibited an odd–even effect with the alkyl chain number [13]. However, regarding *k*, no definite conclusion could be obtained as it has shown neither odd–even effect nor a linear variation. Further, studies on other series of compounds are needed to come to a definite conclusion.

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References

[1] Bahadur B. A brief review of history, present status, developments and market overview of liquid crystal displays. Mol Crystals Liquid Crystals. 1983;99:345–374.
[2] Rananavara SB, Pisipati VGKM, Freed JH. Nematic order near a tricritical N-SA phase transition. Chem Phys Lett. 1987;140:255–262.
[3] Alkeskjold TT, Laegsgaard J, Bjarklev A, Hermann DS, Broeng J, Li J, Wu ST. All-optical modulation in dye-doped nematic liquid crystal photonic band gap fibers. Opt Express. 2004;12:5857–5871.
[4] Wu ST, Efronfron U, Hess LD. Infrared birefringence of liquid crystals. Appl Phys Lett. 1984;44:1033–1036.
[5] de Gennes PG, Prost J. The physics of liquid crystals. New York (NY): Oxford University Press; 1993.
[6] Zywucki BJ, Kuczynski W. Optical phenomena – the orientational order in nematic liquid crystals from birefringence measurements. Dielectr Electr Insul, IEEE Trans. 2001;8:512–515.
[7] Kuczynski W, Zywucki B, Malecki J. Determination of orientational order parameter in various liquid-crystalline phases. Mol Crystals Liquid Crystals. 2002;381:1–19.
[8] Soorya TN, Gupta S, Kumar A, Jain S, Arora VP. Temperature dependent optical property studies of nematic mixtures. Ind J Pure Appl Phys. 2006;44:524–531.
[9] Sreehari Sastry S, Kumari TV, Begum SS, Venkata Rao V. Investigations into effective order geometry in a series of liquid crystals. Liquid Crystals. 2011;38:277–285.
[10] Rao NVS, Potukuchi DM, Pisipati VGKM. Phase transition studies on N-(p-n-butoxy benzylidene)-p-n-alkyl anilines – density and birefringence study. Mol Crystals Liquid Crystals. 1991;196:71–87.
[11] Roushdy M. Effective of the polar substituents on the optical parameters of binary mixtures of 4-substituted

phenyl-4-hexyloxybenzoztes. Mol Crystals Liquid Crystals. 2007;461:53–69.

[12] Palffy-Muhoray P, Balzarini DA. Refractive index measurements and order parameter determination of the liquid crystal *p*-ethoxybenzilidene-*p*-butylaniline. Can J Phys. 1981;59:515–520.

[13] Latha DM, Pisipati VGKM, Pardhasaradhi P, Datta Prasad PV, Padmaja Rani G. Cross over temperature (T_{CO}) and temperature gradient of refractive indices of a number of homologous series of liquid crystal materials. Liquid Crystals. 2012;39:1113–1116.