Dielectric Studies of Three Liquid Crystals HBT, E$_8$ and PCH-1132

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The dielectric behavior of a Schiff base N-(p-Hexyloxybenzylidene)-p-toluidine (HBT) and two technologically important mixtures, E₈ and PCH-1132, are reported in the radio frequency region. The value of the mean dielectric constant increases by ~5% on going from the nematic to the isotropic phase in the case of E₈ and PCH-1132. This may perhaps be due to antiferroelectric arrangement of the molecules in the nematic phase. These mesogens show unusual dielectric behavior and exhibit positive anisotropy at lower frequencies and negative dielectric anisotropy above a critical frequency termed as isotropic frequency. The isotropic frequency is found to be temperature dependent. All these nematogens exhibit single relaxation in the radio frequency region which is due to hindered rotation of the molecules under nematic potential. The relaxation frequencies are 3.98 MHz (at 61.4°C), 2.27 MHz (at 34.3°C), 1.87 MHz (at 33°C) in case of HBT, E₈ and PCH-1132 respectively. The activation energy is found to be 16.7 KCal/mole, 14.6 KCal/mole and 16.1 KCal/mole for HBT, E₈ and PCH-1132 respectively. In smectic B phase of HBT, the dipolar orientations are found to be somewhat "locked" similar to that in solids. The inversion of the sign of dielectric anisotropy in S_B phase of HBT is also discussed.

INTRODUCTION

The recent applications of liquid crystals in various types of electro-optical devices have stimulated the investigations on dielectric behavior of liquid crystals.[1-4] The dielectric studies of liquid crystals not only provide useful information about the molecular structure, intermolecu-

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lar forces and molecular dynamics[5] but also provide useful clues related to the display performance such as threshold and operating voltages, switching times, operating and isotropic frequencies etc.[1-3] Dielectric studies are therefore important from basic as well as applied points of view. In this paper we are reporting dielectric studies on three mesogens HBT, E_8 and PCH-1132. E_8 and PCH-1132 are stable liquid crystal mixtures and are being used for liquid crystal digital displays. The dielectric studies on HBT are expected to provide some information on the smectic B phase which is not very well understood as yet.

EXPERIMENTAL

HBT was procured from M/S. E. Merck (Germany) and was further purified before use.[6] E_8 and PCH-1132 were procured respectively from M/S. BDH (England) and E. Merck (Germany) in purest form.[3] The transition temperatures and the corresponding phases were confirmed using a polarizing microscope and D.S.C. These are listed below

HBT *N*-(*p*-Hexyloxybenzylidene)-*p*-toluidine[6]

$$\text{Solid I} \xrightarrow{57.2^\circ C} \text{Nematic} \xrightleftharpoons{73.7^\circ C} \text{Isotropic}$$

$$\uparrow{\sim}39^\circ C \qquad \Big\Downarrow 52.9^\circ C$$

$$\text{Solid II} \xrightleftharpoons[\sim 46.5^\circ C]{50.1^\circ C} S_B$$
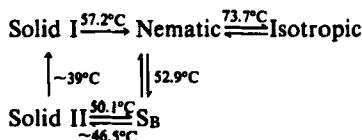
E_8 (an eutectic mixture of three cyanobiphenyls and one cyanoterphenyl)[3]

$$\text{Solid} \xrightleftharpoons{-12^\circ C} \text{Nematic} \xrightleftharpoons{70^\circ C} \text{Isotropic}$$

PCH-1132 (an eutectic mixture of three cyanophenyl cyclohexanes and one cyanobiphenyl cyclohexane).[3]

$$\text{Solid} \xrightleftharpoons{-6^\circ C} \text{Nematic} \xrightleftharpoons{70^\circ C} \text{Isotropic}$$

The dielectric permittivity (ϵ') and loss (ϵ'') of these liquid crystals (HBT, E_8 and PCH-1132) were measured using G.R. Scheering bridge 716C in frequency range 1–100 KHz and using Wayne Kerr R.F. bridge B602 along with G.R. tuned amplifier null detector 1232A and frequency mixer 1232 in frequency range 100 K–3.5 MHz. The dielectric cell was essentially a parallel plate capacitor (effective capacity ${\sim}14.5$

pF) consisting of two gold plated circular copper electrodes separated by a teflon spacer of thickness ~ 300 μm. For measuring $\epsilon'_\parallel$ and $\epsilon'_\perp$, the alignment of the liquid crystal was achieved by a uniform magnetic field of 5–6 KGauss, a field strength much above the saturation value. The temperature control of the cell was better than $\pm 0.2°C$.

