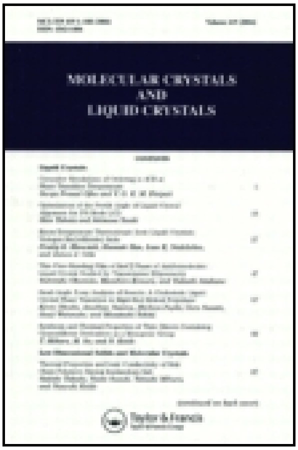

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ORIENTATIONAL ORDER PARAMETER AS A FUNCTION OF TEMPERATURE OF CYANOCYCLOHEXYL CYCLOHEXANES

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Orientational Order Parameter as a Function of Temperature of Cyanocyclohexyl Cyclohexanes

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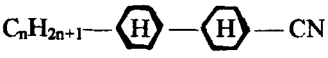
With a view to studying the effect of increasing chain length, texture and optical studies have been conducted on two members of the series cyanocyclohexyl cyclohexanes namely CCH_4 and CCH_5. Refractive index measurements have been conducted at different temperatures by Chatelaine Wedge method using a laser beam. The orientational order parameter $\langle P_2 \rangle$ has been determined as a function of temperature for both the members in the nematic phase. The $\langle P_2 \rangle$values have been compared with the theoretical values predicted by the Maier-Saupe theory.

Keywords: cyanocyclohexylcyclohexanes; temperature; texture; optical anisotropy; $\langle P_2 \rangle$

INTRODUCTION

Much work has been done on the members of the series trans, trans – 4′ – alkyl – bicyclohexyl – 4 – carbonitrites (abbreviated to cyanocyclohexylhexanes or CCH) and having the structural formula



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following their synthesis [1]. Dielectric and optical anisotropy measurements have been conducted [2] on some members of the CCH and they have found to be the first monomeric thermotropic nematic class of liquid crystals with a negative diamagnetic susceptibility [2]. X-ray crystal structure of some members namely CCH_3,CCH_5 and CCH_7 in the solid phase have been determined [3] and diffraction work conducted on some members of the series [4,5]. Elastic constants of CCH_3 and CCH_5 have been determined [6]. IR/Raman scattering studies have also been conducted on some members of the series [7]. Theoretical work on dimer association [8] and molecular dynamic studies have also been done. The variation of order parameter with temperature from birefringence studies has not been reported so far. Also not all the smectic phases exhibited have been identified.

We have determined $<P_2>$ as a function of temperature for two members namely CCH_4 ($C_{17}H_{29}N$) and CCH_5 ($C_{18}H_{31}N$) from optical studies. Texture studies have also been conducted on the above members.

EXPIREMENTAL METHODS

Samples of CCH_4 and CCH_5 were obtained from Merck Ltd. The transition temperatures as supplied (by Merck Ltd.) are

$$CCH_4: \quad \text{solid} \xrightarrow{28^\circ C} \text{smectic} \xrightarrow{54^\circ C} \text{nematic} \xrightarrow{79^\circ C} \text{isotropic}$$

$$CCH_5: \quad \text{solid} \xrightarrow{62^\circ C} \text{nematic} \xrightarrow{85^\circ C} \text{isotropic}$$

$$\text{Smectic1} \xleftarrow[39^\circ C]{} \text{smectic2} \xleftarrow[50^\circ C]{} \text{nematic} \longleftarrow$$

Microscopic studies in conjunction with differential scanning calorimetry (DSC) show the appropriate validity of the above transition temperatures.

Texture Studies

The nature of the changes at different temperatures was examined and transition temperatures noted using a polarizing microscope (Leitz) having a hot stage (Mettler F 82HT). Observation was performed on both the samples under crossed polarizers with a magnification of 150X. However no observations could be made below 30°C due to technical difficulties. Heating and cooling were done at the rate of 1°C/min. Each sample was heated to temperatures well above the isotropic transition temperatures and then allowed to cool.

Compound I: CCH_4

The transition temperatures as obtained from polarizing microscope studies are

$$\begin{array}{l} \text{smectic} \xrightarrow{53^\circ\text{C}} \text{nematic} \xrightarrow{78.8^\circ\text{C}} \text{isotropic} \\ \text{smectic} \xleftarrow[51.4^\circ\text{C}]{} \text{nematic} \xleftarrow[79^\circ\text{C}]{} \end{array}$$

Compound II: CCH_5

The transition temperatures as obtained from polarising microscope studies are

$$\begin{array}{r} \text{solid} \xrightarrow{63.3^\circ\text{C}} \text{nematic} \xrightarrow{85.6^\circ\text{C}} \text{isotropic} \\ \text{smectic1} \xleftarrow[39.9^\circ\text{C}]{} \text{smectic2} \xleftarrow[51.0^\circ\text{C}]{} \text{nematic} \xleftarrow[85.6^\circ\text{C}]{} \quad\quad\quad\; \end{array}$$

Texture photographs were taken.

