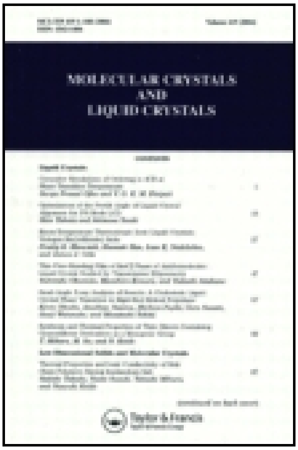

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Kanishka Bhowmick [a] & Anuradha Mukhopadhyay [a]

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

Version of record first published: 22 Sep 2010

To cite this article: Kanishka Bhowmick & Anuradha Mukhopadhyay (2007): Dielectric Behavior of Three Structurally Related Mesogens, Molecular Crystals and Liquid Crystals, 473:1, 31-42

To link to this article: http://dx.doi.org/10.1080/15421400701613482

Mol. Cryst. Liq. Cryst., Vol. 473, pp. 31–42, 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701613482

Dielectric Behavior of Three Structurally Related Mesogens

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

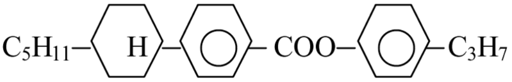
The dielectric properties of three structurally related mesogenic compounds [4′-n-propyl phenyl-4-(4′-n-pentyl cyclohexyl) benzoate (code name HP53), trans-4-propyl cyclohexyl-4-(trans-4-pentyl cyclohexyl) benzoate (code name HH53), and 4-pentyl cyclohexyl-4-(4-propyl cyclohexyl) benzoate (code name HD35)] have been studied as a function of temperature, and their effective molecular dipole moments were determined. The effect of the operating frequency on the dielectric properties has been investigated and the thermal variation of the effective molecular dipole moment μ in the mesophase studied. The dependence of β, the angle of inclination of the dipole axis with the preferred direction on temperature, has been investigated.

Keywords: dielectric permittivity; effective molecular dipole moment; mesogens; thermotropic

INTRODUCTION

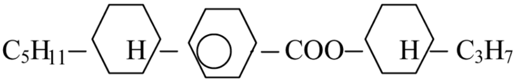
The mesogenic compounds 4′-n-propyl phenyl-4-(4′-n-pentyl cyclohexyl) benzoate (code name HP53), trans-4-propyl cyclohexyl-4-(trans-4-pentyl cyclohexyl) benzoate (code name HH53), and 4-pentyl cyclohexyl-4-(4-propyl cyclohexyl) benzoate (code name HD35) have very similar molecular structures, as evident from their structural formulae.

HP53, molecular formula $C_{27}H_{36}O_2$:

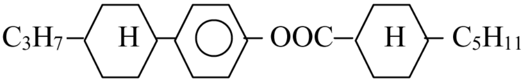


Address correspondence to Anuradha Mukhopadhyay, Department of Physics, Jadavpur University, Kolkata 700032, India. E-mail: anuradha_mukhopadhyay@yahoo.com

HH53, molecular formula $C_{27}H_{42}O_2$:



HD35, molecular formula $C_{27}H_{42}O_2$ (same as in HH53):



The benzene ring in HP53 is replaced by a cyclohexane ring to yield HH53, and an interchange of terminal groups C_nH_{2n+1} in HH53 yield HD35. The compounds exhibit the following mesophases and have the phase-transition temperatures (supplied by Merck Ltd.) given in Table 1.

