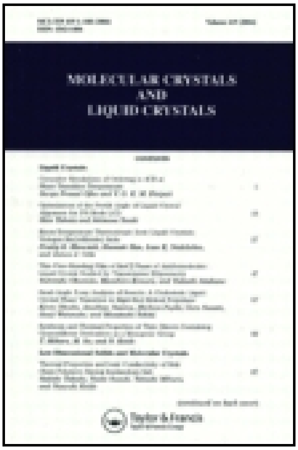

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The Temperature Dependence of the Orientational Order Parameter of the Mesogens : 4'-N-Propyl Phenyl-4-(4'-N-Pentyl Cyclohexyl) Benzoate, Trans-4-propyl cyclohexyl 4-(trans-4-pentyl Cyclohexyl) Benzoate and 4-Pentyl cyclohexyl-4-(4-propyl cyclohexyl) Benzoate from Optical Studies

Kanishka Bhowmick [a], Anuradha Mukhopadhyay [a] & S. K. Roy [b]

[a] Department of Physics, Jadavpur University, Kolkata, India

[b] Department of Spectroscopy, Indian Association for the Cultivation of Science, Kolkata, India

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THE TEMPERATURE DEPENDENCE OF THE ORIENTATIONAL ORDER PARAMETER OF THE MESOGENS : 4′-N-PROPYL PHENYL-4-(4′-N-PENTYL CYCLOHEXYL) BENZOATE, TRANS-4-PROPYL CYCLOHEXYL 4-(TRANS-4-PENTYL CYCLOHEXYL) BENZOATE AND 4-PENTYL CYCLOHEXYL-4-(4-PROPYL CYCLOHEXYL) BENZOATE FROM OPTICAL STUDIES

Kanishka Bhowmick and Anuradha Mukhopadhyay
Department of Physics, Jadavpur University, Kolkata-700032, India

S. K. Roy
Department of Spectroscopy, Indian Association for the Cultivation of Science, Kolkata-700032, India

The birefringence properties of the three mesogenic compounds 4′-n-propyl phenyl-4-(4′-n-pentyl cyclohexyl) benzoate (code name HP53) Trans-4-propyl cyclohexyl 4-(trans-4-pentyl Cyclohexyl) Benzoate (code name HH53) and 4-Pentyl cyclohexyl-4-(4-propyl cyclohexyl) Benzoate (code name HD35) have been studied as a function of temperature. The variation of polarisibilities with temperature of the three mesogens has been calculated from birefringence studies and the orientational order parameter $\langle P_2 \rangle$ *thereby determined as a function of temperature. Texture studies have been conducted to confirm/identify the different mesophases of HP53 and HH53. The two smectic phases 1 and 2 of HD35 have been identified as the smecticE and smecticB phase from texture and x-ray studies [1]. Comparison has been made of* $\langle P2 \rangle$ *values of the three mesogens. Also* $\langle P_2 \rangle$ *values of HD35 obtained from the above study have been compared with* $\langle P_2 \rangle$ *values of the same obtained from x-ray methods [1].*

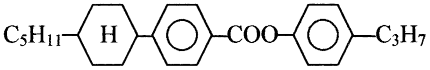
Keywords: birefringence; optical anisotropy; order parameter; thermotropic

We are thankful to Merck Ltd. for supplying the samples. Thanks are due to Prof. P. Nandy and Dr. R. Basu of the Department of Physics, Jadavpur University for helping us with the texture studies.

*Corresponding author. E-mail: arm@juphys.ernet.in, anuradha_mukhopadhyay@yahoo.com

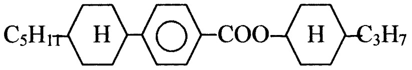
INTRODUCTION

The mesogenic compounds 4′-n-propyl phenyl-4-(4′-n-pentyl cyclohexyl) benzoate (HP53) and trans-4-propyl cyclohexyl-4-(trans-4-pentyl cyclohexyl) benzoate (HH53) having the structural formula



HP 53

Molecular formula: $C_{27}H_{36}O_2$



HH 53

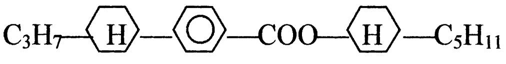
Molecular formula: $C_{27}H_{42}O_2$

are known (supplied by Merck Ltd.) to undergo the following phase transitions:

HP53		HH53	
Melting point	69°C	Melting point	67°C
$S_B \rightarrow S_A$	93°C	$S_B \rightarrow S_A$	43°C
$S_A \rightarrow N$	119°C	$S_A \rightarrow N$	55°C
Clearing point	179°C	Clearing point	155°C

To study the effect of replacing a benzene ring in HP53 by a cyclohexane as in HH53, the variation with temperature of the refractive indices and thereby the orientational order parameter of the two mesogens have been determined using the Chatelain wedge principle. No other determination of order parameter of HP53 as a function of temperature from optical anisotropy has been reported to date.