Refractive Index Measurements

Hollow prisms made from glass slides whose surfaces were treated for surface alignment were used for birefringence measurements. Prior to introduction of the sample the prism angle was determined using a laser beam and measuring the distance between the images formed on a screen kept several meters away due to reflection from front and back surfaces of the prism. Prisms of angles of the order of 1° — 2° were used. The liquid crystal samples were then introduced by melting the sample at the top of the open edge and allowing the melted sample to flow in. The open edge was then sealed. The prism was then placed in brass sample holder with a electrical heating device (fabricated in house), the temperature being regulated with an accuracy of ± 1°C. The combination of rubbing and magnetic field strength of 8 kGauss in the direction of rubbing produced a homogenous nematic specimen with the optic axis parallel to the edge of the prism. Light from a He – Ne laser ($\lambda = 633$ nm) was made incident on the sample normally through a hole drilled in the sample holder. The angular deflections of the refracted beam were measured by observing the positions of the light spots on a screen held several meters away. From the changes in the patterns observed on the screen the transition temperatures may be verified. They were found to be in conformity with the temperatures obtained from texture studies. The sample was heated at the rate of 1°C/min to temperatures beyond the isotropic temperature and allowed to cool at the same average rate. The refractive indices n_e and n_o were calculated at different temperatures from the angular deflections.

The densities of the samples were determined by putting the weighted samples in a glass capillary tube, which was then placed in a heat bath. The length of the column was measured with a travelling microscope.

RESULTS AND DISCUSSIONS

Though there is no significant difference in data on transition temperatures regarding CCH_4, there exist differences regarding transition temperature on CCH_5. Most workers including us have detected two smectic phases of CCH_5, but the existence of only one smectic phase has also been reported [9]. Furthermore, Ibrahim et al [10] have reported more than one crystalline phase:

$$K_2 \xrightarrow{59.2°C} K_1 \xrightarrow{63.4°C} S_1 \xrightarrow{40.5°C} S_2 \xrightarrow{49.1°C} N \xrightarrow{86.4°C} I$$

We were unable to detect any change around 59°C from texture studies but X-ray crystal structure determination shows that the compound exists in two crystal forms [3,10].

Phase Identification

CCH_4: Fig 1 (a) is a typical photograph showing the Schlieren texture of the nematic phase taken at 60°C. Fig 1 (b) of the smectic phase taken at 46.5°C while cooling from the nematic phase compares well with the mosaic texture of the smecticB phase (plate 7, Gray&Goodby [11]). Homeotropic texture is also exhibited in this phase ruling out the possibility of any tilted phase. DSC study reveals that the transition to and from the smectic phase is accompanied with an enthalpy of ~ 4kJ/mole. X-ray studies on a freshly prepared sample at 29°C have shown a six spot configuration [5]. We are thus led to conclude that the smectic phase exhibited by CCH_4 is a smecticB phase.

CCH_5: Fig 2 (a) is a photograph of the texture of the nematic phase at 80°C while cooling the sample from the isotropic phase. Transition from nematic to smectic2 phase while cooling starts at 51.4°C. Fig 2 (b) is a photograph of the texture when this phase begins to separate out. Fig 2 (c) is a photograph of the same phase at 49°C showing the mosaic textures when the phase is completely formed. These two photographs [Fig 2 (b) & (c)] compare well with plates 5&6, Gray & Goodby [11] of the smecticB phase. Though no other corroborative study has been done we are led to believe that the smectic2 phase of CCH_5 is a smecticB phase.

On further cooling, the above phase begins to transform at 39.9°C and a photograph at 37°C when this phase has completely formed is depicted in Fig 2 (d). From the nature of the texture and that it has formed from a smecticB phase we believe this phase is a smecticG phase. However no other corroborative test has been conducted so far. The phase transition from smecticB to this phase is accompanied with an enthalpy change of 2.6 kJ/mole.

