

Translational Order Parameter in a Schiff Base Liquid Crystalline Compound

M. K. Usha¹, N. Bharathi²

¹Department of Physics, M. S. Engineering College (Affiliated to Visvesvaraya Technological University, Belagavi), Bengaluru, Karnataka, India – 560085

²Department of Physics, Mysore Makkala Koota and Shri Dharmasthala Manjunatheshwara Mahila Maha Vidyalaya (Affiliated to University of Mysore, Mysuru), Mysuru, Karnataka, India – 570004
Email address: bharathimysore5@gmail.com

Abstract—Translational order parameter has been computed in the smectic B phase of a Schiff base liquid crystalline compound, namely, *p*-Butoxybenzylidene *p*-Heptylaniline using its X-ray diffraction data. The results obtained have been discussed in terms of molecular ordering present in its Smectic B phase.

Keywords—Liquid crystals, smectic phase, translational order parameter, Schiff base compounds, X-ray diffraction.

I. 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 liquid crystal displays (LCDs). Apart from this, they find innumerable applications in industries, photonics, imaging technology, biomedical field, nanoscience and nanotechnology, etc. [1] Out of several classes of liquid crystals, the most common ones that are majorly used in technical applications are nematics and smectics. In nematic liquid crystals, the molecules orient their long axes along a preferred direction resulting in orientational order. In smectic liquid crystals, molecules exhibit positional order as well as orientational order. Orientational ordering in nematic liquid crystals is numerically measured by orientational order parameter S while positional ordering in smectics is measured by translational order parameter Σ . Both S and Σ are temperature dependent. This ordering plays a major role in deciding the properties of liquid crystals and hence their applications. Thus, experimental determination of order parameter is one of the vital characterizations to be carried out for any liquid crystal. Literature survey reveals that a lot of reports are available on orientational order parameter of nematic liquid crystals while translational order parameter (TOP) of smectics is sparsely reported [2]. Optical method is the most widely employed technique to measure S while X-ray diffraction method is mainly used to compute Σ .

Earlier reports on computation of TOP employed a method proposed by Leadbetter *et al.* [3], [4]. However, this method suffers from two major drawbacks – it requires higher order diffraction peaks which are quite difficult to obtain in most of the liquid crystals, and, all calculations are made by assuming only a single conformation of molecule ignoring vibrational motion (the fluctuations in position of molecules are actually assumed to be Gaussian). Kapernaum and Giesselmann [2] have proposed a new method which overcomes these drawbacks – it requires only (001) X-ray peak which can be

easily recorded for all liquid crystals using small angle X-ray scattering (SAXS).

In the present work, we have adopted the Kapernaum and Giesselmann [2] method to compute TOP in a Schiff base liquid crystalline compound *p*-Butoxybenzylidene *p*-Heptylaniline in its smectic B (SmB) phase. The chemical structure of the compound is shown in Fig. 1. It belongs to Schiff base $nO.m$ class of compounds where n and m represent alkyl chain length on either sides of the rigid core and, hence is abbreviated as 4O.7. Calorimetric [5], [6], X-ray scattering studies [7], [8], NMR [9], refractive index and density measurements [10] of the compound 4O.7 have been reported in literature. Chan *et al.* [11] have estimated the smectic order parameter at the nematic to smectic-A phase transition of 4O.7 using Leadbetter method. Microstructural parameters and pair correlation function, and electrical conductivity studies of 4O.7 are published elsewhere [12], [13].

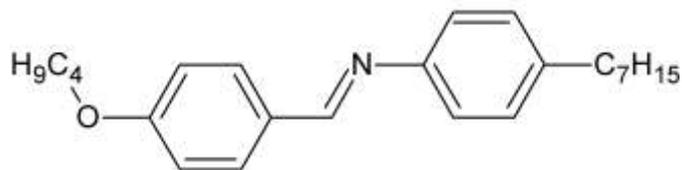


Fig. 1. Chemical structure of 4O.7

II. THEORY

In order to calculate smectic TOP Σ , we have employed the following equations proposed by Kapernaum and Giesselmann [2]:

$$I(T) = I_0 [1 - (T/T_C)]^{2\beta} \quad (1)$$

where $I(T)$ is the temperature dependent X-ray intensity of the liquid crystalline sample recorded at a temperature T , I_0 is the hypothetical intensity which would result from the perfectly ordered (crystalline) smectic phase, $\beta > 0$ is the reduced scattered X-ray intensity exponent and T_C is the phase transition temperature into the smectic phase of interest.

Equation (1) can be expressed in logarithmic form as

$$\ln I = \ln I_0 + 2\beta \ln [1 - (T/T_C)] \quad (2)$$

which represents a straight line. In this equation, $I(T)$ is obtained from the area under the (001) X-ray intensity profiles recorded at different temperatures T in the desired smectic phase. Then, I_0 is estimated by extrapolating $I(T)$ to absolute zero temperature ($T = 0$ K) using Haller extrapolation method [14]. The parameters β and I_0 are obtained by fitting the experimental data to the linear equation (2). Then, TOP can be computed using:

$$\Sigma = [1 - (T/T_c)]^\beta \quad (3)$$

Thus, this method involves much lesser computational effort compared to Leadbetter method and can be applied to any smectic phase provided it has a sufficiently wide temperature range to allow reasonable extrapolation [2].

III. EXPERIMENTAL

The sample 4O.7 was obtained from M/s Frinton Laboratories Inc., USA. Its phase sequence and transition temperatures as determined from DSC and polarizing microscope studies are as given below:

(Smectic B) 45.9 °C (Smectic C) 47°C (Smectic A) 54°C (Nematic) 80.8°C (Isotropic)

A texture photograph of 4O.7 recorded in its smectic B phase is shown in Fig. 2. Focal conic texture was obtained which is a clear indication of SmB phase.