The temperature variation of the effective capacity of the cell was monitored. The capacity of the cell was found to be fairly constant up to 2 MHz and hence no correction was required up to this frequency. In higher frequency side errors can arise due to small resistence and inductance (mainly contributed by long connecting leads and empty space of the cell in series with the dielectric cell. The contribution due to series resistance R_s was negligible as with our $R_s \lll 1\Omega$ and capacity ~ 200 pF (for the cell filled with E₈ or PCH-1132), $(R_s C)^{-1} \ggg 10$ MHz, the highest frequency which can be utilized with the bridge. However the contribution of the inductance L to the total impedence, which is negligible at low frequencies, becomes more and more significant at higher frequencies (i.e. above 2 MHz) and bridge balances at significantly higher values than the actual capacity of the cell. The measured value Cp is related to the actual capacity, C, by the relation

$$Cp = C\left(1 + x^2 - \frac{1}{Q^2}\right)$$

where x is ω/ω^*, $\omega^* = (LC)^{-1/2}$, $Q = R\sqrt{L/C}$ and other symbols have their usual meanings.[7] $\epsilon'_\perp$ was assumed to remain constant in the frequency range studied (i.e. up to 4 MHz) and using above relation a correction was applied to get the correct values of $\epsilon'_\parallel$.

The loss factor was evaluated by subtracting the conductance of empty cell (i.e. filled with air) from the conductance of the cell filled with liquid crystal material. This procedure thus eliminates the losses due to R_s and L.[7] However, this loss factor, measured from the actual conductance of the dielectric material, contains dielectric as well as d.c. conduction losses. The dielectric loss was evaluated by subtracting d.c. conduction loss from the total loss of the dielectric material.[5]

The absolute accuracy of dielectric constant and loss measurements using a Wayne–Kerr bridge were $\sim 2\%$ and $\sim 5\%$ respectively, while the relative accuracy was found to be much better. The accuracy of static dielectric constant measurements using Scheering bridge was still better i.e. the absolute accuracy was $\sim 1\%$ and relative accuracy was better than $\sim 0.2\%$.

RESULTS AND DISCUSSIONS

The behavior of dielectric permittivity will be discussed in two parts (i) the temperature variation of the static dielectric permittivity and (ii) the dielectric dispersion in the liquid crystals.

(I) Static permittivity studies

The static dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ in the nematic phase and ϵ_{iso} in the isotropic phase for HBT, E_8 and PCH-1132 are shown in Figures 1–3 respectively. ϵ in the isotropic phase increases with decrease in temperature in all the three mesogens which is in fact a normal behavior of an organic substance. At the isotropic–nematic transition temperature, isotropy of the material vanishes and anisotropy sets in discontinuously in accordance with a first-order transition. In the nematic phase, in all the three materials, $\epsilon_{\parallel}$ is greater than $\epsilon_{\perp}$ indicating positive dielectric anisotropy. The dielectric anisotropy in HBT is
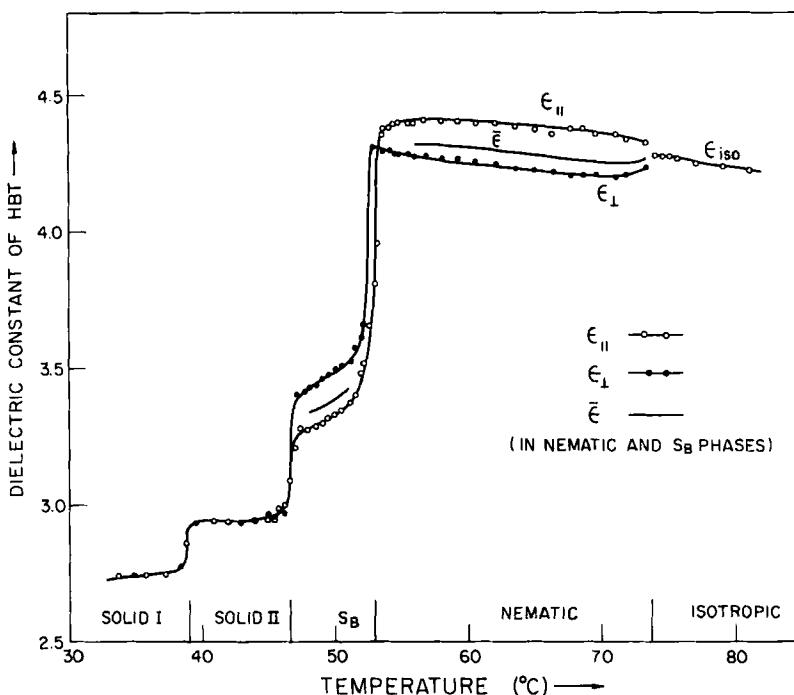
FIGURE 1   Temperature variation of the components of the dielectric permittivity ($\epsilon_{\parallel}$, $\epsilon_{\perp}$) of HBT in isotropic, nematic, S_B and solid phases at 10 KHz.
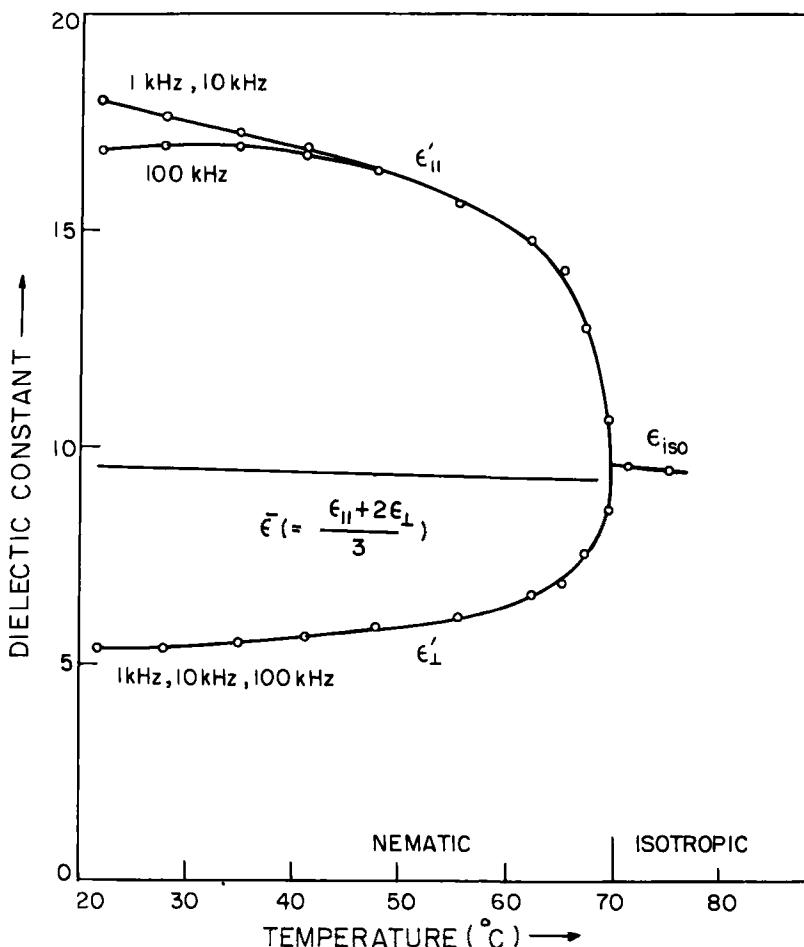
FIGURE 2 Temperature variation of the components of the dielectric permittivity ($\epsilon_\parallel$, $\epsilon_\perp$) of E$_8$ in the nematic and isotropic phases.