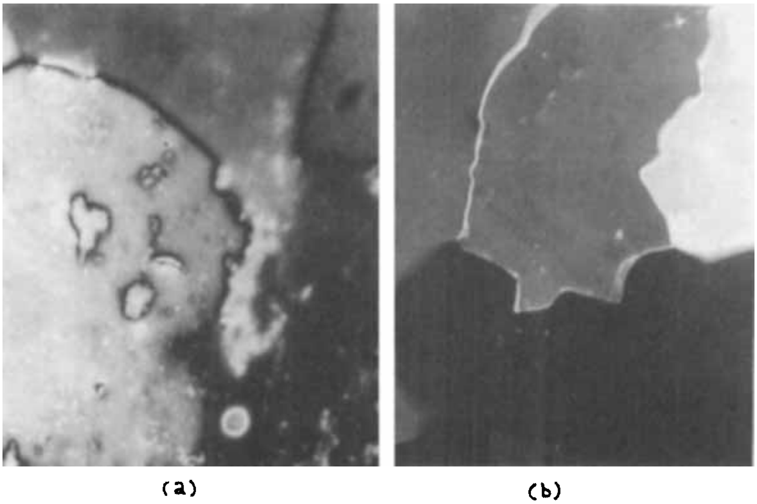

(a) (b)

FIGURE 1(a) Schlieren texture of the nematic phase of CCH_4 at 60 °C
(b) Smectic phase of CCH_4 at 46.5°C

See Color Plate V at the back of this issue.

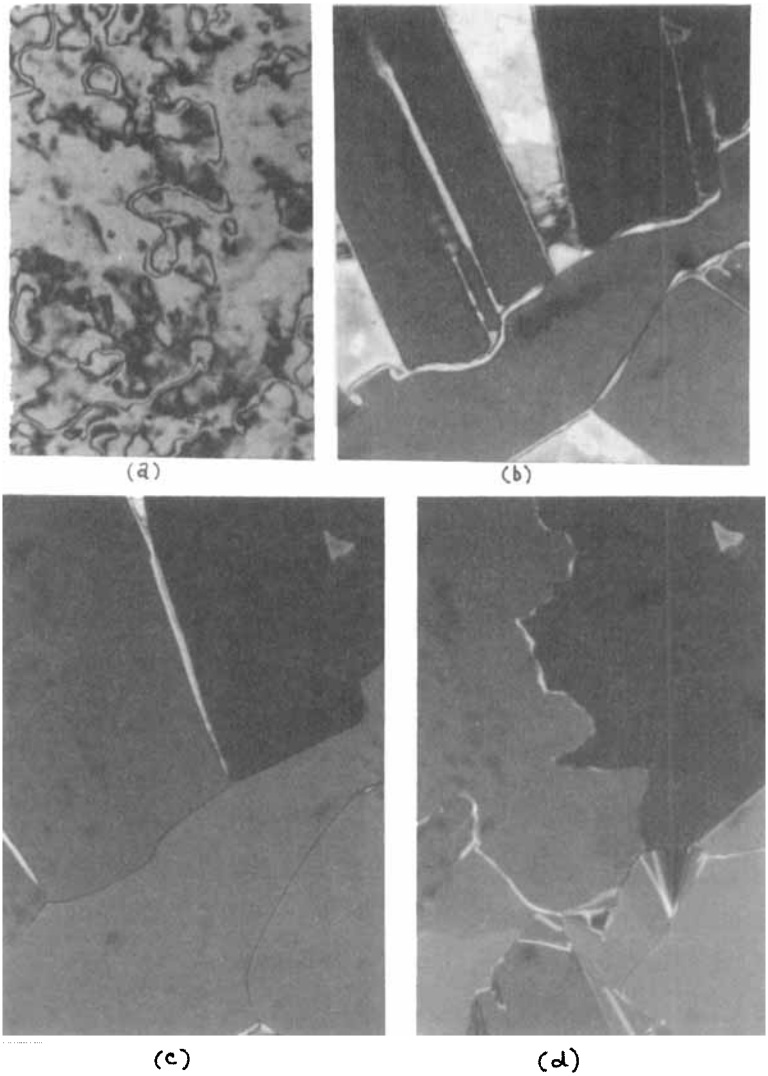


FIGURE 2 (a) Nematic phase of CCH$_5$ at 80°C
(b) Smectic2 phase of CCH$_5$ separating out at 51°C
(c) Mosaic texture of the Smectic2 phase of CCH$_5$ at 49°C
(d) Smectic1 phase of CCH$_5$ at 37°C
See Color Plate VI at the back of this issue.

