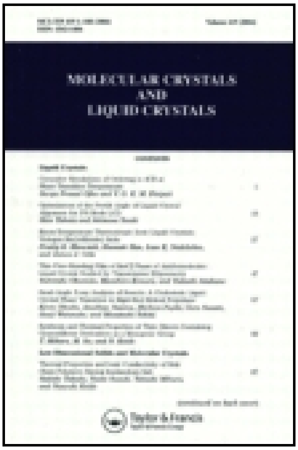

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Macroscopic Properties and Their Temperature Dependence of the Mesogen 4-(4-Propylcyclohexyl)phenyl 4-Butylcyclohexanecarboxylate

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Macroscopic Properties and Their Temperature Dependence of the Mesogen 4-(4-Propylcyclohexyl) phenyl 4-Butylcyclohexanecarboxylate

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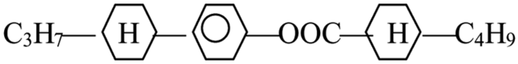
The thermal dependence of optical and dielectric properties of one member namely 4-(4-propylcyclohexyl)phenyl 4-butylcyclohexanecarboxylate (HD34) of the mesogenic homologous series 4-(4-propylcyclohexyl)phenyl 4-alkylcyclohexanecarboxylate is reported. In particular, the thermal variation of orientational order parameter and the effect of temperature on the effective molecular dipole moment μ *and the angle of inclination* β *of the dipole axis with the prefered direction are investigated. The experimental order parameter values have been compared with theoretical Maier–Saupe values. Comparison of these electro-optical properties have been made with those of the next higher member (HD35) of the series to study the effect of increasing chain length .*

Keywords: birefringence; dielectric permittivity; dipole moment; mesogen; order parameter

INTRODUCTION

As a part of our investigation on the mesogenic properties of the series 4-(4-propylcyclohexyl)phenyl 4-alkylcyclohexanecarboxylate, optical and dielectric studies have been conducted on one member of the series, namely, 4-(4-propylcyclohexyl)phenyl 4-butylcyclohexanecarboxylate (HD34) having the structural formula



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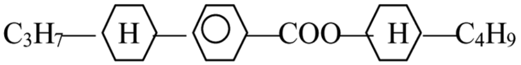
and molecular formula $C_{26}H_{40}O_2$. The compound HD34 is known to undergo the following phase transitions (Merck Ltd.):

$$\text{solid} \xrightarrow{64^\circ\text{C}} \text{smecticB} \xrightarrow{97^\circ\text{C}} \text{smecticA} \xrightarrow{116^\circ\text{C}} \text{nematic} \xrightarrow{189^\circ\text{C}} \text{isotropic}$$

Another mesogenic compound 4-butylcyclohexyl 4-(4-propylcyclohexyl) benzoate having identical molecular formula as HD34 but differing slightly in molecular structure



and exhibiting only/a nematic phase had been synthesized and studied as early as 1979 [1]. Optical and dielectric studies [2,3], molecular modelling [4], and X-ray studies [5] on the next higher member HD35 have been reported. Infrared spectroscopy has also been conducted [6] on compounds obtained by interchanging the terminal groups of some members of the series.

The phase transition from the crystalline to smecticB phase of the sample has been studied using differential scanning calorimetry and low-frequency internal friction technique [7]. However, no systematic study of the optical and dielectric properties of the sample have been reported. In the present work, we report the results of optical and dielectric studies carried out on HD34 in a temperature range spanning the smecticB, smecticA, and nematic phases. The thermal variation of order parameter from birefringence study has been determined. We have also calculated the variation of dipole moment μ with temperature and angle of inclination β from dielectric study.

The above results for HD34 have been compared with those of HD35 to study the effect of increasing chain length.

EXPERIMENTAL METHODS

Texture Studies

Prior to undertaking optical and dielectric studies, routine texture studies of the compound were conducted in the entire solid to isotropic temperature range using a polarizing microscrope (Leitz) having a hot stage (Mettler FP 82 HT) to confirm the different phases as well as the phase transition temperatures. Observations were performed under crossed polarizer with a magnification of 150X. Powdered crystals were melted on a clear glass surface and a cover slip was used. Photographs of the sample were taken. Heating and cooling were done at the rate of 1.5°C/min.

