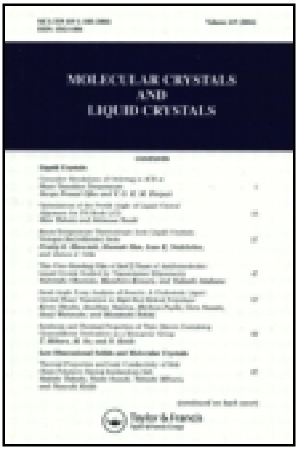

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B. R. Ratna [a] & R. Shashidhar [a]
[a] Raman Research Institute, Bangalore, 560006, India

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Dielectric Dispersion in 4′-*n*-Alkyl-4-Cyanobiphenyls†

B. R. RATNA and R. SHASHIDHAR

Raman Research Institute, Bangalore 560006, India

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The dispersion of $\varepsilon_{\parallel}$ in the frequency range of 1–10 MHz has been studied for 4′-*n*-alkyl-4-cyanobiphenyls (pentyl to octyl) at different temperatures in the nematic phase. It is established for the first time that the relaxation frequency at a common relative temperature ($T_{NI} - T$) for the successive homologues shows an alternation similar to that exhibited by the nematic–isotropic transition point or the orientational order parameter. The activation energy evaluated from the Arrhenius plot is found to be the same ($\sim$0.56 eV) for all the compounds.

INTRODUCTION

The dielectric constant of nematic liquid crystals for measuring field parallel to the optic axis ($\varepsilon_{\parallel}$) is usually characterized by a dispersion in the radio frequency region.[1] This is because of the strong hindering of the rotations of the longitudinal component of the dipole moment of the molecule about its transverse axis. Meier and Saupe[2] and Martin *et al.*[3] have extended the Debye theory of dielectric relaxation in liquids to account for this behaviour in nematics. There have also been a number of experimental studies of the dielectric dispersion in this region.[1,4–11]

In an earlier paper we presented the static dielectric constants of 4′-*n*-alkyl-4-cyanobiphenyls.[12] These are compounds of very large dielectric anisotropy owing to the presence of a strong permanent dipole moment (C≡N) along the long molecular axis. In the present paper we report dielectric dispersion measurements of $\varepsilon_{\parallel}$ of these compounds up to 10 MHz and an estimate of their activation energies.

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EXPERIMENTAL

The experimental set up as well as the methods adopted to obtain homogeneous and homeotropic alignments are the same as those used in the static measurements and have already been described in detail[12] except that in the present case aluminium coated glass plates were used as electrodes instead of tin oxide coated plates. A GR1606B R.F. bridge with a frequency range of 400 KHz–60 MHz was used, in conjunction with a Radart 923A signal generator. A Philips 15 MHz PM3231 oscilloscope and a Philips 7 MHz AC millivoltmeter were used as detectors. The reactance and resistance of the sample were measured and from this the dielectric constant and the dielectric loss could be calculated. The measured reactance was corrected for the series inductance. The loss $\varepsilon''_\perp$ for measuring field normal to the director was measured at each frequency and used to correct $\varepsilon''_\parallel$, as suggested by Rondelez and Mircea-Roussel.[6] The maximum error in the measurement is estimated to be 3% for the dielectric constant and 7% for the dielectric loss. The relaxation frequency could be determined to an accuracy of 2–3%.

RESULTS AND DISCUSSION

For each compound the dispersion was measured at four or five temperatures in the 400 KHz–10 MHz range. In Figures 1–4 we have plotted the frequency dependence of $\varepsilon''_\parallel$ at different temperatures. As is to be expected the maximum of $\varepsilon''_\parallel$ decreases with increasing temperature while the frequency at which the maximum occurs increases with temperature.

Figures 5–8 present the plots of $\varepsilon'_\parallel$ versus $\varepsilon''_\parallel$ to give the Cole–Cole arcs for different temperatures. The points lie on a semicircle with its centre on the $\varepsilon'_\parallel$-axis. With increasing temperature the radius of the semicircle decreases and the centre shifts to a lower $\varepsilon'_\parallel$. According to Debye's relaxation theory[13] this describes a single relaxation with the relaxation time (τ_R) determined by the maximum of $\varepsilon''_\parallel$, which decreases with increasing temperature. It is well known[2,11] that $\tau_R \propto \exp(W/kT)$, where the 'activation energy' $W = W_\eta + q$, W_η is the activation energy due to viscosity effects and q the height of the nematic potential. Since no viscosity data are available for these compounds, we could evaluate only W. Figure 9 shows f_R (where $f_R = 1/2\pi\tau_R$) versus $1/T$. The value of W calculated from the slope of the straight line is found to be about the same for all compounds (see Table I). The activation energies of 5CB[9] and 7CB[10] have been measured previously. Our results for these two compounds agree with the earlier data.