Birefringence studies have also been conducted as a function of temperature on 4-pentyl cyclohexyl-4-(4-propyl cyclohexyl) benzoate (HD35) and the order parameters obtained there from compared with those of HH53, which is obtained on interchanging the terminal groups of HD35. HD35 having the molecular formula $C_{27}H_{42}O_2$ (same as HH53) and structural formula



has been investigated at different temperatures by texture studies and x–ray methods by Mukhopadhyay *et al.* [1]. The phase transition temperatures supplied by Merck Ltd. are as follows:

$$\text{Solid} \xrightarrow{42^\circ C} \text{Sm1} \xrightarrow{72^\circ C} \text{Sm2} \xrightarrow{128^\circ C} \text{Nematic} \xrightarrow{193^\circ C} \text{Isotropic}$$

The DSC measurements confirm the approximate validity of the quoted transition temperatures while heating, but during cooling the Isotropic–Nematic transition takes place at 188.2°C. The Smectic1 and Smectic2 phases have been identified to be the SmecticE and SmecticB phase respectively. From x–ray photographs the orientational distribution function f(θ) has been determined and the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been calculated in the temperature range of 80°C to ~110°C when the mesogen exhibits the SmecticB phase [1]. In the nematic temperature range, extending from 128°C to ~190°C the order parameter could not be determined due to the diffuse nature of the x–ray diffraction pattern in that high temperature region. No other observations on order parameter of HD35 as a function of temperature have been reported to date.

EXPERIMENTAL METHODS

Texture Studies

The behaviour of the compounds at different temperatures was examined using a polarising microscope (Leitz) having a hot stage (Mettler FP82HT). Observations were performed under crossed polarisers with a magnification 150x. 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. Texture photographs were taken. The approximate validity of the phase transition temperatures were confirmed from polarising microscope studies.

Birefringence Studies

Refractive Index measurements were conducted on the samples at different temperatures covering the entire nematic phase by Chatelain wedge method using a laser beam. The samples were introduced in the isotropic liquid phase into glass prisms, which were formed from glass slides cut to the required size and surface treated for alignment with polyvinyl alcohol. The treated surfaces were rubbed in a direction parallel to the edge of the prisms and forms the inner surfaces of the prisms. The prism angles – characteristically of the order of 1°–2° were accurately determined prior to the introduction of the samples by directing a He-Ne laser beam ($\lambda = 630\,\text{nm}$) on the prisms at near normal incidence and measuring the position of spots reflected from the front and back surfaces of the prisms on a screen held approximately 350 cm away. The open edges of the prisms were sealed after introduction of the samples. The prisms thus formed were placed in a brass sample holder whose temperature may be regulated upto

250°C. The sample encapsulated in the sample holder was placed in an aligning magnetic field of 8 KGauss, the direction of the field being parallel to the direction of rubbing of the internal surface of the prism. Repeated temperature cycling in the presence of the magnetic field ensured a monodomain homogeneous sample. The He-Ne laser beam ($\lambda = 630\,\mathrm{nm}$) was directed normally on the sample through a hole drilled in the holder. Details of the experimental arrangement have been enumerated by Bhowmick *et al.* [2]. The refractive indices of the ordinary and extraordinary rays were determined from the angular deflections of the spots on a screen held at a distance $\sim$4 meters away. 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 densities of the samples were determined at various temperatures by introducing the weighed samples in a glass capillary tube which was then placed in a heat bath, the length of the column being measured with a travelling microscope. From refractive indices and density measurements the polarisabilities α_e and α_o were determined as a function of temperature.