The smectic 1 and smectic 2 phases of HD35 have been identified by Mukhopadhyay *et al.* [1] to be smectic E and smectic B phases, respectively. Optical studies have been conducted on the three compounds (HP53, HH53, and HD35) and their orientational order parameters determined as a function of temperature [2]. Molecular modeling [3] and X-ray studies [1] have been conducted on HD35. From X-ray photographs, orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been calculated in the smectic 2 range for HD35. From routine texture studies conducted prior to the optical and dielectric studies [1], the observed phase-transition temperatures are found to be in conformity with the quoted values (for HP53 and HH53):

HP53

$$\mathrm{Cryst}\ \underset{39^{\circ}\mathrm{C}}{\overset{67^{\circ}\mathrm{C}}{\rightleftarrows}}\ \mathrm{SmecticB}\ \underset{91.8^{\circ}\mathrm{C}}{\overset{92.8^{\circ}\mathrm{C}}{\rightleftarrows}}\ \mathrm{SmecticA}\ \underset{118^{\circ}\mathrm{C}}{\overset{119^{\circ}\mathrm{C}}{\rightleftarrows}}\ \mathrm{Nematic}\ \underset{178^{\circ}\mathrm{C}}{\overset{178.8^{\circ}\mathrm{C}}{\rightleftarrows}}\ \mathrm{Iso}$$

TABLE 1 Phase Transitions of HP53, HH53 and HD35

Property	HP53	HH53	HD35
Melting point	69°C	67°C	42°C
$S_B \rightarrow S_A$	93°C	43°C	72°C
$S_A \rightarrow N$	119°C	55°C	128°C
Clearing point	179°C	155°C	193°C

HH53

$$\text{Cryst} \xrightarrow{67.8^{\circ}\text{C}} \text{Nematic} \xrightarrow{154^{\circ}\text{C}} \text{Iso}$$
$$\text{SmecticB} \xleftarrow[43^{\circ}\text{C}]{} \text{SmecticA} \xleftarrow[55^{\circ}\text{C}]{} \qquad\qquad \xleftarrow[153.2^{\circ}\text{C}]{}$$

HD35

$$\text{Cryst} \xrightarrow{42^{\circ}\text{C}} \text{Smectic1} \xrightarrow{72.4^{\circ}\text{C}} \text{Smectic2} \xrightarrow{126.7^{\circ}\text{C}} \text{Nematic} \xrightarrow{193^{\circ}\text{C}} \text{Iso}$$
$$\xleftarrow[38^{\circ}\text{C}]{} \qquad \xleftarrow[63.4^{\circ}\text{C}]{} \qquad \xleftarrow[120.8^{\circ}\text{C}]{} \qquad \xleftarrow[188.2^{\circ}\text{C}]{}$$

In the case of HD35, each of the states passes through a supercooled state during cooling, and the isotropic →nematic transition takes place at a lower temperature of 188°C. This observation is supported by DSC measurements [1]. Srinivasa *et al.* [4] and Shashidhara Prasad *et al.* [5] have conducted birefringence studies and determined order parameter of HH53 at $\lambda = 4358\,\text{Å}$. No systematic studies of the dielectric properties of the three samples have been carried out to date; the molecular dipole moments in the liquid-crystalline state have also not been determined.

EXPERIMENTAL METHODS

A pair of Indium Tin Oxide (ITO)-coated conducting glass plates separated by thin cover slips on three sides was used to form the sample cell (capacitor). The effective sample cell size is of the order of $4.0\,\text{cm} \times 2.5\,\text{cm} \times 0.05\,\text{cm}$, and its capacitance (air) is 21 pF (approximately). Each cell was calibrated using standard liquid (p-xylene) with the help of a LCR meter (6471 Forbes Tinsley). The sample was introduced into the cell as an isotropic liquid, and the open end was sealed. It was then placed in a sample holder whose temperature can be regulated (±1°C) using a temperature controller. The sample was taken through a number of temperature cycles in the presence of a magnetic field of approximately 10 kGauss to get an aligned monodomain sample. The sample was then heated to more than isotropic temperature at the rate of 1°C per min and cooled to the desired temperature at the same average rate in the presence of the magnetic field (~10 kGauss). Readings for the parallel and perpendicular components of capacitance were taken at regular temperature intervals during cooling at frequencies of 1, 10, and 100 kHz. It is the normal practice to keep the frequency low (*i.e.*, 1–10 kHz); other frequencies have been considered to study the effect of operating frequency on the dielectric permittivity. The values of the parallel and perpendicular components of dielectric permittivity were obtained from the capacitance values by standard procedure. The bridge voltage across the sample was maintained sufficiently low (0.3 V) so as not to produce any electric field–induced instabilities.