Optical Studies

Birefringence studies were conducted using the Chatelain Wedge principle in which the sample was introduced into a glass prism of angle between 1–2° formed with glass slides whose inner surfaces were treated with polyvinyl alcohol and rubbed along the prism edge for planar surface alignment. The open end of the prism was then sealed and the prism encapsulated in a sample holder whose temperature may be regulated up to ±1°C with the help of a temperature controller. The sample holder was placed in an aligning field of ~ 8 kGauss with the direction of the aligning field parallel to the direction of rubbing. The treatment of the inner surfaces of the sample cell is an additional measure taken, to ensure alignment. A He-Ne laser beam ($\lambda = 633$ nm) was directed onto the sample, through a hole in the sample holder and the refracted beams (ordinary and extraordinary) emerging from the sample prism were projected on a screen placed 5.0 m away. From measurements on the screen, the angular deviation and consequently the refractive indices n_e and n_o of the extraordinary and ordinary rays may be determined with the knowledge of the prism angle. The prism angle was determined using the same method, prior to the introduction of the sample. In this method, the refracted extraordinary and ordinary beams are projected on a screen several meters away without any appreciable loss of intensity (laser beam) thereby increasing the angular separation and resolution of the refracted beams and providing an accurate method of refractive index determination. Details of the experimental arrangement are given in [8]. All readings were taken at intervals of 5°C.

To determine the polarizability and thereby the order parameter from birefringence studies, the densities of the samples had to be determined as a function of temperature. The density of the sample at various temperatures was determined by introducing the weighed sample in the molten form in a dilatometer, which was then placed in a heated bath. The length of the sample column in the dilatometer tube was measured with a travelling microscope at intervals of 1°C and the density of the sample material calculated. The polarizability values were determined using Vuk's formula [9].

Dielectric Studies

Sample cells (capacitor) were formed with a pair of ITO coated conducting glass plates separated by thin cover slips on three sides. The sample cell thus formed was calibrated using standard liquids: benzene and p-xylene with the help of an LCR meter (6471 Forbes

Tinsley). The sample was introduced into the cell as an isotropic liquid and the open end then sealed. The sample cell, encapsulated within a sample holder with a heating device (fabricated in-house) was placed in a magnetic field of approximately 8 kGauss. The sample was taken through a number of temperature cycles in the presence of the magnetic field to obtain an aligned monodomain sample. Readings for the parallel and perpendicular components of the capacitance were taken at intervals of 5°C from about 108°C (immediately before the smecticB–smecticA transition) to beyond the nematic–isotropic transition temperature at frequencies of 10 and 100 kHz. The values of the parallel and perpendicular components of the dielectric permittivity $\varepsilon_{||}$ and $\varepsilon_{\perp}$ were obtained from the capacitance values by standard procedure of calibration. The bridge voltage across the sample was maintained sufficiently low ($\sim 0.3\,\text{V}$) so as not to produce any electric field induced instabilities.

RESULTS AND DISCUSSION

Texture Studies

The transition temperatures for HD34 as observed from texture studies are as follows:

$$\text{solid} \underset{85^\circ\text{C}}{\overset{100.5^\circ\text{C}}{\rightleftarrows}} \text{smeticB} \underset{111^\circ\text{C}}{\overset{110^\circ\text{C}}{\rightleftarrows}} \text{smecticA} \underset{116^\circ\text{C}}{\overset{116^\circ\text{C}}{\rightleftarrows}} \text{nematic} \underset{185^\circ\text{C}}{\overset{187^\circ\text{C}}{\rightleftarrows}} \text{isotropic.}$$

The transition temperatures from smecticA to nematic and nematic to isotropic liquid phase are in excellent agreement with the quoted values supplied by Merck Ltd. However there exists a discrepancy between the experimentally observed and quoted values of the transition temperature between the solid to smecticB and smecticB–smecticA phase. Repeated observations, however, gave the same results. Also, during cooling the phase change from smecticB to solid phase takes place at a lower temperature of 85°C indicating a supercooled state.

At this juncture, it may be mentioned that HD35 having an extra CH_2 moiety and the molecular formula $C_{27}H_{42}O_2$ has the following phase transitions (Merck Ltd. also confirmed by experiment [5]):

$$\text{solid} \xrightarrow{42^\circ\text{C}} \text{smectic1} \xrightarrow{72.4^\circ\text{C}} \text{smectic2} \xrightarrow{128^\circ\text{C}} \text{nematic} \xrightarrow{193^\circ\text{C}} \text{isotropic.}$$

Though the nematic–isotropic transition temperatures of HD34 and HD35 are comparable, the mesogenic ranges are not at all similar.