RESULTS & DISCUSSIONS

Texture Studies

The phase transition temperatures observed from texture studies are in confirmity with the quoted values and are as follows for HP53 and HH53

HP53

$$\mathrm{K}\underset{\xleftarrow[39^\circ\mathrm{C}]{}}{\xrightarrow{67^\circ\mathrm{C}}}\ \mathrm{S_B}\underset{\xleftarrow[91.8^\circ\mathrm{C}]{}}{\xrightarrow{92.8^\circ\mathrm{C}}}\ \mathrm{S_A}\underset{\xleftarrow[118^\circ\mathrm{C}]{}}{\xrightarrow{119^\circ\mathrm{C}}}\mathrm{N}\underset{\xleftarrow[178^\circ\mathrm{C}]{}}{\xrightarrow{178.8^\circ\mathrm{C}}}\mathrm{Iso}$$

and

HH53

$$\begin{tikzcd}
 & \mathrm{K} \arrow[r, "67.8^\circ\mathrm{C}"] & \mathrm{N} \arrow[r, "154^\circ\mathrm{C}"] \arrow[dl, "55^\circ\mathrm{C}"] & \mathrm{Iso} \arrow[dl, "153.2^\circ\mathrm{C}"] \\
\mathrm{S_B} & \mathrm{S_A} \arrow[l, "43^\circ\mathrm{C}"'] & &
\end{tikzcd}$$

The samples were cooled till 35°C. At 39°C the mesogen HP53 underwent a transition from S_B phase to the crystalline phase. No such observation was noticed for HH53, which maintained its S_B phase till 35°C. In case of HD35 however, the isotropic – nematic transition temperature during cooling was found to occur at 188°C, which is in agreement with the result obtained from DSC measurements [1].

Refractive Index and Order Parameter

The refractive indices and polarisabilities of HP53, HH53 and HD35 are tabulated in Tables 1, 2 & 3 respectively. Figures 1(a), 2(a) & 3(a) depict the variation of the refractive indices n_e and n_o with temperature for compounds HP53, HH53 and HD35. $\bar{n} = \sqrt{(n_e^2 + 2n_o^2)/3}$ is seen to be virtually independent of temperature and is continuous at T_{NI} for HP53. This is commonly indicative of a strong antiparallel ordering of molecules commonly found in cynosystems. $\bar{n}$ for both HH53 & HD35 increases slightly as T_{NI} is approached and shows no significant discontinuity with the n_{iso} value just after the completion of nematic–isotropic The refractive indices are higher for HP53 compared to the values for HH53. The value of $\Delta n = 0.131$ (at 120°C) for HP53 at the start of the nematic phase agrees well with the quoted values of 0.137 at 20°C ($\lambda = 598\,nm$) by Merck Ltd. The value of Δn for HH53 at 55°C (at the commencement of the nematic phase) is 0.083, the quoted value being $\Delta n = 0.097$ at 20°C ($\lambda = 598\,nm$) by Merck Ltd. The lowering of the anisotropy value in HH53 in comparison to the value for HP53 when the benzene ring is replaced by a cyclohexane is expected; the benzene ring being more polarisable (in the plane of the ring due to delocalised π-electrons) than the cyclohexane rings. The interchanging of the terminal chains in HH53 to produce HD35 decreases the value of refractive indices as is evident from Table 2 and 3. The optical anisotropy $\Delta n = 0.113$ is however \higher at 135°C (which agrees with the quoted value of 0.11 by Merck) and drops to 0.035 at 185°C near the nematic–isotropic transition. The molecular polarisabilities (αe, αo) have been calculated using Vuk's formula [3]. Figures 1(b), 2(b) and 3(b) depict

TABLE 1 Refractive Indices and Polarisabilities of HP53 in the Nematic Phase

Temp °C	n_o	n_e	$\alpha_0 \times 10^{-23}\,cm^3$	$\alpha_e \times 10^{-23}\,cm^3$
120	1.529 (4)	1.660 (4)	3.90 (6)	5.12 (7)
125	1.529 (4)	1.660 (4)	3.91 (6)	5.13 (7)
130	1.529 (4)	1.660 (4)	3.94 (6)	5.17 (7)
135	1.538 (4)	1.660 (4)	4.02 (6)	5.17 (7)
140	1.538 (4)	1.660 (4)	4.04 (6)	5.20 (7)
145	1.538 (4)	1.660 (4)	4.03 (6)	5.18 (7)
150	1.538 (4)	1.660 (4)	4.05 (6)	5.21 (7)
155	1.538 (4)	1.660 (4)	4.07 (6)	5.23 (7)
160	1.538 (4)	1.643 (4)	4.11 (6)	5.12 (7)
165	1.546 (4)	1.635 (4)	4.19 (6)	5.04 (7)
170	1.558 (4)	1.609 (4)	4.33 (6)	4.83 (7)
175	1.567 (4)	1.601 (4)	4.42 (6)	4.75 (7)