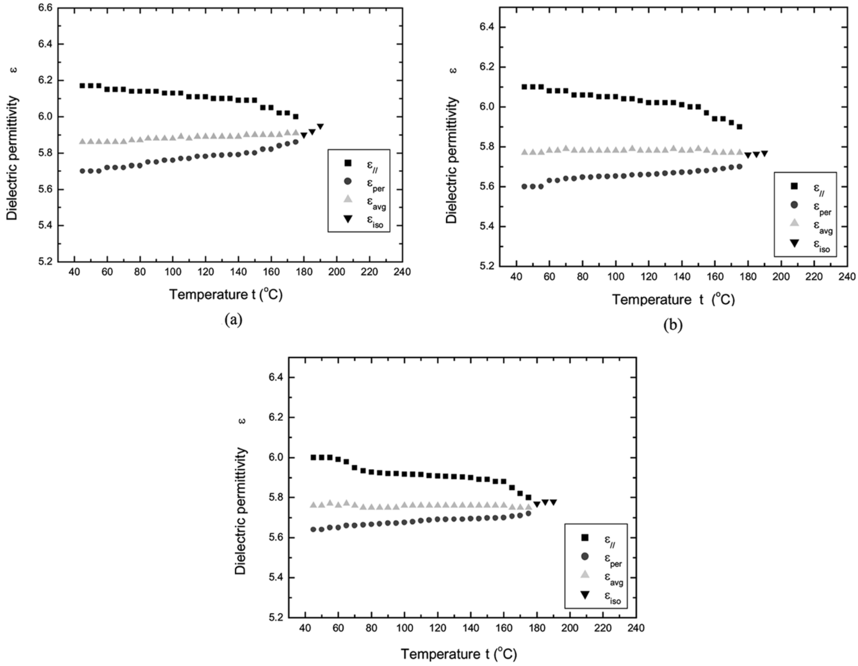
From results of dielectric studies, μ and β have been calculated using the values of polarizability and order parameter from our optical studies [2].

RESULTS AND DISCUSSION

Dielectric Permittivity

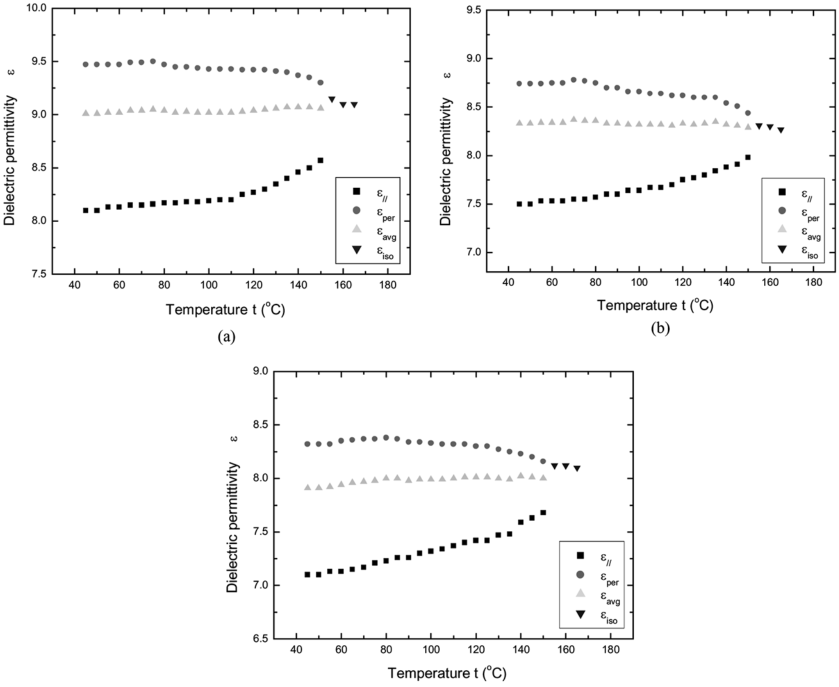
The variation of $\varepsilon_{||}$ and $\varepsilon_{\perp}$ with temperature at frequencies of 1, 10, and 100 kHz for the three compounds HP53, HH53, and HD35 are depicted in Figs. 1a–c, 2a–c, and 3a–c, respectively.

