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Dielectric Studies of S_B Phase and Solid II Phases of the Liquid Crystal HBT

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Dielectric Studies of S_B Phase and Solid II Phases of the Liquid Crystal HBT

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The dielectric permittivity and relaxation were studied in S_B and solid II phases of a Schiff base HBT. Dielectric studies indicate a somewhat molecular locking and the existence of strong antiparallel molecular arrangement in S_B phase. The activation energies are found to be 14.64, 27.74 and 14.0 K cal/mole for $\epsilon_{\|}$, $\epsilon_{\perp}$ (both in S_B phase) and ϵ (in solid II phase), respectively.

INTRODUCTION

The dielectric studies provide useful information about molecular structure, molecular dynamics, phase transition and display performance of liquid crystals.[1–5] Most of the dielectric studies on liquid crystals are concerned with nematic phase and nematic-isotropic phase transition.[4] The dielectric studies on smectic phases are very scanty.[4] In our previous paper[6] we have reported the dielectric permittivity of HBT in its S_B phase at low frequencies along with the dielectric

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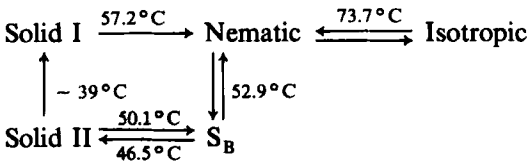
studies on E_8 and PCH-1132. In this paper we are reporting the dielectric relaxation studies in S_B and solid II phases of HBT to cast more light on the nature of these phases.

EXPERIMENTAL

N(-*p*-Hexyloxybenzylidene)-*p*-toluidine (HBT) exhibits the following phase transitions.[6]



It exhibits a monotropic S_B phase, so all the observations were recorded in cooling cycle. Dielectric permittivity and loss were measured by a General Radio Scheering bridge type 716 C in range 1 to 100 KHz. $\epsilon_{\|}$ and $\epsilon_{\perp}$ were measured by aligning the liquid crystals properly using a strong magnetic field (~ 6 KG). The temperature regulation was better than $\pm 0.1°C$. The absolute accuracy of loss measurements was 5% while that of permittivity measurement was better than 1%. The experimental details are described in our earlier paper.[6,7]

RESULTS AND DISCUSSIONS

The static dielectric constants, $\epsilon'_{\|}$ and $\epsilon'_{\perp}$ (at 10 KHz) are plotted as a function of temperature in Figure 1. These values are in good agreement with those reported in our earlier paper.[6] Besides the normal dielectric behaviour of liquid crystals, the Figure 1 exhibits two important results (1) $\bar{\epsilon}$[i.e. $(\epsilon_{\|} + 2\epsilon_{\perp})/3$] in S_B phase is appreciably lesser than that in nematic phase (2) the dielectric anisotropy reverses its sign on passing from nematic to S_B phase.

The appreciable fall (~ 25%) of $\bar{\epsilon}$ from nematic to S_B phase reflects that dipolar orientations are somewhat locked in this phase similar to that of solids. The reversal of sign of dielectric antisotropy during nematic to S_B transition can be understood on the basis of dipolar correlation in S_B phase. For a central polar molecular in S_B phase the