HD35 has a much longer mesogenic range commencing from 42°C and the smectic1 and smectic2 phases of HD35 have been identified as the smecticE and smecticB phases, respectively [5], whereas HD34 exhibits smecticB and smecticA phases (Merck Ltd.).

Optical Studies

Figures 1 and 2 show the variation of refractive indices n_e and n_o and polarizabilities α_e and α_o, respectively, with temperature. The estimated errors for determination of refractive index and polarizability are 2% and 3%, respectively. The refractive indices remain constant with temperature throughout the nematic range and no appreciable discontinuity is observed as the phase changes from smecticA to nematic. The average refractive index n_{ave} (average n)is seen to be virtually independent of temperature and continuous with n_{iso} at the nematic–isotropic transition temperature, a feature which is also shown by ε_{ave} in Figure 4. Optical anisotropy Δn is seen to remain fairly constant in the temperature range 108°C–185°C at 0.08, the quoted value being 0.11 (temperature unspecified). The optical anisotropy Δn for the next higher member HD35 is 0.113 [2] at 135°C which agrees well with the quoted value of 0.11 supplied by Merck. On comparison with HD35 [2] we find that with an increase in chain length the refractive indices decrease.

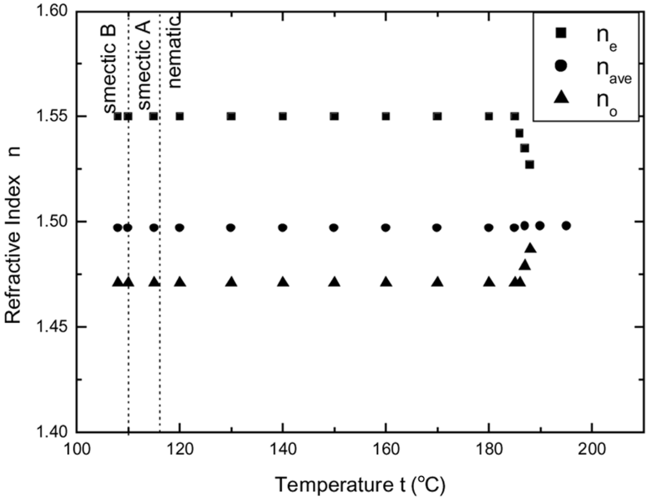


FIGURE 1 Variation of refractive index with temperature of HD34.

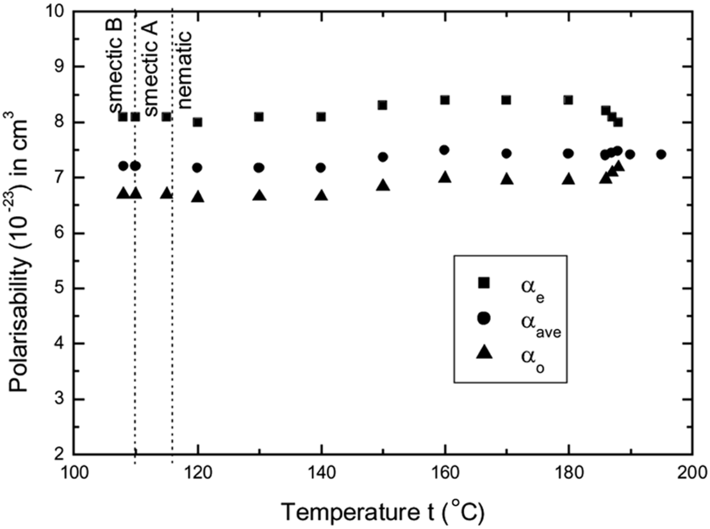


FIGURE 2 Variation of polarizability with temperature of HD34.

Polarizability shows a discontinuity at around 116°C which is the smecticA–nematic transition temperature but remains fairly constant within the nematic range. No discontinuity, however, is observed in the values of the refractive indices at the smecticA–nematic transition.

