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# Orientational order parameter determination of the liquid crystal: 4 propyl paraethoxy phenyl cyclohexyl carboxylate by X-ray studies

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**ABSTRACT**

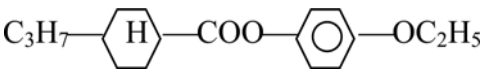
The compound 4 propyl paraethoxy phenyl cyclohexyl carboxylate (code name D302) is a member of a homologous series and exhibits liquid crystalline (nematic) behavior in the temperature range 48°C to 78°C. An experiment has been set up for conducting X-ray studies of liquid crystal samples at various temperatures. From X-ray studies conducted at different temperatures on D302, the apparent molecular length and inter-molecular distance and their temperature dependence have been determined. The variation of the orientational-order parameter $<P_2>_{xray}$ has been determined from the intensities of the scanned X-ray photographs taken at different temperatures. The results have been compared with the $<P_2>_{opt}$ values obtained by us from birefringence studies.

**KEYWORDS**

Nematic; orientational order parameter; mesogen

## Introduction

The mesogen 4 propyl paraethoxy phenyl cyclohexyl carboxylate (code name D302), having the molecular formula $C_{18}H_{26}O_3$ and the structural formula as given below




has been studied by X-ray method at various temperatures.

The compounds are known to posses the following phase transition temperatures

$$\text{Solid} \xrightarrow{48^\circ\text{C}} \text{Nematic} \xrightarrow{78^\circ\text{C}} \text{Isotropic}$$

The compound D302 (supplied by Merck Ltd.) exhibits only a nematic phase spanning a temperature range of 30°C, from 48°–78°C. Three photographs of the sample were taken in the nematic phase at 55°C, 60°, and 70°C of which only most prominent one has been reproduced here. The photographs were taken at the desired temperatures while cooling the sample from the isotropic phase in the presence of the aligning (magnetic) field.

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NMR studies on D302[1,2] have been reported and the formation of a new phase (either a plastic or a cubic) on cooling each of the mesogens has been discussed[1]. It has been reported[2] from NMR studies that in case of D302, the benzene rings have a local molecular motion around the benzene plane in the solid state as compared to the carbons of the cyclohexane ring which has a rigid conformation. Optical studies (λ unspecified) by the standard procedure using Abe's refractometer have also been conducted on the samples[3] and the order parameter calculated. Dielectric studies have also been conducted at a frequency of 1 kHz[3]. Optical studies have been conducted using a He-Ne laser beam on D302 and polarisability and orientational order parameter of the compounds have been determined therefrom[4]. The dielectric experiments have been done at operating frequencies of 10 and 100 kHz and the variation of the mesogenic molecular dipole moment $\mu_{eff}$ with temperature has been obtained from the results of dielectric and optical studies[5]. Now X-ray diffraction study is a powerful tool to study the structural characteristics of mesogens. Lingen [6] and Friedel[7] were the first to perform X-ray diffraction experiment on liquid crystals. Theoretical interpretation were given by Vainshtein[8] and Leadletter[9]. The present work has been undertaken with a view to corroborate our experimental findings of order parameter from x-ray studies with that obtained from optical studies and thereby to attempt an explanation of the nature of molecular-molecular interaction in the mesophase.

## Experimental arrangement and procedure

In our arrangement, X-ray diffraction photographs are taken on a flat plate camera using $CuK_\alpha$ radiation. The sample is introduced into a capillary tube of approximately 1 mm diameter. The two ends of the capillary are then sealed and the capillary introduced into a bore of the sample holder. Preliminary photographs are taken to adjust the orientation and alignment of the sample holder such that the length of the capillary is parallel to the plane of the flat plate-camera and both are at right angles to the incident beam.

The sample holder Figure 1 (designed and fabricated in-house) is made of a brass cylinder of 1.0 cm diameter and screwed on a base such that its height may be adjusted. A hollow bore of diameter 1.5 mm allows the X-ray beam to be incident on the sample capillary which is inserted along another bore perpendicular to the former.

The sample holder may be heated up to ∼250°C and its temperature regulated with the help of a thermostat with an accuracy of ±1°C. The brass block is coated with white cement to ensure there is no heat loss through dissipation. An electromagnet is so positioned, such that the sample lies between its pole pieces (of strength ∼ 7kGauss), the magnetic field direction being along the length of the sample capillary.