With increasing frequency, the dielectric permittivity decreases; ε_{ave} has values of 5.88, 5.78, and 5.75 at 1, 10, and 100 kHz frequencies respectively at 100°C for HP53. Corresponding values for HH53 and



(a) (b) (c)

FIGURE 1 Variation of dielectric permittivity with temperature for HP53 at (a) 1 kHz, (b) 10 kHz, and (c) 100 kHz.



(a)

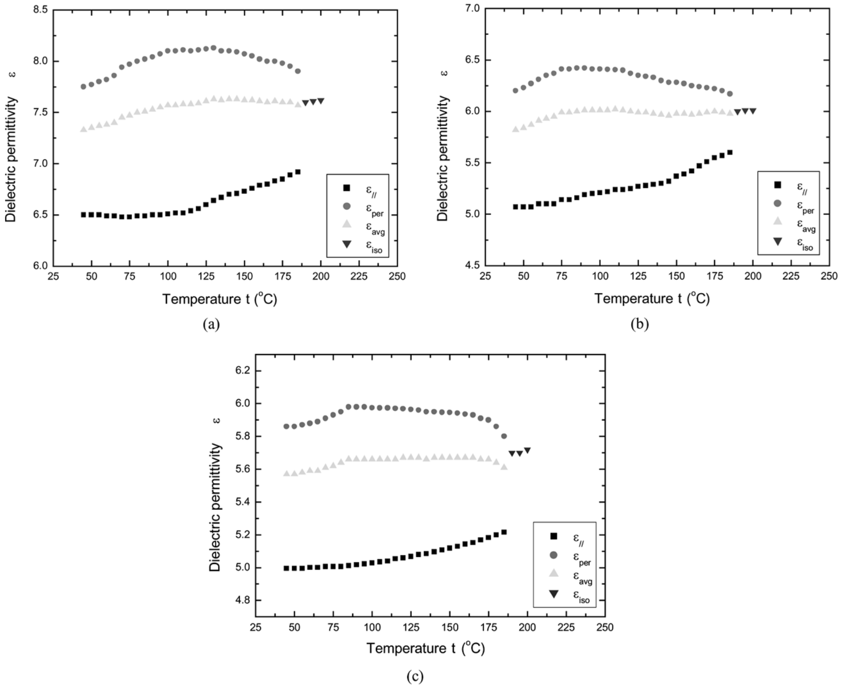
(b)

(c)

FIGURE 2 Variation of dielectric permittivity with temperature for HH53 at (a) 1 kHz, (b) 10 kHz, and (c) 100 kHz.

HD35 are 9.02, 8.32, 7.99 and 7.57, 6.01, 5.66 respectively at 100°C. The percentage decrease of ε_{ave} for HP53 is less than 2% of the initial value for an increase in operating frequency from 1 to 10 kHz and slightly greater than 2% for a change in operating frequency from 1 to 100 kHz. The corresponding values for HH53 are 7% and 11% and for HD35, 20% and 25%. The decrease in ε, attributed to dielectric loss (the effect of other parasitic phenomena being cancelled out during the process of standardization of the cell) is greater for HH53 than for HP53. However, the effect is much greater in the case of HD35.