TABLE 2 Refractive Indices and Polarisabilities of HH53 in the Nematic Phase

Temp °C	n_o	n_e	$\alpha_0 \times 10^{-23}$ cm^3	$\alpha_e \times 10^{-23}$ cm^3
55	1.406 (4)	1.488 (4)	3.03 (4)	3.77 (3)
60	1.406 (4)	1.488 (4)	3.07 (4)	3.83 (3)
65	1.406 (4)	1.483 (4)	3.11 (4)	3.81 (3)
70	1.406 (4)	1.483 (4)	3.14 (4)	3.85 (3)
75	1.406 (4)	1.483 (4)	3.15 (4)	3.87 (3)
80	1.406 (4)	1.483 (4)	3.16 (4)	3.89 (3)
85	1.406 (4)	1.483 (4)	3.18 (4)	3.90 (3)
90	1.406 (4)	1.483 (4)	3.19 (4)	3.91 (3)
95	1.411 (4)	1.480 (4)	3.24 (4)	3.89 (3)
100	1.411 (4)	1.480 (4)	3.26 (4)	3.92 (3)
105	1.411 (4)	1.480 (4)	3.28 (4)	3.94 (3)
110	1.411 (4)	1.480 (4)	3.28 (4)	3.94 (3)
115	1.413 (4)	1.478 (4)	3.31 (4)	3.93 (3)
120	1.413 (4)	1.478 (4)	3.35 (4)	3.98 (3)
125	1.413 (4)	1.478 (4)	3.36 (4)	3.99 (3)
130	1.415 (4)	1.477 (4)	3.39 (4)	4.00 (3)
135	1.415 (4)	1.477 (4)	3.41 (4)	4.02 (3)
140	1.418 (4)	1.472 (4)	3.46 (4)	4.00 (3)
145	1.420 (4)	1.469 (4)	3.50 (4)	3.99 (3)
150	1.426 (4)	1.464 (4)	3.55 (4)	3.93 (3)

the variations of polarisability of HP53, HH53 and HD35 with temperature. The order parameters $\langle P_2 \rangle$ were calculated using the relation $\langle P_2 \rangle = (\alpha e - \alpha o)/(\alpha_{||} - \alpha_{\perp})$ [4] where $\alpha_{||}$ and $\alpha_{\perp}$ are the polarisabilities parallel and perpendicular to the long axis and have been obtained using Haller's [5] extrapolation procedure. Variation of $\langle P_2 \rangle$ with temperature

TABLE 3 Refractive Indices and Polarisibilities of HD35 in the Nematic Phase

Temp °C	n_o	n_e	$\alpha_0 \times 10^{-23}$ cm^3	$\alpha_e \times 10^{-23}$ cm^3
135	1.302 (5)	1.415 (5)	1.81 (3)	2.60 (4)
140	1.302 (5)	1.412 (5)	1.81 (3)	2.58 (4)
145	1.305 (5)	1.408 (5)	1.83 (3)	2.56 (4)
150	1.312 (5)	1.405 (5)	1.88 (3)	2.54 (4)
155	1.322 (5)	1.402 (5)	1.94 (3)	2.51 (4)
160	1.322 (5)	1.402 (5)	1.95 (3)	2.52 (4)
165	1.332 (5)	1.398 (5)	2.03 (3)	2.50 (4)
170	1.339 (5)	1.398 (5)	2.07 (3)	2.50 (4)
175	1.349 (5)	1.395 (5)	2.14 (3)	2.47 (4)
180	1.349 (5)	1.395 (5)	2.15 (3)	2.48 (4)
185	1.355 (5)	1.388 (5)	2.19 (3)	2.44 (4)