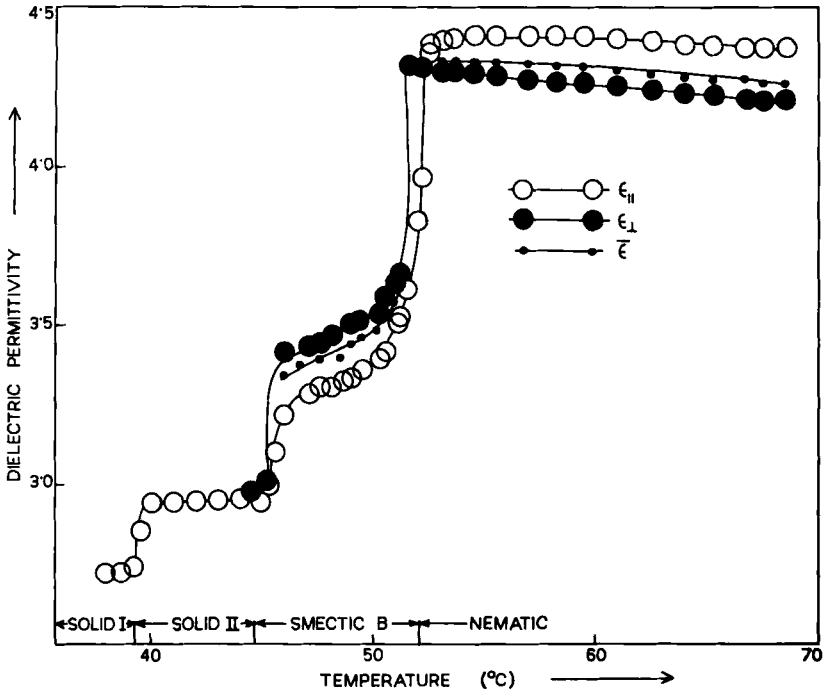


FIGURE 1 Temperature dependence of static dielectric constants ($\epsilon_{\parallel}$, $\epsilon_{\perp}$ and $\bar{\epsilon}$) at 10 KHz.

distance between the dipoles of molecules in different smectic layers is much larger than the distance between the neighboring dipoles in the same layer.[8] This leads to an increased antiparallel correlation along the preferred axis. Hence effective dipole moment in preferred direction is reduced and that in perpendicular direction is enhanced, thus resulting in a decrease in $\epsilon'_{\parallel}$ and increase in $\epsilon'_{\perp}$. If these changes are prominent they can change the sign of the dielectric anisotropy. However, in our case the two effects should be examined jointly. Due to locking of permanent dipoles in S_B phase $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ both fall and we get lower value in S_B phase compared to that in nematic phase. But because of the superimposition of dipolar correlation of smectic B phase on the locking of permanent dipoles, $\epsilon_{\parallel}$ falls more steeply than $\epsilon_{\perp}$ during nematic-S_B transition and we get the reversal of the sign of dielectric anisotropy.

The relaxation of both $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ were studied in S_B phase of HBT. The Cole–Cole plots of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ in S_B phase are drawn in Figure 2 and Figure 3 respectively. It is observed that relaxation of both $\epsilon_{\parallel}$ and

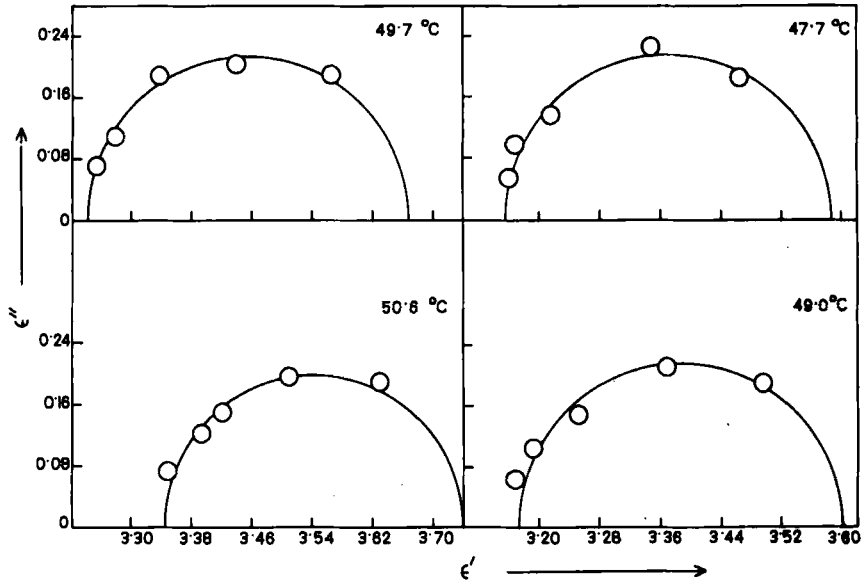


FIGURE 2 Cole–Cole plots at various temperatures of $\epsilon_{\parallel}$ in smectic B phase.

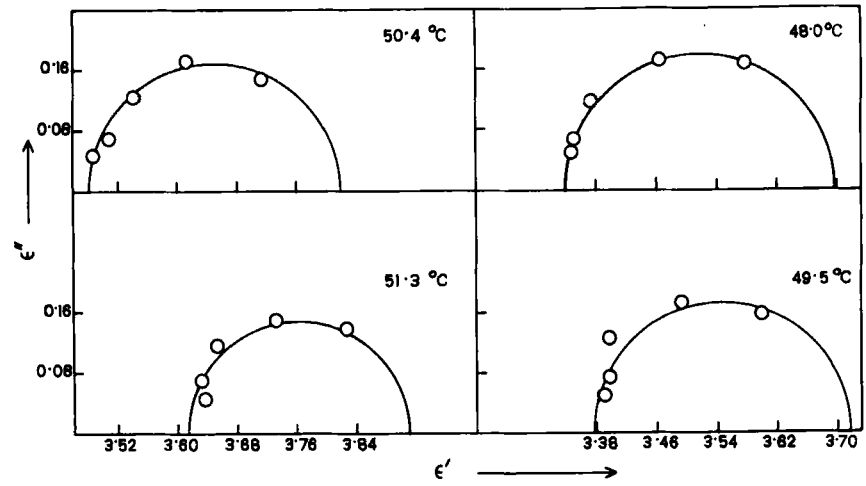


FIGURE 3 Cole–Cole plots at various temperatures of $\epsilon_{\perp}$ in smectic B phase.