It is observed that $\varepsilon_{||}$ and $\varepsilon_{\perp}$ vary in an opposite manner in the nematic phase (*i.e.*, if $\varepsilon_{||}$ increases, $\varepsilon_{\perp}$ decreases and vice versa), an observation that is also supported by Bata and Buka [6]. The dielectric anisotropy $\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$ increases with decreasing temperature according to the Maier and Meier theory [7]. From our observation, $\Delta\varepsilon$ for HP53 is positive and varies from 0.47 at 45°C to 0.14 at 175°C at 1 kHz, the quoted value being 0.4 (temperature unspecified). The replacement of a benzene ring in HP53 by a cyclohexane ring in HH53 and HD35 causes a reversal in the sign of $\Delta\varepsilon$. The cyclohexane



(a) (b) (c)

FIGURE 3 Variation of dielectric permittivity with temperature for HD35 at (a) 1 kHz, (b) 10 kHz, and (c) 100 kHz.

groups have their direction of polarization transverse to the length of the molecules, and the polarization direction of the benzene ring causes an increase of $\varepsilon_\perp$ [4]. The value of $\Delta\varepsilon$ for HH53 is found to vary from -1.34 at 60°C to -0.73 at 150°C (1 kHz); the value quoted by Merck Ltd. is -1.2 at 1 kHz (temperature not specified). In case of HD35, $\Delta\varepsilon$ varies from -1.52 at 125°C to -0.98 at 185°C (1 kHz); quoted value is -1.1 at 1 kHz.

In the smectic phase, neither the permittivities nor the dielectric anisotropy have such a simple nature. If the temperature is decreased, the dipole correlation in the smectic phases increases (mostly by steps) at the phase transitions. The increasing antiparallel setting of the longitudinal components of the dipole moments decrease the value of $\varepsilon_{||}$. The value of $\varepsilon_\perp$ increases for compounds with negative dielectric anisotropy and decreases for compounds with positive $\Delta\varepsilon$ values. This observation is also corroborated by Bata and Buka [6]. The discontinuities at the smectic A and smectic B phase transitions are also present in the optical data [2].

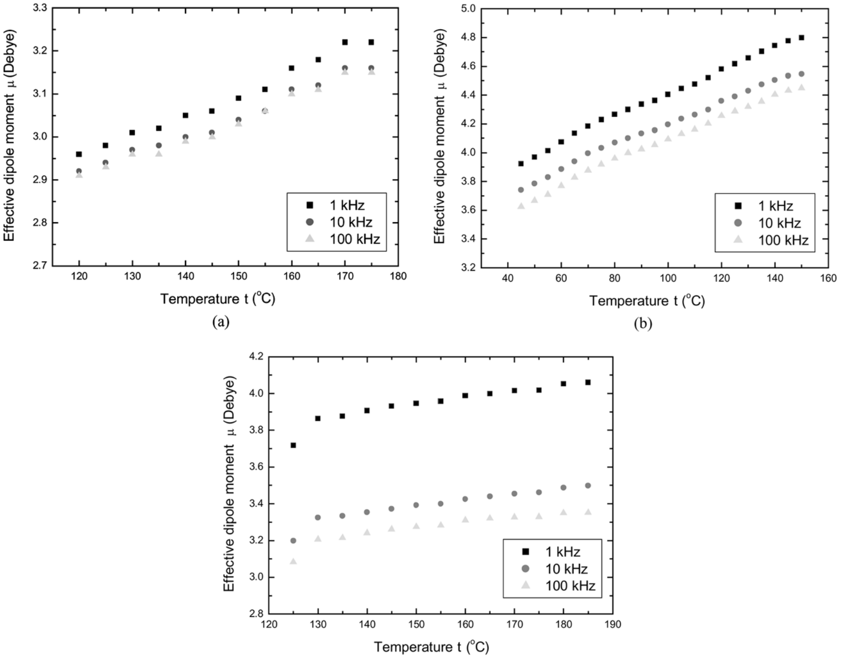
Dipole Moment

The effective dipole moment μ and the angle of inclination β have been calculated using the following relations (which have been obtained from expressions for $\varepsilon_{||}$ and $\varepsilon_{\perp}$ [7]):