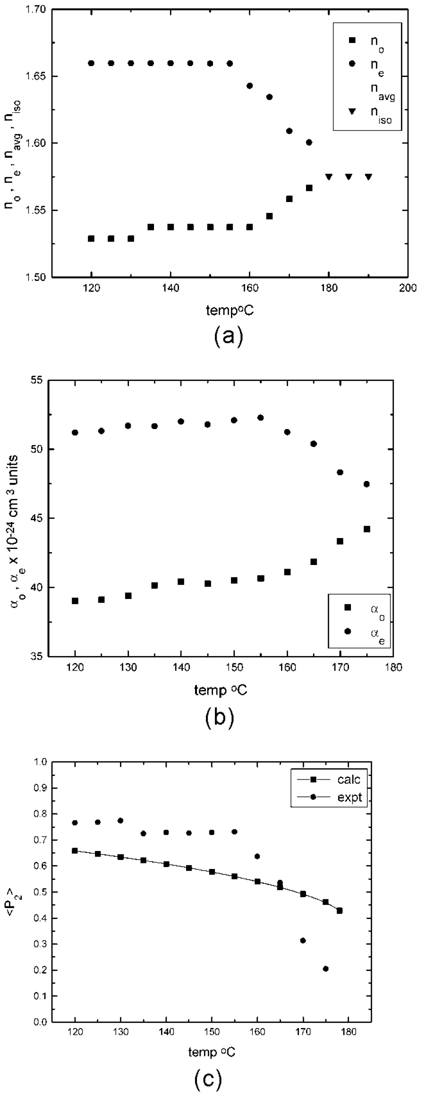


FIGURE 1 Variation with temperature of (a) refractive indices (b) polarisabilities (c) order parameter of HP53.

for three mesogens along with the theoretically calculated Maier–Saupe $\langle P_2 \rangle_{MS}$ values have been depicted in Figure 1(c), 2(c) and 3(c). The order parameter values for HP53 are higher than the theoretical values but drops more sharply in the high temperature region as the nematic-isotropic

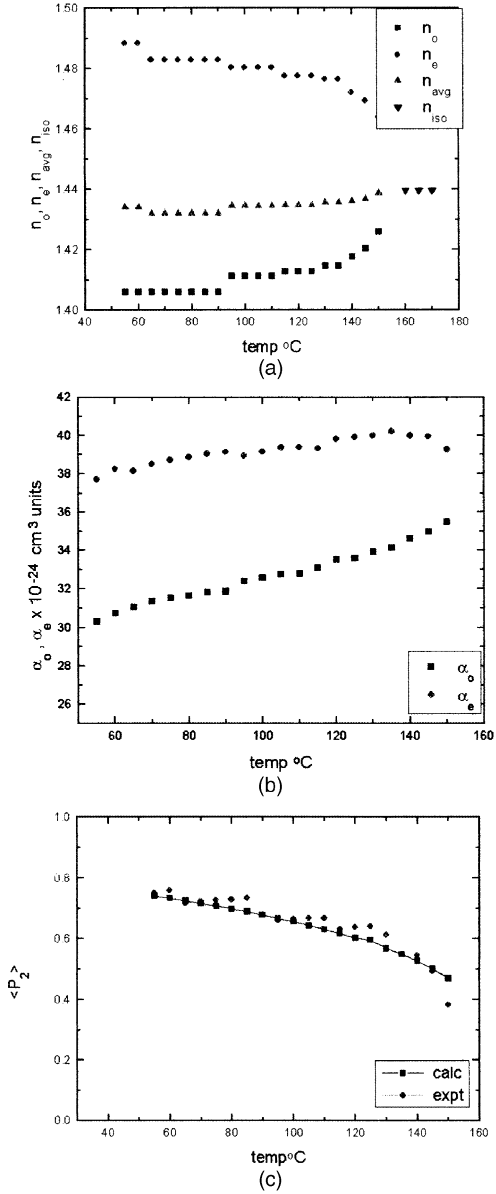


FIGURE 2 Variation with temperature of (a) refractive indices (b) polarisabilities (c) order parameter of HH53.