The orientational order parameter $\langle P_2 \rangle$ was calculated using the relation $\langle P_2 \rangle = (\alpha_e - \alpha_o)/(\alpha_{||} - \alpha_{\perp})$ [10], where $\alpha_{||}$ and $\alpha_{\perp}$ are the polarizabilities parallel and perpendicular to the long axis corresponding to the solid phase and have been obtained using Haller's [11] extrapolation procedure. Variation of $\langle P_2 \rangle_{expt}$ together with theoretical Maier–Saupe (MS) [12] values of the order parameter have been depicted in Figure 3(a). The experimental order parameter values are in close agreement with calculated MS values and varies from 0.7 at 108°C to 0.4 before nematic–isotropic transition. The variation of the experimental order parameter of HD35 in the nematic range obtained from birefringence studies [2] by the same method and reproduced in Figure 3(b) shows, on the contrary a much steeper descent than that predicted by the MS theory and falls from values slightly greater than 0.6 at 135°C to 0.2 near the clearing temperature (of 193°C) for HD35. In the smecticB region, thermal variation of order parameter of HD35 obtained from the X-ray study [5] is seen to drop from 0.75 at 80°C to ~0.6 at 110°C as smecticB–nematic transition is approached at which a discontinuity is observed. The variation for HD35 has been reproduced in Figure 3(b) for easy comparison. The close agreement

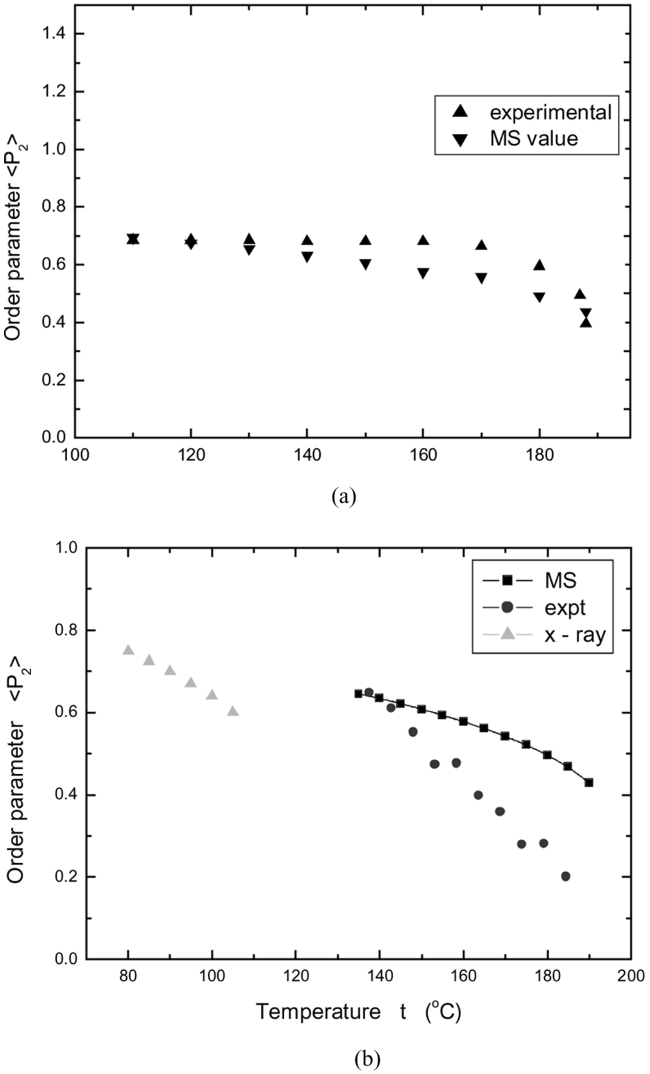
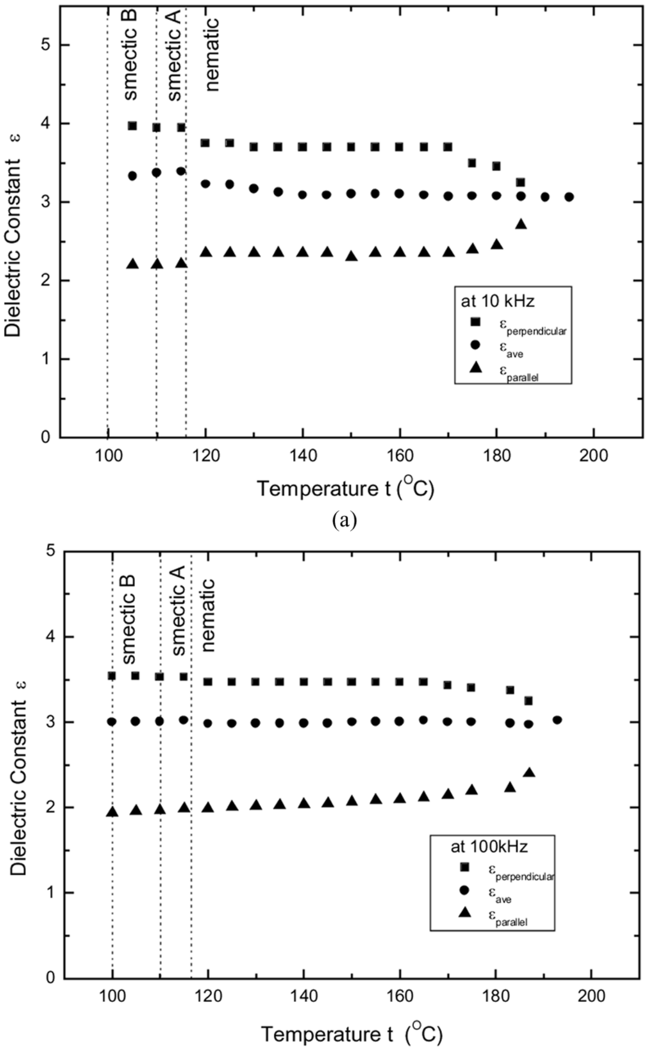