small ($\sim$0.15 in entire temperature range) whereas it is large in the case of E$_8$ and PCH-1132 (it is about 7 for both E$_8$ and PCH-1132 at $T - T_c = 5°$). The cause of high dielectric anisotropy of E$_8$ and PCH-1132 is the presence of a cyano end group on the para position of the benzene ring. Our room temperature values of $\epsilon_\parallel$, $\epsilon_\perp$ and $\Delta\epsilon$ of E$_8$ and PCH-1132 are in good agreement with those reported by M/s. BDH and E. Merck.[3]

The dielectric anisotropy was found to increase with decreasing temperature in nematic phase of E$_8$ and PCH-1132 while it was found
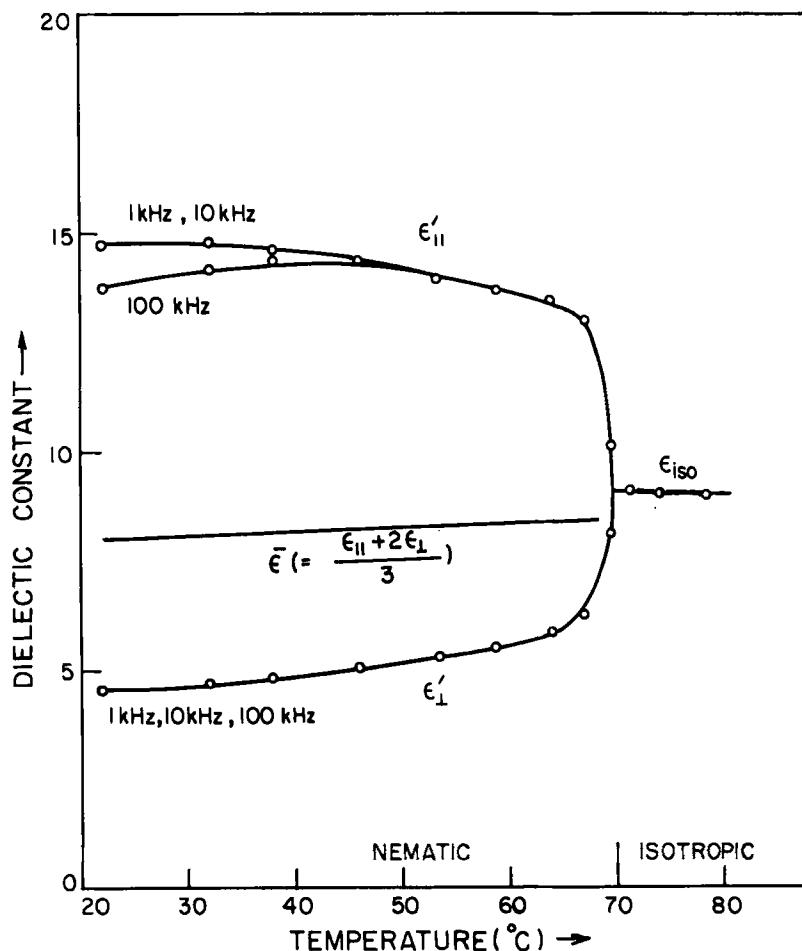
FIGURE 3   Temperature variation of components of the dielectric permittivity ($\epsilon_\parallel$, $\epsilon_\perp$) of PCH-1132 in the nematic and isotropic phases.