Refractive Index and Order Parameter

Fig 3 shows the variation of refractive indices with temperature for both the compounds. $\bar{n}$ is seen to be virtually independent of temperature and discontinuous at T_{NI}. Similar is the nature of variation of the dielectric permitivity $\bar{\varepsilon}$ of CCH's [6]. This is indicative of the strong antiparallel local ordering of molecules found in cyanosystems. Bradshaw and Raynes [6] have reported ε as a function of temperature for the odd members CCH_3, CCH_5, CCH_7. With increasing chain length, both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ decreases. In our refractive indices measurements n_o and n_e are greater for CCH_5 than for CCH_4. Evidently the odd – even effect rather than the chain length effect has made its contribution. From birefringence and density measurements, the principal molecular polarisations (ae, ao) were calculated using Vuks' formula [12]. Fig 4 depicts the variation of polarisibilities with temperature. The order parameters were calculated using the relation $\langle P_2 \rangle = (a_e - a_o)/(a_{\parallel} - a_{\perp})$ [13], where $a_{\parallel}$ and $a_{\perp}$ are the polarisibilities parallel and perpendicular to the long axis. $a_{\parallel}$ and $a_{\perp}$ could not be directly obtained due to lack of solid state phase data and Haller's [14] extrapolation procedure was adopted for this purpose. log $(a_e - a_o)$ vs log $(T_C - T)$ was plotted and the straight line portion at low temperature region was extrapolated to logT_C ($T = 0$) to obtain the limiting value of $(a_e - a_o)$ which is assumed to correspond to $(a_{\parallel} - a_{\perp})$.

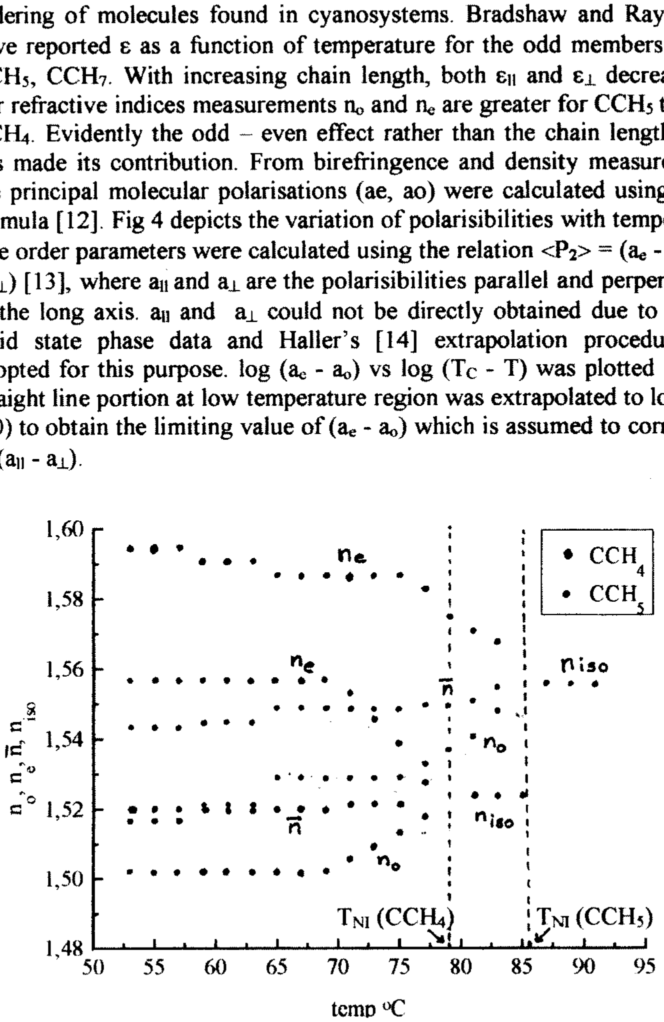


FIGURE 3 Variation of refractive indices with temperature
See Color Plate VII at the back of this issue.

