

Orientalional order parameter of a liquid crystalline compound by optical studies

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Abstract—The paper reports the refractive indices and density measurements at different temperatures in the nematic and liquid phases of liquid crystalline p-butoxybenzylidene p-propylaniline (4O.3). From these data, the orientational order parameter S has been estimated employing different approaches. The results obtained are compared and discussed.

Key words: *Liquid crystal, refractive index, density, nematic, orientational order parameter.*

1. Introduction

Liquid crystals possess a combination of properties of both crystalline solids and isotropic liquids, thus, providing scientists and engineers with one of the most active and fascinating fields of scientific and industrial research. The major application of liquid crystals is in construction of liquid crystal displays (LCDs). They also find innumerable applications in industries, photonics, imaging technology, biomedical field and in nanoscience and nanotechnology [1]. To understand the suitability and applicability of liquid crystalline systems in different applications, their basic characterization is very essential.

The orientational order parameter, S defines the long-range orientational order in the liquid crystalline phase and plays an important role in the determination of the applicability of nematic liquid crystals in electro-optical devices. It can be estimated using techniques such as dielectric, diamagnetic susceptibility, elastic constants, X-rays, NMR, ESR, IR, etc. [1, 2]. However, optical method is most widely used for this purpose. Optical method involves the measurement of refractive indices and/or density as a function of temperature usually accompanied by calculation of polarizabilities.

The molecular structure of the compound p-butoxybenzylidene p-propylaniline (4O.3) studied here is shown in Figure 1. The compound belongs to Schiff's base $nO.m$ class where n and m denote the alkoxy and alkyl chain lengths on either side of the rigid core.

Literature survey reveals that extensive studies have been carried out on $nO.m$ series compounds [3-5]. Rao et al. [3] have reported refractive index and density measurements of

4O.m compounds with $m = 4$ to 10, 12 to 16. Recently, Trivikaram Rao [4] has studied the dynamic molecular processes of 4O.2, 4O.3, 4O.4 and mixture of 4O.2 and 4O.4 through frequency dispersion measurements using field cycling NMR process.

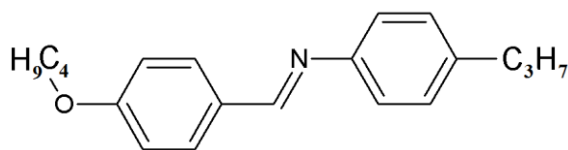


Figure 1: Molecular structure of 4O.3

2. Experimental

The compound 4O.3 was procured from M/s Frinton Laboratories Inc., USA (purity 98%). The refractive indices were measured for $\lambda=5893\text{\AA}$ employing small angle hollow prism technique and density measurements were carried out employing capillary tube technique [3]. The average errors in the measurements of the temperatures, densities, refractive indices are estimated to be $\pm 0.1^\circ\text{C}$, $\pm 0.0005\text{ gm/cc}$ and ± 0.0004 respectively.

The phase sequence and transition temperatures exhibited by the compound as observed from polarizing microscope and DSC studies is:

(Crystal) 28.64°C (Smectic G) 49.96°C (Nematic) 79.22°C (Isotropic)

3. Theoretical background

Orientational order parameter can be expressed in terms of polarizability as

$$S = \frac{\alpha_e - \alpha_o}{\alpha_{\parallel} - \alpha_{\perp}} \quad (1)$$

where α_e and α_o are respectively the average effective polarizabilities for the extraordinary and ordinary ray, and α_{\parallel} and α_{\perp} are the polarizabilities of the molecule when the electric vector is respectively parallel and perpendicular to the long axis of the molecule.

In the present work, the values of α_e and α_o at different temperatures in the nematic phase of the compound 4O.3 has been estimated from refractive index and density data employing Vuks and Neugebauer local field models. The value of $(\alpha_{\parallel} - \alpha_{\perp})$ has been estimated using Haller approximation, Lippincott δ -function model and molecular vibration methods. From these values, S can be estimated using Equation (1). Further, S has been estimated using the refractive index data employing Vuks scaling factor method, Neugebauer $f(B)$ parameter, and, birefringence method proposed by Kuczyński et al.[6] A detailed description of these methods is given elsewhere [7].

4. Results and discussion

The variation of the refractive indices (n_e , n_o) of 4O.3 with temperature measured for $\lambda=5893\text{\AA}$ is shown in Figure 2(a). Figure 2(b) shows the variation of density with temperature in the nematic and isotropic (liquid) phase.