to be almost constant in the entire nematic range of HBT. The behavior of dielectric anisotropy with change in temperature in HBT, E$_8$ and PCH-1132 can be explained on the basis of Maier–Meier theory[8] which yield that

$$\Delta\epsilon = NhF\left\{\Delta\alpha + \frac{F\mu^2}{2kT}\,(3\cos^2\beta - 1)\right\}S$$

where the symbols have their usual meanings. $\Delta\alpha$ is generally positive and arises mainly due to anisotropy of benzene rings. A material can

be of high positive dielectric anisotropy if the dipolar contribution $(F\mu^2/2kT)(3\cos^2\beta - 1)$ is large and positive. For materials of negative dielectric anisotropy or very small positive dielectric anisotropy this term is negative. In case of PCH-1132 and E₈, which have high positive $\Delta\epsilon$, the S/T dependence of dipole contribution to $\Delta\epsilon$ is predominant and is additive to $S\Delta\alpha$. Consequently $\Delta\epsilon$ increases with decreasing temperature. On the other hand in HBT, where $\Delta\epsilon = \sim 0.15$, the anisotropy of induced polarization is approximately equal to that of orientational polarization. Just below nematic–isotropic temperature, the temperature dependence of S is most important and increases with decreasing temperature. At lower temperature, the counteracting S/T dependence of the orientational polarization predominates and hence we get almost constant $\Delta\epsilon$.

Another observation of importance is that the value of the mean dielectric constant increases by ~5% on going from nematic to isotropic phase in case of E₈ and PCH-1132 (Figures 2 and 3). This difference in ϵ_{iso} and $\bar{\epsilon}(\epsilon = [\epsilon_{\parallel} + 2\epsilon_{\perp}]/3$ in nematic phase) at T_{NI}, nematic–isotropic transition temperature, in highly polar E₈ and PCH-1132 may be due to antiferroelectric short range order of the molecules in the nematic phase as proposed by Chandrasekhar et al.[9] A similar trend is observed in case of HBT too but the difference in $\bar{\epsilon}$ at T_{N-I} and ϵ_{iso} is very small which is due to weak polarity of HBT.

We will now discuss the temperature variation of dielectric permittivity in the smectic B phase of HBT. The observations were recorded on a sample cooled to S₈ phase in the presence of magnetic field (~6–8 KG). From the Figure 1 it is clear that values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ both fall rapidly on cooling from nematic to S₈ phase, the decrease being more in $\epsilon_{\parallel}$ compared to $\epsilon_{\perp}$. One can easily observe that $\bar{\epsilon}$ in S₈ phase of HBT is considerably less than that of nematic and isotropic phases. This indicates that dipolar orientations in S₈ phase are not free as in liquids but are somewhat "locked" similar to that in the solids. Moreover, the temperature variation of $\bar{\epsilon}$ in S₈ phase resembles to that of solid phase. A partial contribution to this decrease in the value of $\bar{\epsilon}$ in S₈ phase compared to nematic phase may be attributed to the increase in the number of pairs of antiparallel oriented dipoles in S₈ phase than nematic phase. However, the change in $\bar{\epsilon}$ is very large (~25%) and cannot be accounted only by this. On going to the solid state, a further decrease in $\bar{\epsilon}$ is observed at S₈–solid II transition which may be due to further locking of the permanent dipoles. A small decrease in ϵ is observed during solid II to solid I transition. In solid I phase ϵ decreases with decrease in temperature which is the normal behavior of solids.

During nematic to smectic B transition of HBT, the $\Delta\epsilon$ exhibits an inversion of sign i.e. $\Delta\epsilon$ is positive in nematic phase while it is negative in the S_B phase. Similar behavior of $\Delta\epsilon$ during nematic–smectic transition has been reported by de Jeu et al.[4,10]