FIGURE 3 (a) Variation of order parameter with temperature of HD34; (b) Variation of order parameter with temperature of HD35.

of experimental $\langle P_2 \rangle$ values with MS values for HD34 in contrast to the discrepancy in case of HD35 is indicative of the molecular interactions being such as to satisfy the assumptions of the MS theory in the former case as opposed to the latter.

Dielectric Studies and Dipole Moment

The variation of dielectric permittivity with temperature at two different frequencies of 10 and 100 kHz is depicted in Figsures 4(a) and (b). Dielectric anisotropy is negative and is found to be −1.35 and −1.4 at 10



(a)

(b)

FIGURE 4 Variation of dielectric constant with temperature of HD34 at (a) 10 kHz and (b) 100 kHz.

and 100 kHz, respectively, at 150°C, the quoted value at 1 kHz being -1.4. The discontinuities observed in the polarizability curves at 116°C at the smecticA–nematic transition persist, though the transition from smecticB to smecticA at 110°C is smooth. As mentioned earlier, ε_{ave} is continuous with ε_{iso} at the nematic–isotropic temperature. This is a feature that is exhibited by nonpolar molecules like di-alkyl azobenzene [13] and has been explained assuming the presence of short range antiferroelectric order in the nematic state [14,15]. With an increase in frequency, the dielectric permittivity decreases; ε_{ave} having values of $\sim$4.33 and 3.90 at 10 and 100 kHz, respectively, at 120°C, *i.e.,* the percentage decrease is $\sim$10% of the value at 10 kHz and is attributed to dielectric loss. In case of HD35, ε(average) has values of 7.59, 6.00 and 5.67 at 1, 10, and 100 kHz, respectively, at the same temperature [3]. Thus the dielectric constant is seen to increase with the chain length in this case.

Using the expressions for $\varepsilon_{||}$ and $\varepsilon_{\perp}$ of Maier and Meier [16] the effective molecular dipole moment μ in the mesophase and angle of inclination β between the director direction and the molecular axis have been calculated from the expressions

$$\varepsilon_{\text{ave}} = 1 + 4\pi \text{NhF}(\alpha_{\text{ave}} + \text{F}\mu^2/3\text{KT}) \tag{1}$$

and

$$\Delta\varepsilon = 4\pi\text{NhF}\{\Delta\alpha - \text{F}\mu^2(1 - 3\ \text{Cos}^2\beta)/2\text{KT}\}\langle \text{P}_2\rangle, \tag{2}$$

where

$$\varepsilon_{\text{ave}} = (\varepsilon_{||} + 2\varepsilon_{\perp})/3, \alpha_{\text{ave}} = (\alpha_{\text{e}} + 2\alpha_0)/3,\ \text{f} = 4\pi\text{N}(2\varepsilon_{\text{ave}} - 2)/3(2\varepsilon_{\text{ave}} + 1)$$

$$\text{h} = 3\varepsilon_{\text{ave}}/(2\varepsilon_{\text{ave}} + 1), \quad \text{F} = 1/(1 - \alpha_{\text{ave}}\ \text{f})$$

Values of α_{ave}, $\Delta\alpha$ and $\langle \text{P}_2\rangle$ have been taken from the birefringence studies to calculate μ and β at various temperatures.