The sample is taken through a number of temperature cycles in presence of the magnet field to obtain a aligned monodomain sample. X-ray exposure is given at the desired temperature. Accurate film to sample distance is measured by making measurements on the (111) reflection of an Al sample placed in the position of the liquid crystal sample prior to the actual experiment. The angle of reflection $\theta'$ for the liquid crystalline sample is obtained from the diameter of the halo due to diffraction from the sample using the equation

$$\tan 2\theta' = \text{Radius of the halo/sample to the film distance.}$$

The $\theta'$ values obtained from above are used to give the molecular parameters.

To obtain the order parameter in case of aligned samples the X-ray photographs are scanned linearly using HP scanjet 2200c Scanner and intensity plot obtained using Image Pro

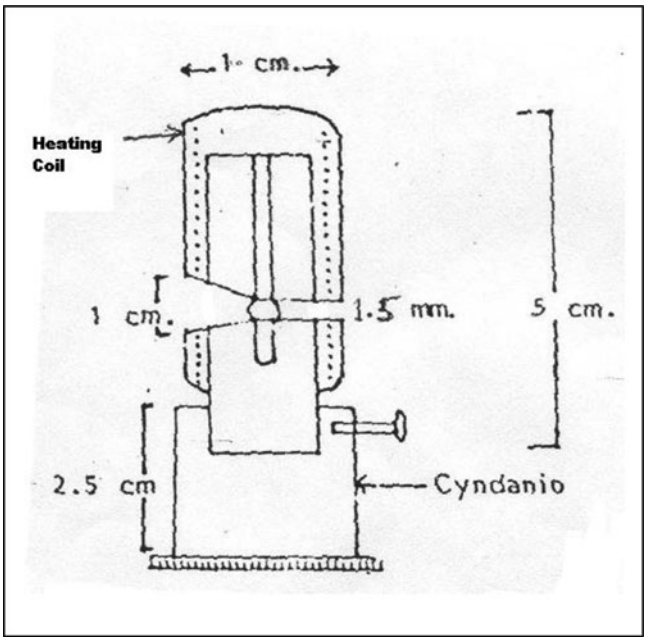


**Figure 1.** Schematic diagram of sample holder used for X-ray studies.

Plus software. The intensities relative to the background intensity is obtained by deducing the latter from the former. The intensity values are then expressed as a function of the angle $\psi$ at the crescent radius and then fed to a computer program for calculating $<P_2>$ and $P_4$.

In the present work X-ray study has been conducted on one sample and its order parameter determined at various temperatures.

## Experimental observation

The room temperature photograph at 35°C shows a spotted, discontinuous outer ring indicating a semi crystalline nature of the sample at this temperature. No measurement could be done on this photograph.

For photograph at 55°C, the outer ring was broken up into two segments indicating ordering of the sample. The diameter of the outer arcs/ segments and that of the inner rings were measured from which the intermolecular distance D and apparent molecular length could be obtained. The inner ring however is not too distinct.

For photograph at 60°C, the variation of intensity in the outer ring indicates good ordering of the sample. The photograph shows a segment outer ring two bright arcs in diametrically opposite positions. Both the outer arc and inner ring radii were measured to obtain D and l. Photograph at 70°C This photograph appeared slightly blurred compared to the previous one and no appreciable change was observed in the diameter of the inner ring, the outer radius corresponding to the arcs was slightly smaller.

## Results and discussion

It is evident that the intermolecular distance D increases slightly with temperature varying from 5.14 Å at 55°C to 5.98 Å at 70°C. This is expected, since with rise in temperature, the molecules vibrate more vigorously and the effect of binding forces decrease. The molecular

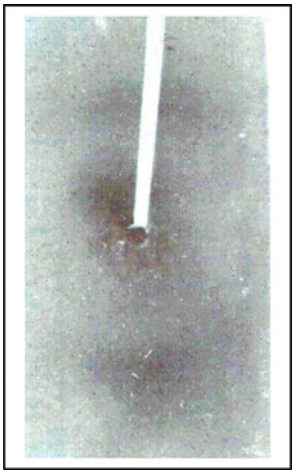

**Figure 2.** Photo at 60°C.

length (apparent) also increases from 16.08 Å (55°C) to 17.68 Å (60°C) but remains the same with further increase of temperature (Fig. 2).