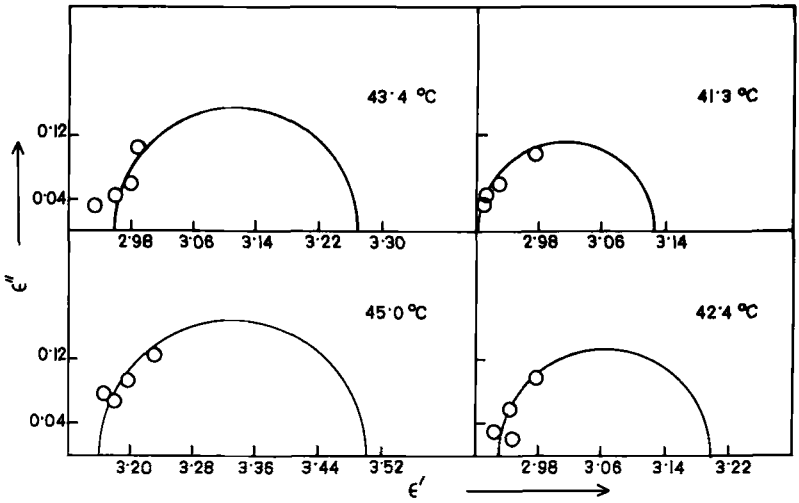


FIGURE 4 Cole–Cole plots at various temperatures in solid II phase.

$\epsilon_\perp$ occurs in S_B phase. It seems somewhat surprising as in nematic phase the relaxation of only $\epsilon_\parallel$ is observed and $\epsilon_\perp$ remain unaffected in radio frequency region.[4] Relaxation of $\epsilon_\perp$ in nematic phase lies in GHz region.

In S_B phase molecules are arranged in layers orthogonal to layer plane and a hexagonal or herringbone type of packing exists within the layer.[9] The relaxation of $\epsilon_\perp$ in S_B phase in low frequency region exhibits that unlike nematic phase molecules are not much free to rotate along their long molecular axes. The relaxation frequency of $\epsilon_\parallel$ and $\epsilon_\perp$ both are found to be nearly of the same magnitude in S_B phase but much less than that of $\epsilon_\parallel$ in nematic phase. This implies that rotation along both $\parallel$ and $\perp$ axes in S_B phase are much more restricted compared to those in nematic and isotropic phases. In smectic B phase the relaxation times are of the same order as in solid II phase. This clearly confirms that the molecules in S_B phase are somewhat locked similar to solids. The same conclusion has been drawn from the static permittivity studies.

Both $\epsilon_\parallel$ and $\epsilon_\perp$ exhibit single Debye type relaxation in S_B phase which may be due to hindered rotation of the molecules under S_B potential. The relaxation frequencies are 10.15 KHz (at 49°C) and 8.33 KHz (at 49.5°C) in case of $\epsilon_\parallel$ and $\epsilon_\perp$ respectively.

On going from S_B phase to solid II phase the discrimination in $\epsilon'_\parallel$ and $\epsilon'_\perp$ decreases and $\bar{\epsilon}$ decreases substantially. The fall in dielectric constant is due to further locking of dipoles in solid II phase. The dielectric constant, ϵ, in solid II phase also exhibits Debye type single

TABLE I

Temp°C	ϵ_0	ϵ_∞	$\tau_R \times 10^5$	$f_{R(KHz)}$
$\epsilon_\parallel$ in S_B Phase of HBT				
50.6	3.74	3.34	1.41	11.28
49.7	3.67	3.24	1.53	10.39
49.0	3.60	3.17	1.57	10.16
47.7	3.58	3.15	1.95	8.16
46.2	3.53	3.18	2.19	7.26
$\epsilon_\perp$ in S_B phase of HBT				
52.0	4.08	3.85	1.66	9.58
51.3	3.91	3.61	1.78	8.94
50.4	3.80	3.48	1.91	8.33
49.5	3.71	3.38	2.24	7.10
48.0	3.69	3.34	2.75	5.78
ϵ in Solid II phase of HBT				
43.4	3.27	2.96	2.85	5.58
42.4	3.20	2.93	3.08	5.15
41.3	3.13	2.90	3.31	4.81
40.0	3.09	2.89	3.71	4.28