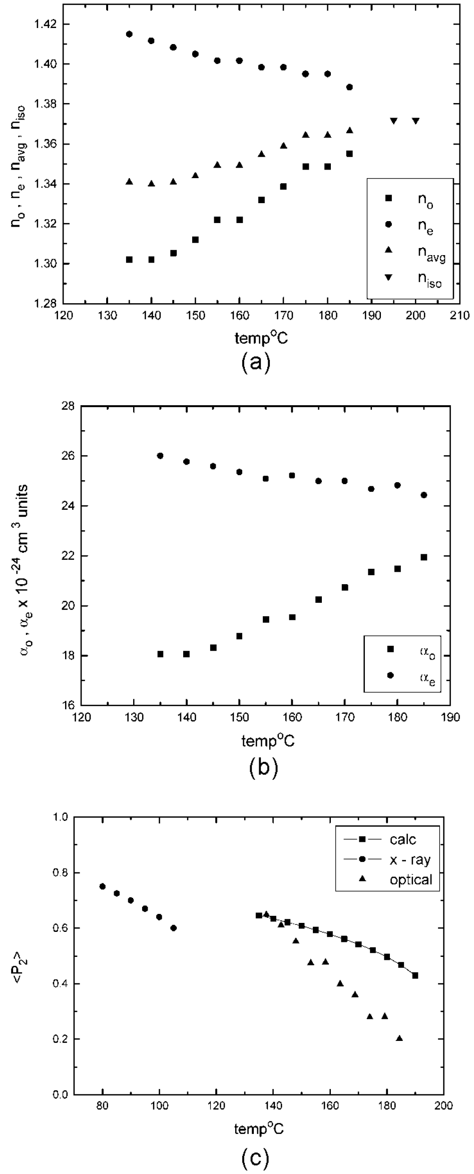


FIGURE 3 Variation with temperature of (a) refractive indices (b) polarisabilities (c) order parameter of HD35.

transition is approached. In fact the temperature variation of $\langle P_2 \rangle$ for HP53 exhibits two definite trends; one depicting a very gradual variation with temperature up to 160°C and another immediately after 160°C when the fall is much sharper than the predicted nature. At this juncture we are unable to comment on this particular nature of variation. In contradistinction the order parameter values for HH53 are in very good agreement with theoretically predicted Maier–Saupe values and are higher than the $\langle P_2 \rangle$ values of HP53. Srinivasa *et al.*[6] have conducted birefringence studies using an Abbe refractometer and determined order parameter values of HH53 at $\lambda = 4358Å$. In the nematic phase $\langle P_2 \rangle$ values of HP53 are higher than those of HH53. We have mentioned that in HP53 the optical anisotropy and T_{NI} is higher than in HH53. For higher nematic–isotropic transition temperature leading to higher thermal stability, optical anisotropy plays a dominant role and overtakes the role played by cylindrical symmetry – the discrepancy increasing with increasing temperature. This may be a plausible explanation as to why the order parameter of HP53 plunges to low values in sharp disagreement with the theoretical Maier – Saupe $\langle P_2 \rangle_{MS}$ values where assumption of cylindrical symmetry is one of the main features of Maier – Saupe theory.

The order parameter $\langle P_2 \rangle_{opt}$ from birefringence studies for HD35 is depicted in fig 2(c) and is seen to vary from 0.8 at 50°C to 0.4 at 150°C. The variation of $\langle P_2 \rangle$ in SmecticB phase obtained from X-ray study [1] has been included in the fig. $\langle P_2 \rangle$ in SmB phase drops from 0.75 at 80°C to 0.53 at 115°C as smecticB–nematic transition approached. A discontinuity is observed in the $\langle P_2 \rangle$value in the region immediately prior to the smecticB – nematic phase transition and at 130°C when the transition to the nematic phase is complete. $\langle P_2 \rangle_{opt}$ at 135°C is $\sim$0.7 which is higher than the value of $\langle P_2 \rangle_{X\text{-}ray}$ at 115°C in the smecticB phase prior to smecticB – nematic transition. At the commencement of the nematic phase the $\langle P_2 \rangle_{opt}$ values are in good agreement with $\langle P_2 \rangle_{MS}$ values. However the drop in $\langle P_2 \rangle_{opt}$ value is much faster than that predicted by Maier–Saupe theory and is 0.2 near the clearing temperature. This is probably due to the predominant effect of thermal vibration at this high temperature counteracting the effect of ordering. The main distinguishing feature in the nature of variation of $\langle P_2 \rangle_{opt}$ between HD35 and HH53 is that$\langle P_2 \rangle_{opt}$ for HD35 falls steeply contrary to the trend predicted by Maier – Saupe theory where as for HH53 the variation of$\langle P_2 \rangle_{opt}$ is in close agreement with Maier – Saupe values corroborating the explanation given above that for compounds with lower nematic–isotropic transition temperature i.e., lower thermal stability, the effect of cylindrical symmetry is more dominant than for compounds of higher thermal stability as in HD35.

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