$$\varepsilon_{ave} = 4\pi NhF\left(\alpha_{ave} + \frac{F\langle\mu^2\rangle}{3k_BT}\right)$$

$$\Delta\varepsilon = 4\pi NhF\left\{\Delta\alpha - \frac{F\langle\mu^2\rangle}{2k_bT}\left(1 - 3\cos^2\beta\right)\right\}\langle P_2\rangle$$

$$\varepsilon_{ave} = \frac{\varepsilon_{||} + 2\varepsilon_{\perp}}{3}, \quad \alpha_{ave} = \frac{\alpha_{||} + 2\alpha_{\perp}}{3}, \quad f = \frac{8\pi N(\varepsilon_{ave} - 1)}{3(2\varepsilon_{ave} + 1)},$$
$$h = \frac{3\varepsilon_{ave}}{2\varepsilon_{ave} + 1}, \quad F = \frac{1}{(1 - f\alpha_{ave})}$$

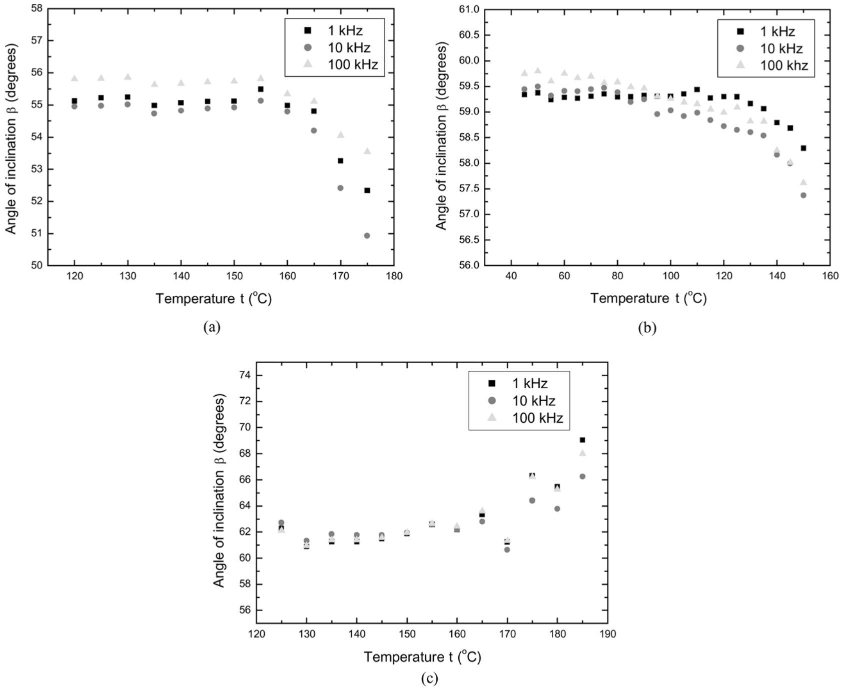


(a) (b) (c)

FIGURE 4 Variation of the dipole moment μ with temperature at frequencies of 1, 10, and 100 kHz for (a) HP53, (b) HH53, and (c) HD35.

Values of $\Delta\alpha$, α_{ave}, and orientational order parameter $\langle P_2 \rangle$ at different temperatures have been taken from our experimental findings based on birefringence data [2], which have been reproduced in Figs. 6a,b, 7a,b, and 8a,b for the sake of easy reference.

The variation of dipole moment with temperature at the three frequencies for HP53, HH53, and HD35 are presented in Figs. 4a–c. For HP53, μ varies in the nematic range from 2.96D at 120°C to 3.22D at 175°C at 1 kHz. For HH53, the variation in the nematic range (from 60°C to 150°C at 1 kHz) is 4.07 D to 4.80 D, whereas for HD35, μ varies from 3.72 D at 125°C to 4.06 D at 185°C. Evidently, the replacement of the benzene ring in HP53 by a cyclohexane ring in HH53 has increased the effective molecular dipole moment. For all the three samples, μ increases steadily with temperature at all frequencies, μ values being lowest at 1 kHz. However, the increase in μ values for an increase in operating frequency from 1 kHz to 10 kHz is more marked in the case of HD35 as compared to the other compounds.