There are two main factors which govern the nature of the dielectric anisotropy. The first is the polarizability anisotropy $\Delta\alpha$ which is approximately proportional to Δn and the other is the dipolar contribution. In the case of HBT too, Δn (and hence $\Delta\alpha$) exhibits normal behavior i.e. it increases in the S_B phase.[11] So it seems that it is the dipolar part which is responsible for such an anomaly. For a central polar molecule in a smectic phase the distance between the dipoles of molecules in different smectic layers is much larger than the distance between the neighboring dipoles in the same layer.[10] This leads to an increased antiparallel coorelation between the dipole components along the preferred axis. Hence the effective dipole moment in pre-
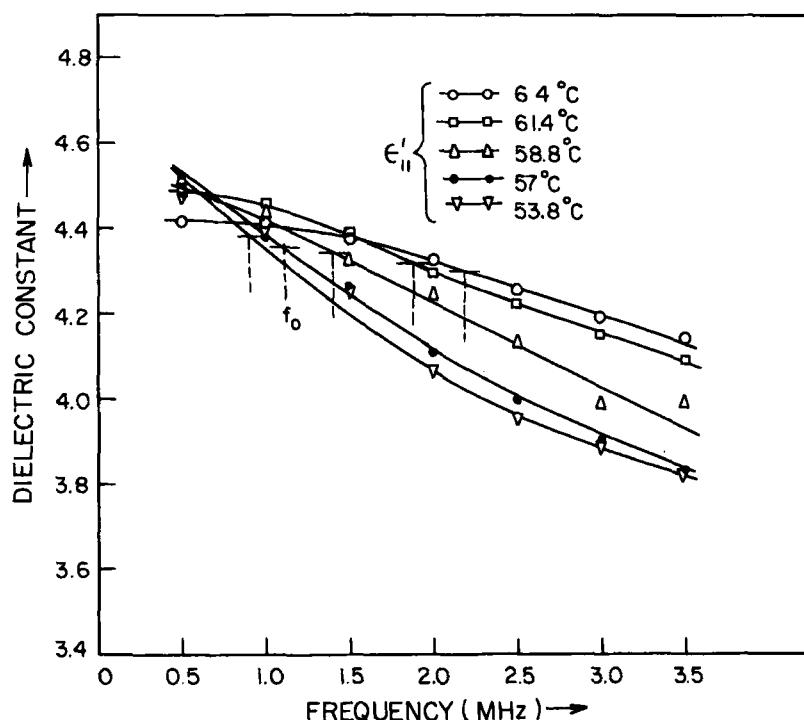
FIGURE 4   Variation of the parallel components of dielectric permittivity, $\epsilon'_{\parallel}$ of liquid crystal HBT as a function of frequency at various temperatures. ϵ'_i(——) cuts the $\epsilon'_{\parallel}$ curve at isotropic frequency, f_0.
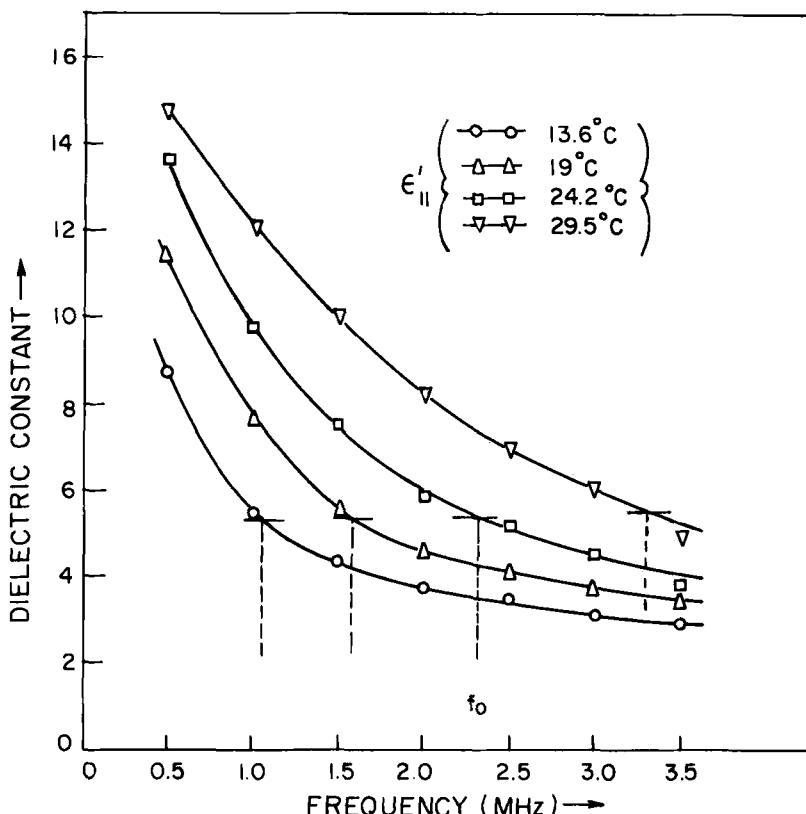
FIGURE 5   Variation of the parallel components of dielectric permittivity, $\epsilon'_{\parallel}$, of liquid crystal E$_8$ as a function of frequency at various temperatures. $\epsilon'_{\perp}$(——) cuts the $\epsilon'_{\parallel}$ curve at isotropic frequency, f_0.