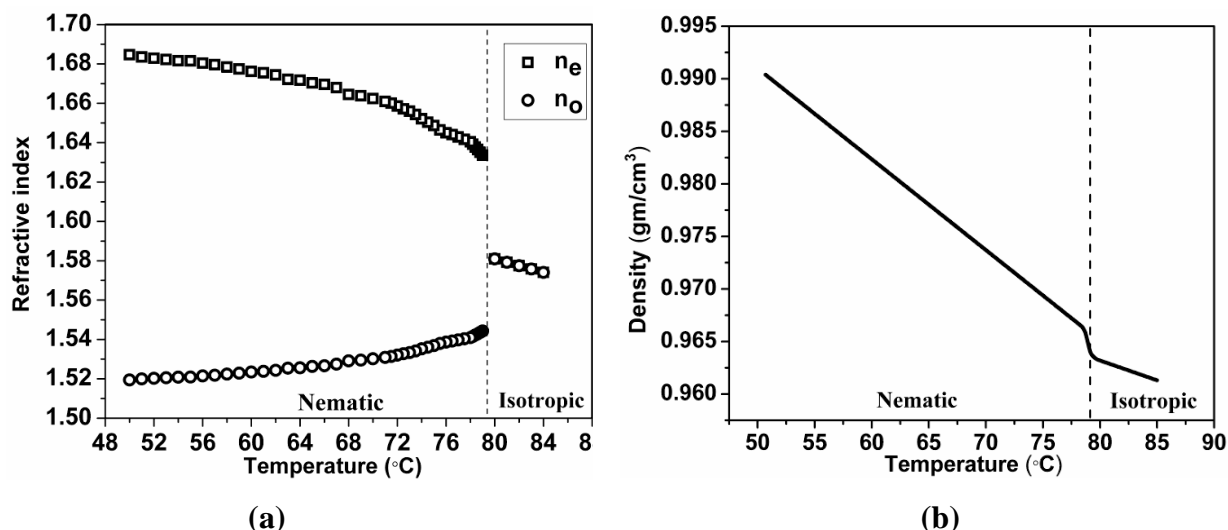


Figure 2. (a) Variation of refractive indices and (b) density with temperature in 4O.3.

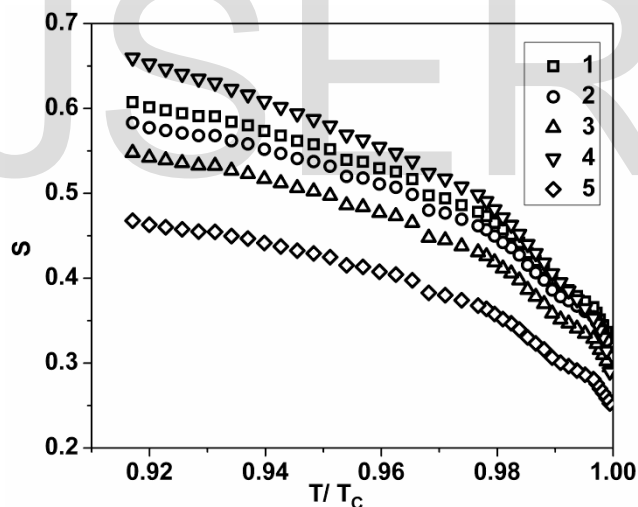


Figure 3. Variation of order parameter with reduced temperature in 4O.3. S determined from: (1) Birefringence method, (2) Using polarizabilities estimated from Vuks model and polarizability anisotropy determined from Haller method, (3) Vuks scaling factor method, (4) Using polarizabilities estimated from Neugebauer model and polarizability anisotropy determined from Haller method, and, (5) Neugebauer $f(B)$ parameter.

The values of polarizability anisotropy ($\alpha_{||} - \alpha_{\perp}$) estimated using Lippincott δ - function model, vibrational method and Haller extrapolation method employing Vuks and Neugebauer models are 24.88, 25.11, 24.15 and 25.29 ($\times 10^{-24} \text{ cm}^3$) respectively.

5. Conclusions

With increase in temperature, n_e decreases while n_o increases, but at a different rate [Figure 1]. It may be seen from Figure 2, that the density increases uniformly with the decrease in temperature in the nematic and isotropic phases, except at the vicinity of the isotropic-nematic transition temperature T_c , where the increase is steep. However, the slope of density variation in nematic phase is higher than that in the isotropic phase indicating the growth of long range orientational order from a completely disordered molecular arrangement in the isotropic phase.

The values of polarizability anisotropy estimated using Lippincott δ -function model, molecular vibration method and Haller extrapolation method (for Vuks and Neugebauer models) are reasonably in good agreement with each other.

The values of S estimated from different methods agree well near the nematic-isotropic transition (T_c) and diverge as the nematic phase attains equilibrium [Figure 3]. Further, the S values obtained from the birefringence method lies in the middle of the plots due to other methods and is comparable with those estimated using Vuks model rather than Neugebauer model. The S values estimated using Neugebauer $f(B)$ parameter has lowest value compared to other methods. These observations agree well with those reported in literature for similar liquid crystalline compounds [3,5].

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