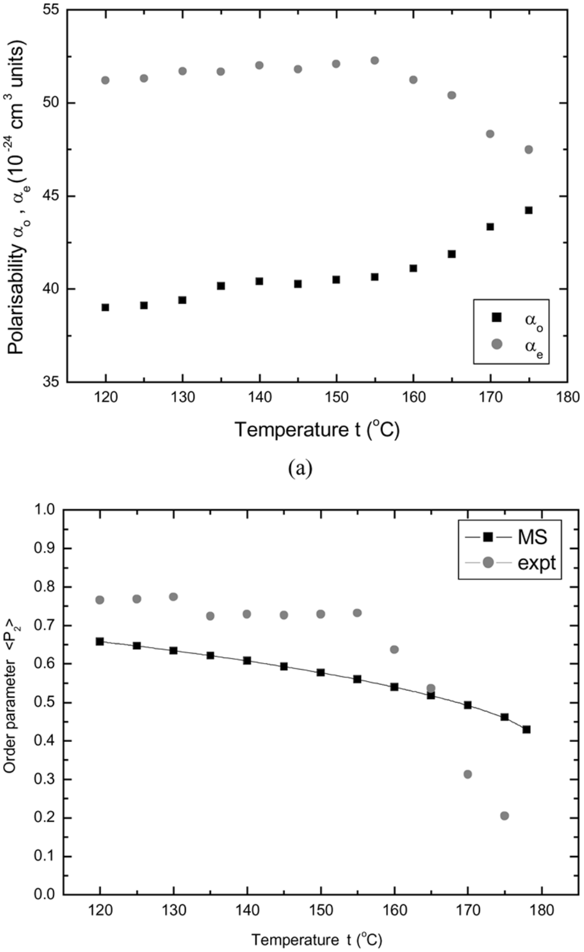


(a)

(b)

(c)

FIGURE 5 Variation of angle of inclination β with temperature at the three frequencies for (a) HP53, (b) HH53, and (c) HD35.



(a)

(b)

FIGURE 6 Variation of (a) polarizabilities with temperature for HP53 and (b) order parameter with temperature for HP53.

Angle of Inclination

The variation of the angle of inclination β with temperature at the three frequencies are shown in Figs. 5a–c. β is approximately 55° for HP53, 59° for HH53, and 62° for HD35. The nature of variation of β with temperature follows similar trends for HP53 and HH53 (*i.e.*, it remains fairly constant for a wide range of temperature and drops sharply as the nematic to isotropic temperature is approached).