The variations of μ and β with temperature are depicted in Figures 5 and 6. At frequencies of both 10 and 100 kHz, a discontinuity in dipole moment is observed in the smecticA to nematic transition at 116°C. Within the smectic phase, even as the sample goes from smecticB to smecticA, μ increases gradually without any discontinuity. From smecticA to nematic phase, there is a drop in μ value for both frequencies. Within the nematic range, μ increases slightly from 2.27 D to 2.43 D for 10 kHz. For 100 kHz, μ is slightly less than its corresponding values at 10 kHz and increases slightly but steadily from 2.10 D to 2.19 D. For HD35, μ is appreciably higher (3.4 D at 10 kHz, 150°C)

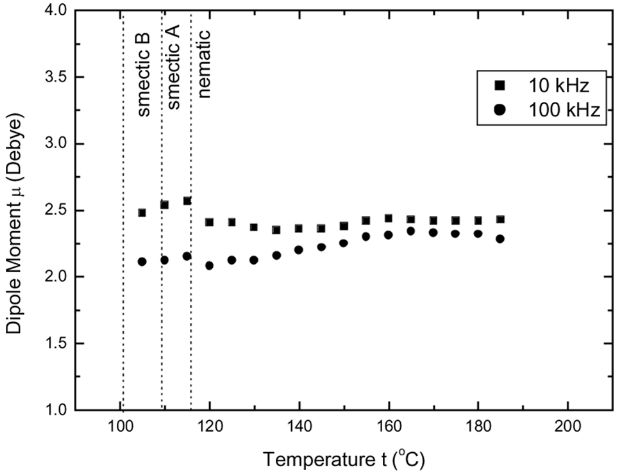


FIGURE 5 Variation of molecular dipole moment with temperature of HD34.

and increases with temperature but decreases with are increase in operating frequency [3].

However, β for HD34 remains fairly constant with temperature at an angle of 77° in the nematic range at 10 kHz, except when nearing the isotropic transition, and is slightly higher at a higher frequency of 100 kHz as compared to that at 10 kHz in nematic phase. In the

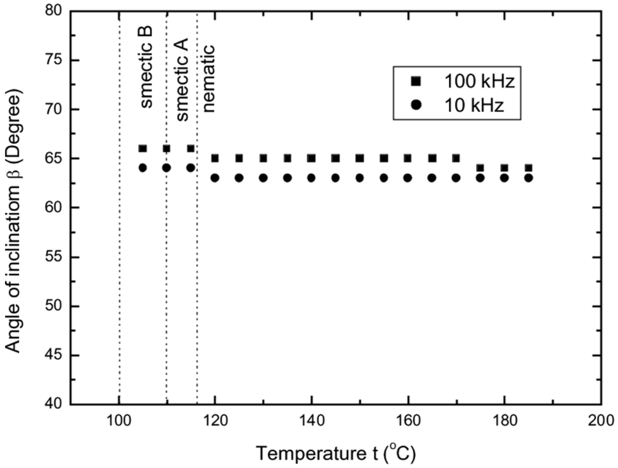


FIGURE 6 Variation of angle of inclination with temperature of HD34.

smectic phase, however, the trend is reversed. The discontinuity from smecticA to nematic phase is also exhibited by β. The percentage error in the determination of μ and β are calculated to vary between 3–4%. In case of HD35, β has a slightly lower value of about 62 at 10 kHz, which rises significantly as the isotropic temperature is approached [3].

Comparison of μ obtained as above with the value of the isolated molecular dipole moment (obtained in extremely dilute solution) may be made to obtain an idea regarding the nature of association of molecules in the liquid crystalline phase. The correlation factor 'g' may also be calculated, and work on determination of μ in solution is in progress.

CONCLUSION

In conclusion, it may be said that the addition of a CH_2 moiety to HD34 has caused a significant alteration in the nature of variation of the orientational order parameter $\langle P_2 \rangle$. In case of HD34, the thermal variation of $\langle P_2 \rangle$ agrees completely with the predicted theoretical MS values, whereas that for HD35 shows significant difference as the clearing temperature is approached, indicating substantial deviation from the mean field theory in the high-temperature region. Also, the average dielectric constant and effective molecular dipole moment for HD35 are significantly higher, indicating a perceptible change in the nature of the molecular charge distribution due to increase in chain length.

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