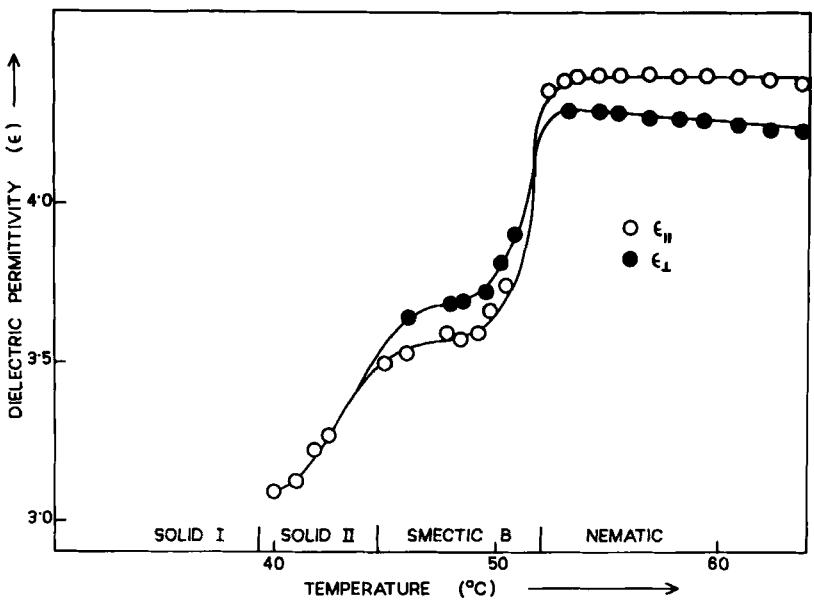


FIGURE 5 Temperature dependence of static dielectric permittivity (from Cole–Cole plots).

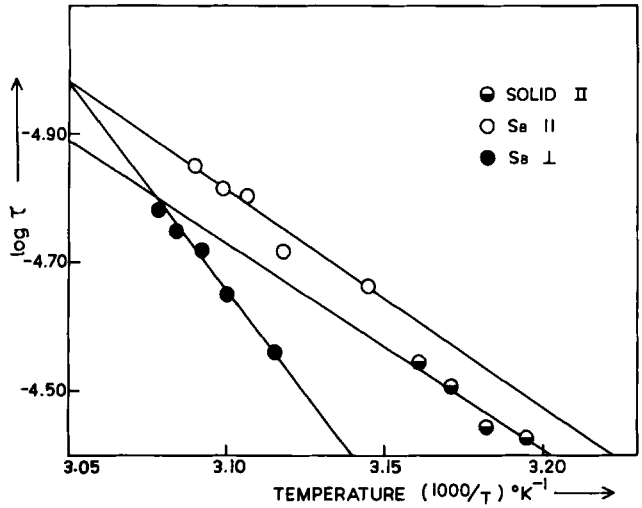


FIGURE 6 Temperature dependence of the relaxation time in various phases.

relaxation. The Cole–Cole plots in solid II phase are exhibited in Figure 4. The relaxation frequency is found to be 5.15 KHz (at 42.4°C.)

Although 10 KHz is very low frequency and can be treated as static frequency (Figure 1) our relaxation measurements on S_B and solid II phases indicate that relaxation region starts well below 10 KHz. So it would be better to compute the value of static dielectric constant from Cole–Cole plots in these phases instead of taking 10 KHz measurements as static frequency. These results are plotted in Figure 5. Figure 5 is qualitatively very much similar to Figure 1. This confirms our predictions that dipolar motion in S_B phase is somewhat locked and strong antiferroelectric arrangement of the molecules exists in S_B phase.

The activation energies were computed from the plot of $\log \tau$ vs $1/T$ curve as shown in Figure 6. These were found to be 14.6 and 27.7 K cal/mol for $\epsilon_{\|}$ and $\epsilon_{\perp}$ respectively in S_B phase. The temperature range of S_B phase is small so it may lead to some uncertainties in activation energies of $\epsilon_{\|}$ and $\epsilon_{\perp}$ in this phase. The activation energy of ϵ in solid II phase is found to be 14.0 K cal/mol.

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