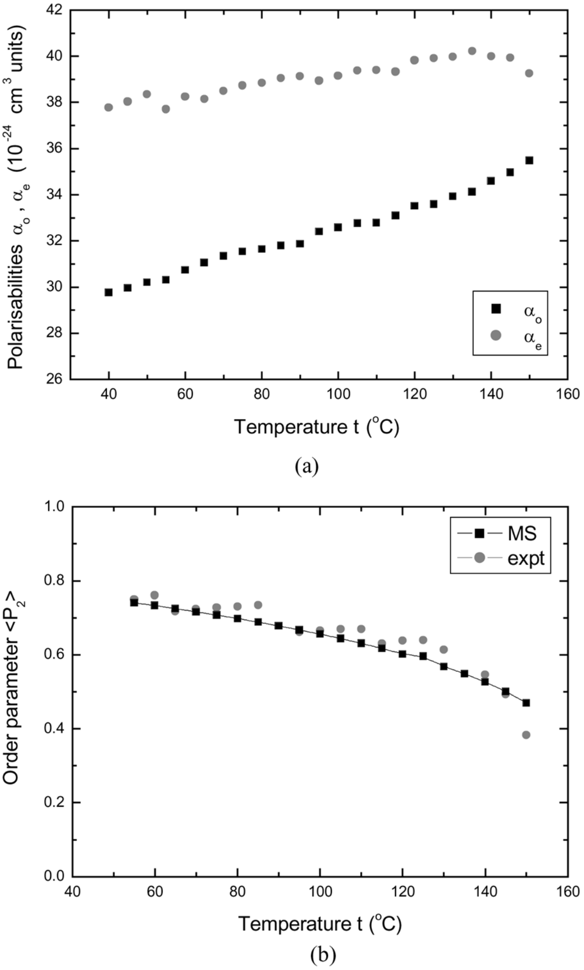
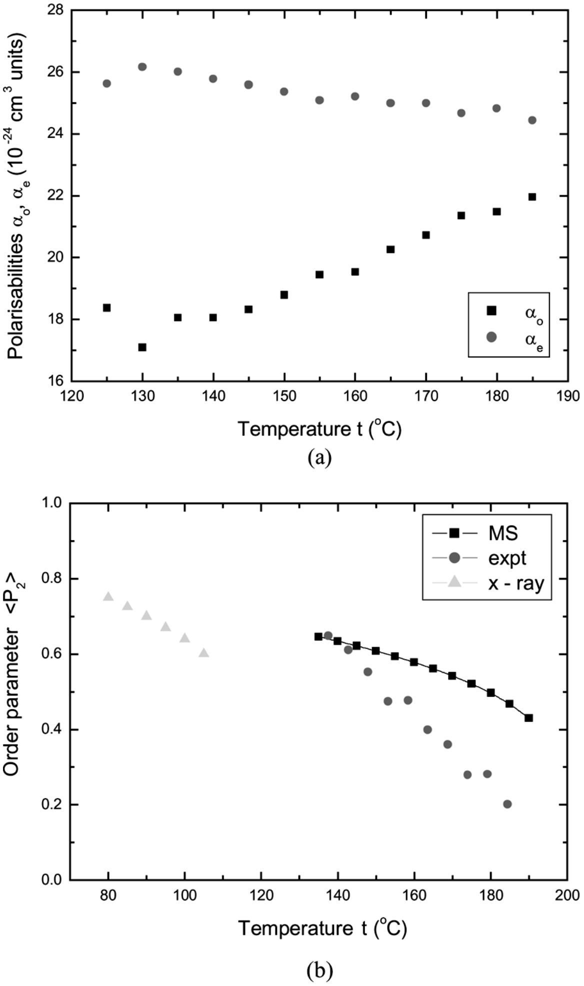


FIGURE 7 Variation of (a) polarizabilities with temperature for HH53 and (b) order parameter with temperature for HH53.

For HD35, the trend is quite the reverse. β values increase in general for all the frequencies as the temperature is raised. That HD35 behaves differently from HP53 and HH53 in its optical properties as well is corroborated in the nature of orientational order parameter $\langle P_2 \rangle$ (determined from birefringence) in the nematic range [2]; $\langle P_2 \rangle_{expt}$ matches very well with $\langle P_2 \rangle_{MS}$ (theoretical Maier Saupe [8] values) for HP53 but falls very sharply in total disagreement with theoretical Maier Saupe values for HD35. This is probably due to the predominant



(a)

(b)

FIGURE 8 Variation of (a) polarizabilities with temperature for HD35 and (b) order parameter with temperature for HD35.

effect of thermal vibration at the high clearing point temperature of 198°C, counteracting the effect of ordering.

CONCLUSION

In conclusion, the effect of replacing a benzene ring in HP53 by the more polarizable cyclohexane ring not only increases the molecular dipole moment but causes a reversal in the sign of the dielectric anisotropy. The effect of dielectric loss with increasing operating frequency is more marked in HD35, however (obtained by interchanging the terminal chains in HH53). Also, the behavior of other parameters of HD35 such as μ and $\langle P_2 \rangle$ with temperature show a trend distinctive from the other two compounds (HP53 and HH53).

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