One dimensional X-ray diffraction patterns (Fig. 3) were recorded using PANalytical Empyrean X-ray diffractometer (Model No. DY1042) and a PIXcel^{3D} detector with CuK_α radiation ($\lambda=1.5406$ Å) at different temperatures in the SmB phase of the sample at Raman Research Institute (RRI), Bengaluru. X-ray intensity profiles of the low angle (001) SmB peak recorded at different temperatures (in steps of 2° C) is shown in Fig. 4. X-ray data was not recorded in SmA and SmC phases of the sample since their temperature range is not wide enough for calculation of TOP with desired accuracy.



Fig. 2. Focal conic texture of smectic B phase in 4O.7 recorded at 35°C (40x)

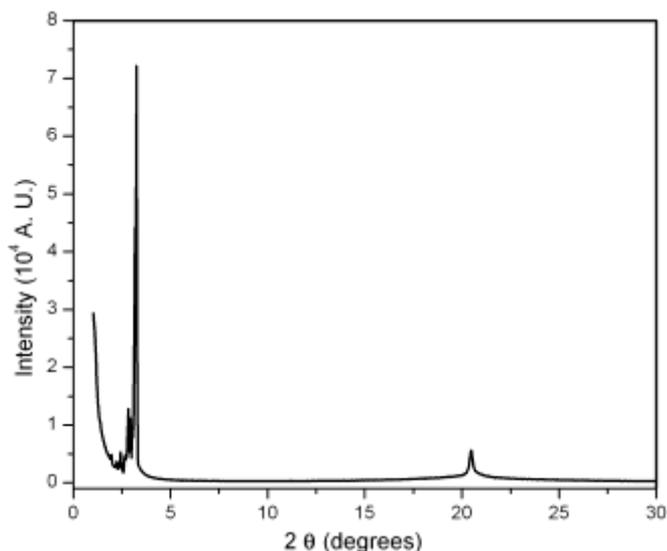


Fig. 3. Representative X-ray pattern recorded at 42 °C in SmB phase of 4O.7

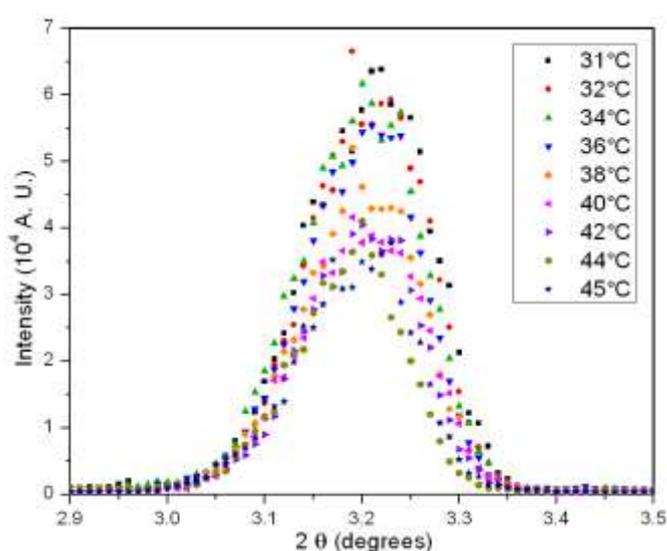


Fig. 4. X-ray diffraction patterns in the SmB phase of 4O.7 recorded at different temperatures

IV. RESULTS AND DISCUSSION

The TOPs computed at various temperatures in the SmB phase of 4O.7 within error of ± 0.05 are shown in Fig. 5. The β value is found to be 0.075. Reported values of β varies from 0.037 to 0.103 for similar liquid crystalline materials exhibiting SmA and nematic phases [2]. The smectic TOP varies from 0.63 to 0.80 which is slightly high. This may be attributed to the interaction of intermolecular hydrogen bonds between the terminal hydroxyl groups of the molecules as in another liquid crystalline compound CBOOA [15]. In fact a high smectic order of the magnitude of 0.8 and above is associated with a phase of anticlinic structure which is expected to smoothen out layer fluctuations [16]. Thus, the values of TOP obtained are in conformity with similar liquid crystalline compounds.

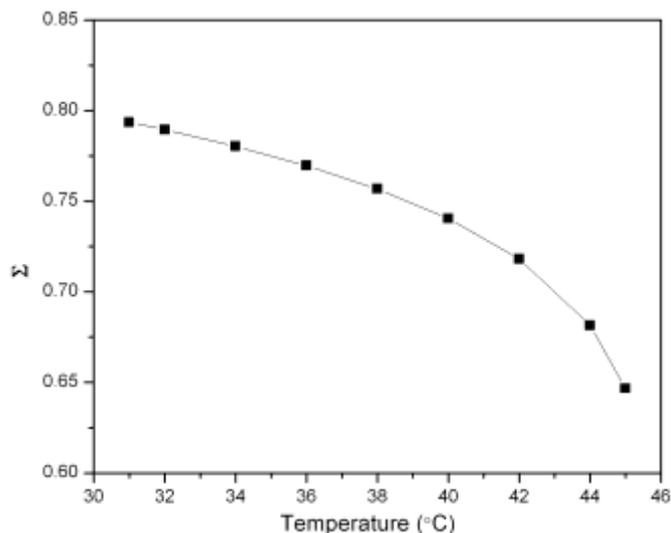


Fig. 5. Temperature variation of translational order parameter S in the SmB phase of 4O.7

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