ferred direction is reduced and that in a direction perpendicular to the preferred axis is enhanced, thus resulting in a decrease in $\epsilon_{\parallel}$ and increase in $\epsilon_{\perp}$. If these changes are prominent, it may also change the sign of dielectric anisotropy. In nematic phase the dipole–dipole interactions are almost smeared out as a result of uniform density of the molecules and effect is much less important than that in smectic phase. However, in our case the two effects i.e. the locking of permanent dipoles and dipolar correlation in S$_B$ phase of HBT should be examined jointly. Due to restricted motion or locking of permanent dipoles in S$_B$ phase, $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ both fall and we get lower value of $\bar{\epsilon}$ in S$_B$ phase compared to that in nematic phase. But because of the superimposition of dipolar correlations of smectic B phase on the locking of permanent
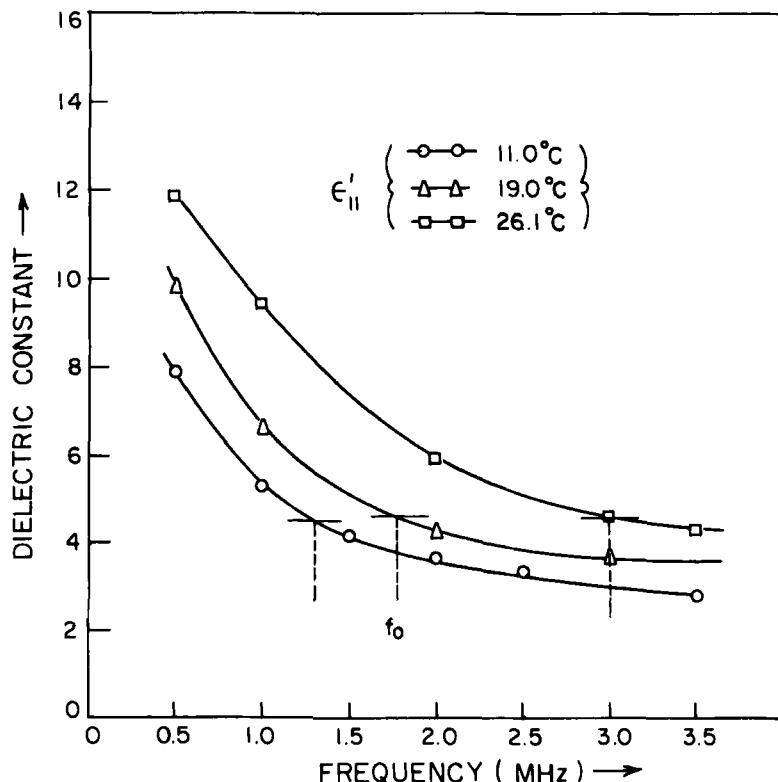
FIGURE 6   Variation of the parallel components of dielectric permittivity, $\epsilon'_{\parallel}$, of liquid crystal, PCH-1132 as a function of frequency at various temperatures. $\epsilon'_{\perp}$(——) cuts the $\epsilon'_{\parallel}$ curve at isotropic frequency, f_0.

dipoles, $\epsilon_{\parallel}$ falls more steeply than $\epsilon_{\perp}$ during nematic–S_B transition and we get the negative dielectric anisotropy in S_B phase.

(II) Dielectric dispersion

The frequency dependence of the dielectric constants, $\epsilon'_{\parallel}$ and $\epsilon'_{\perp}$ of HBT, E_8 and PCH-1132 was studied in their nematic phases in frequency range 0.5–3.5 MHz and are shown in Figures 4–6. $\epsilon'_{\perp}$ was found to be constant in the entire frequency range studied while $\epsilon'_{\parallel}$ exhibited relaxation behavior. This low frequency dispersion of $\epsilon'_{\parallel}$ which occurs at frequency much less compared to relaxation frequency of an isotropic liquid is due to strongly hindered rotation of the permanent dipole around the short molecular axis in the nematic phase.[8] The decrease in $\epsilon'_{\parallel}$ with increasing frequency as a result of orientational
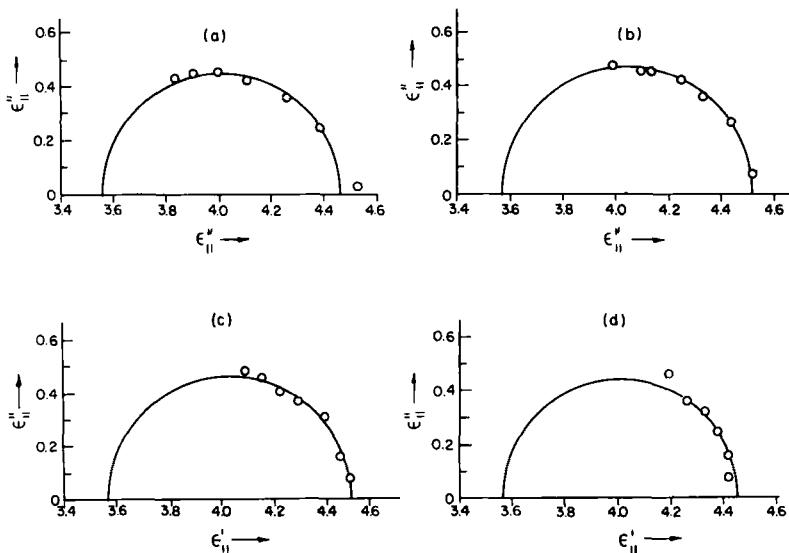
FIGURE 7   Cole–Cole plots for HBT in nematic phase (a) 57°C (b) 58.8°C (c) 61.4°C and (d) 64°C.