The order parameters at the three temperatures of 55°C, 60°C, and 70°C were obtained by scanning the photographs as discussed earlier. The scanned intensities I were obtained as a function of rectangular Cartesian co-ordinates i.e. I(x,y) which were converted to intensity values $I(r,\psi)$ where r has the value of the segment (crescent) radius. These intensity values are corrected after making background corrections and one fed in to a computer to calculate the orientational order parameters $<P_2>$ and $<P_4>$. The order parameter values at the three temperatures have been plotted in Fig. 5. Comparing the trend of $<P_2>$ values obtained from X-ray i.e. $<P_2>_{X\text{-ray}}$ with our values obtained from birefringence[4] study of $<P_2>_{expt}$ we note that the trends are similar expect that $<P_2>_{X\text{-ray}}$ values are slightly less than that of $<P_2>$ values obtained from optical studies.

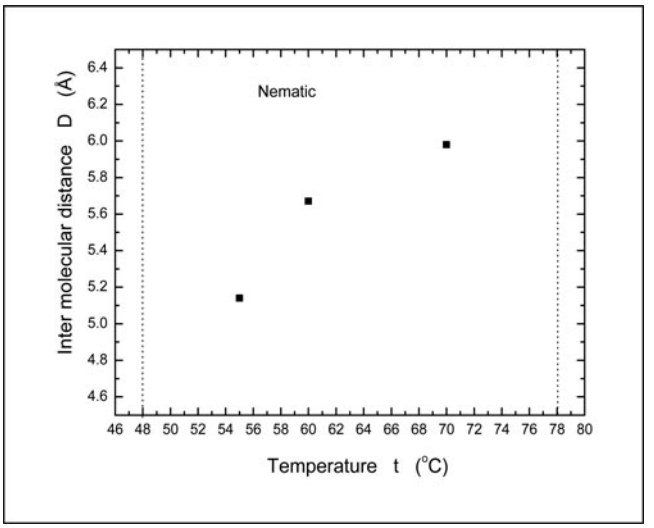


**Figure 3.** Variation of intermolecular distance with temperature for D302.

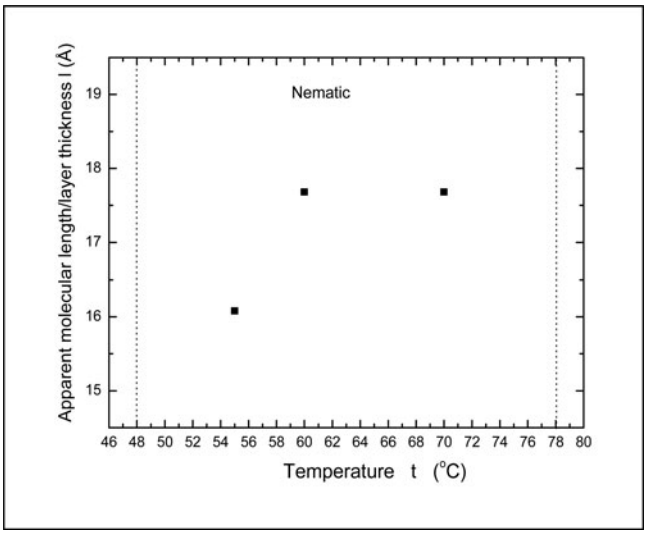


**Figure 4.** Variation of layer thickness with temperature for D302.

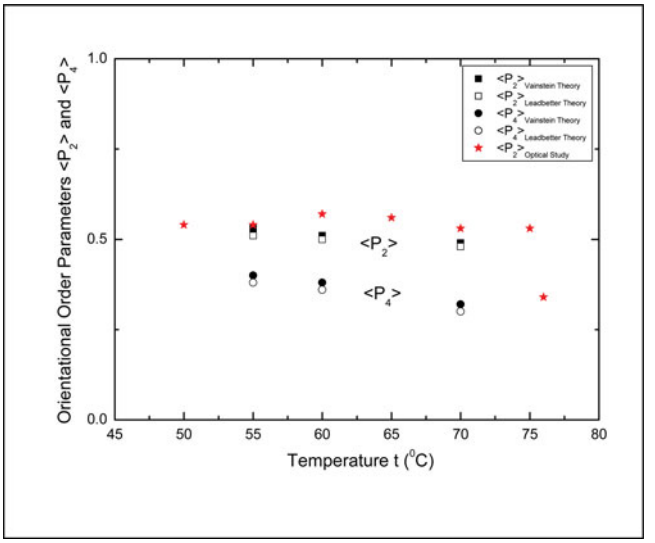


**Figure 5.** Variation of order parameter with temperature of D302 from X-ray study.

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