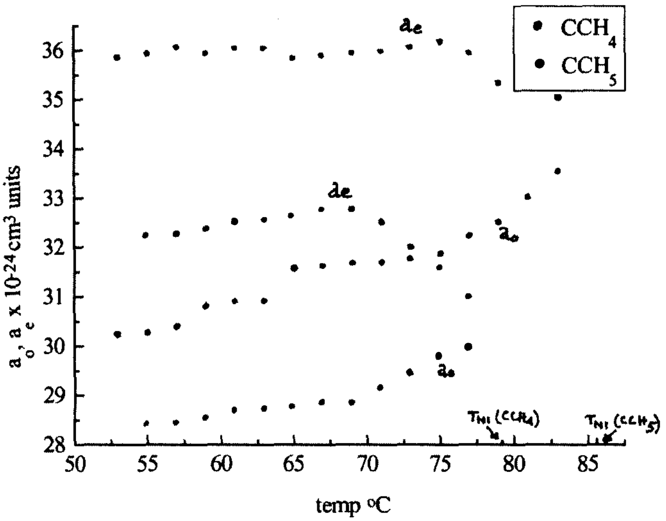
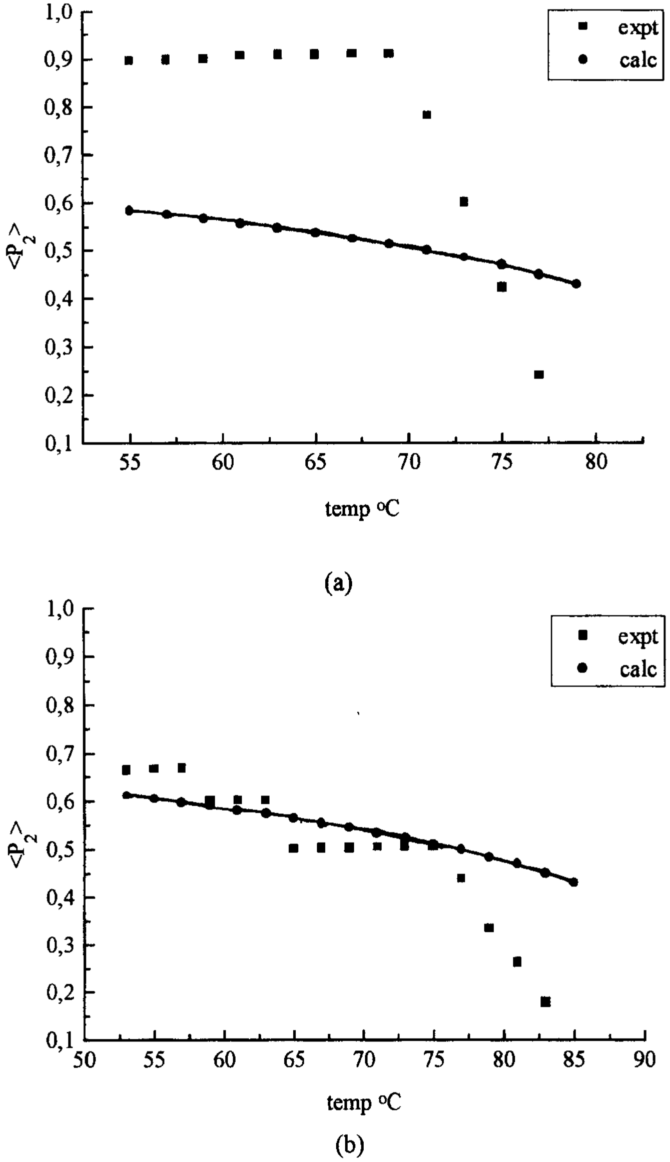


FIGURE 4 Variation of polarisibilities with temperature

See Color Plate VIII at the back of this issue.

Variation of $\langle P_2 \rangle$ with temperature along with Maier – Saupe theoreticalvalues are depicted in Fig 5(a) & (b). $\langle P_2 \rangle$ values for CCH_4 are abnormally high before they plunge to low values preceeding the nematic – isotropic transition temperature. These high values are accorded to low value of $a_{\parallel} - a_{\perp}$ obtained by extrapolating the low temperature region data which actually pertains to the smectic phase data (in this case). Also this may be an instance where the validity of Vuks' formula is not strictly true and it may be worthwhile to try Neugebauer's approach [15]. $\langle P_2 \rangle$ values of CCH_5 are more close to theoretically predicted values except near the nematic – isotropic transition when the drop is much sharper. Regarding the discontinuities at 63°C and 58°C which also persists in n and a curves of CCH_5 we note that 63°C is the melting point and all data taken below this temperature during cooling, is of the sample in a supercooled nematic state. We are unable to comment on the discontinuity at ~ 58°C except that as reported by Ibrahim et al [10], the compound transforms from one crystalline phase to another around ~ 59°C during heating.



(a)

(b)

FIGURE 5 Variation of $<P_2>$ with temperature, ● show Maier – Saupe theoretical curves. (a) CCH_4 (b) CCH_5

Acknowledgements

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