relaxation process led to the value of $\epsilon'_{\parallel}$ less than $\epsilon'_{\perp}$ at higher frequencies in all the three liquid crystals. Thus the dielectric anisotropy, $\Delta\epsilon$, changed its sign from positive to negative at higher frequency side. The dielectric isotropic frequency f_0, (the frequency at which $\epsilon'_{\parallel} = \epsilon'_{\perp}$) was found to increase with increase in temperature. The inversion of the sign of the dielectric anisotropy of E₈ and PCH-1132 may make them suitable for use in two frequency mode operation to shorten the decay time of the display.[3,12,14] The activation energy can be evaluated from the plot of log f_0 vs $1/T$.

For demonstration of the dielectric properties, Cole–Cole plots are very instructive.[5] Typical plots for HBT, E₈ and PCH-1132 at various temperatures are shown in Figures 7, 8 and 9 respectively. Since the centers of the Cole–Cole plots in all these cases lie on the real axis ($\epsilon'_{\parallel}$ axis), there is only single relaxation mechanism which can be described by the relaxation time τ_R. The activation energy w was evaluated from the plots of log τ_R vs $1/T$. Meier and Saupe[15] and Martin et al.[16] have extended the Debye theory of dielectric relaxation in liquids to nematics and showed that the relaxation time in liquid crystals is larger than the ordinary Debye relaxation time τ_D by a factor

$$g \simeq \frac{kt}{q} \exp\left(\frac{q}{kT}\right)$$
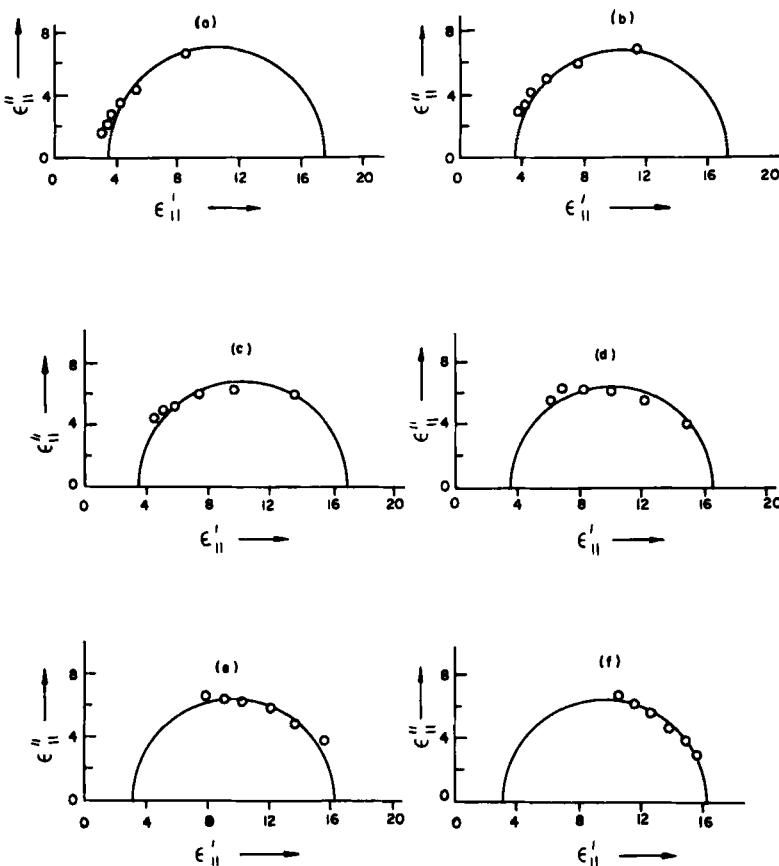
FIGURE 8   Cole–Cole plots for E_s in nematic phase (a) 13.6°C (b) 19.3°C (c) 24.2°C (d) 29.5°C (e) 34.3°C and (f) 40.3°C.

called the retardation factor such that

$$\tau_R = g\tau_D$$

$\tau_R(=1/2\text{-}f_R)$ is proportional to $\exp(w/kT)$, where $w = q + w_\eta$, q being the nematic potential i. e. the height of the potential barrier due to the molecular forces hindering the reorientation of the molecules in the parallel direction and w_η is the activation energy due to viscosity effects. Therefore a plot of log τ_R versus $(1/T)$ yields the total activation energy w.

The activation energy was evaluated by both approaches i.e. log τ_R
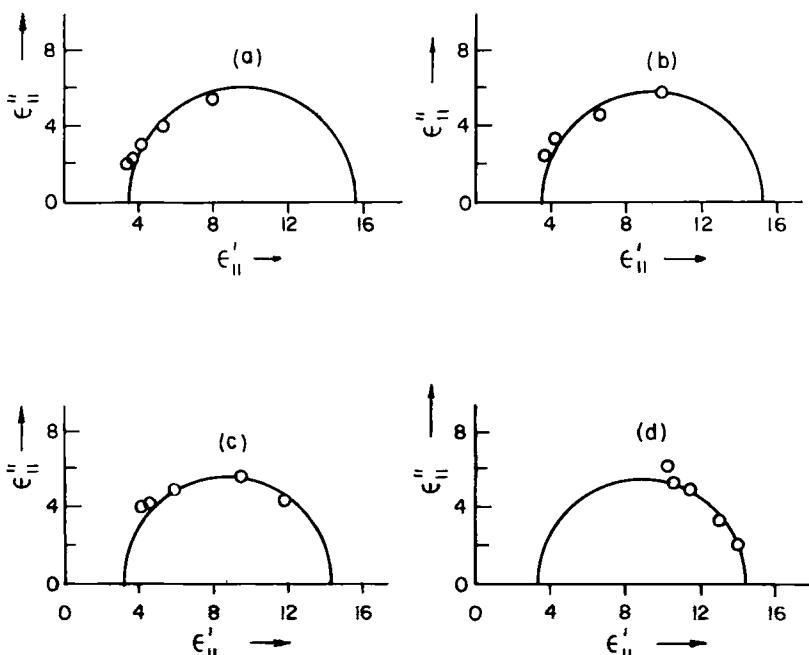
FIGURE 9   Cole–Cole plots for PCH-1132 in the nematic phase (a) 11°C (b) 19°C (c) 26.1°C and (d) 40.6°C.

vs $1/T$ and log f_0 vs $1/T$ in case of HBT and E$_8$ while only by log τ_R vs $1/T$ in case of PCH-1132 as sufficient points were not available for dielectric isotropic frequency. Both these approaches (Table I) give nearly the same value. The values of limiting dielectric permittivity at low frequency ($\epsilon_{\parallel 0}$), the extrapolated permittivity at high frequency ($\epsilon_{\parallel \infty}$) obtained from Cole–Cole plot and relaxation time τ_R obtained from Cole–Cole equation for $\epsilon_{\parallel}$ of HBT, E$_8$ and PCH-1132 at various temperatures are also given in Table I.

The physical interpretation of the energy barrier leading to the retardation factor g is not very clear. Some workers[3,17] have made an attempt to identify whether a group of molecules is rotating together or an individual molecule is rotating and is hindered in its rotation around a transverse axis because of the nematic order. Baessler et al.[17] found it plausible that a rotation around a transverse axis is determined more by the short range order than by the nematic (long range) order. We feel that such a rotation will always be associated with local disorder which in turn could lead to rotation of other molecules and therefore it

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TABLE I

Values of $\epsilon_{\parallel 0}$, $\epsilon_{\parallel\infty}$, τ_R, f_R and f_0 for HBT, E$_8$ and PCH-1132

Temp. (°C)	$\epsilon_{\parallel 0}$	$\epsilon_{\parallel\infty}$	$\tau_R \times 10^7$ in sec.	f_R in MHz	f_0 in MHz	Activation energy w in K Cal/Mol. from log τ_R vs $1/T$	from log f_0 vs $1/T$
HBT							
53.8	4.54	3.57	0.76	2.09	0.89	16.7	18.9
57.0	4.46	3.56	0.63	2.52	1.10		
58.8	4.52	3.57	0.50	3.18	1.38		
61.4	4.49	3.57	0.40	3.98	1.89		
64.0	4.45	3.57	0.35	4.55	2.20		
E$_8$							
13.6	17.6	3.4	4.12	0.39	1.03	14.6	12.5
19.3	17.3	3.4	2.40	0.66	1.59		
24.2	17.0	3.5	1.72	0.93	2.29		
29.5	16.4	3.6	1.06	1.50	3.30		
34.3	16.2	3.2	0.70	2.27	—		
40.3	16.0	3.2	0.46	3.46	—		
PCH-1132							
11.0	15.6	3.5	4.46	0.36	1.29	16.1	—
19.0	15.2	3.5	2.91	0.55	1.77		
26.1	14.2	3.2	1.47	1.08	2.85		
33.0	14.6	3.4	0.85	1.87	—		
40.6	14.2	3.4	0.41	3.88	—		

seems more correct to assume groups of molecules rotating together. This could lead to a low frequency dispersion for $\epsilon_{\parallel}$, while the relaxation of $\epsilon_{\perp}$ is still determined by the easy rotation of individual molecules around the long axis.

Acknowledgment

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