From their dielectric relaxation measurements on 4,4′-di-*n*-alkoxy azoxy benzenes, Mircea-Roussel and Rondelez[14] have shown that the activation

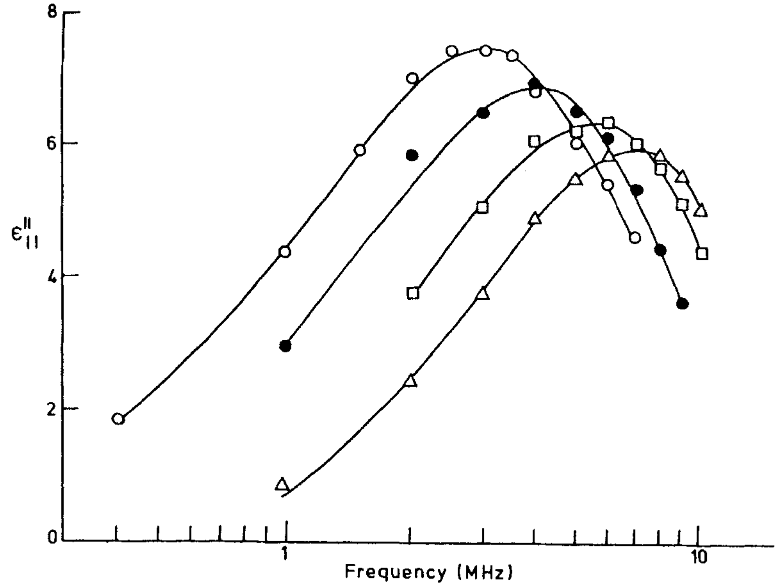

FIGURE 1 Dielectric loss ($\varepsilon''_{\parallel}$) as a function of frequency for 5CB at temperatures 19.5°C (○), 24°C (●), 28°C (□) and 31°C (△).

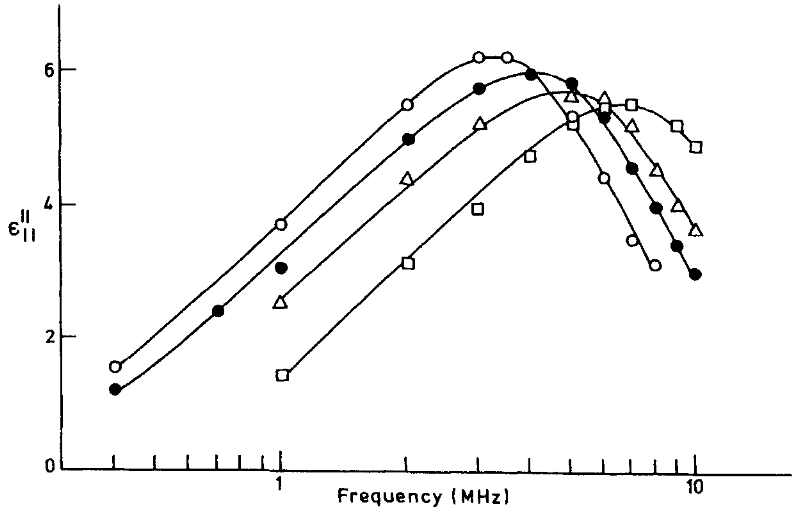

FIGURE 2 $\varepsilon''_{\parallel}$ as a function of frequency for 6CB at 18°C (○), 20.2°C (●). 22.5°C (△) and and 25.5°C (□).

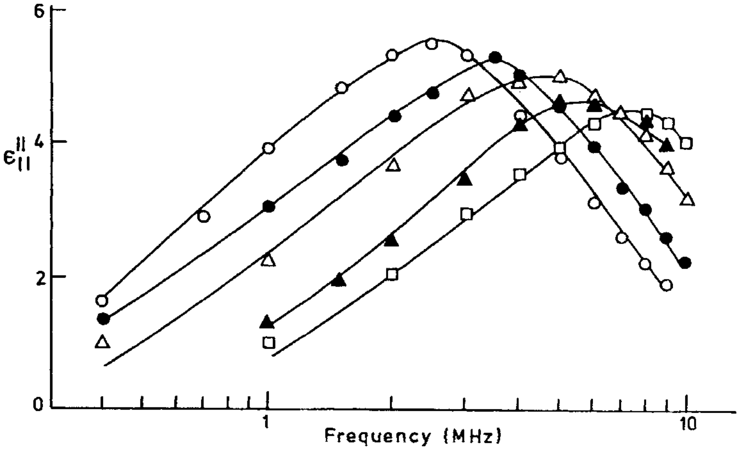

FIGURE 3 $\epsilon''_{\parallel}$ as a function of frequency for 7CB at 23°C (○), 27.5°C (●), 31.5°C (△), 35°C (▲) and 38°C (□).

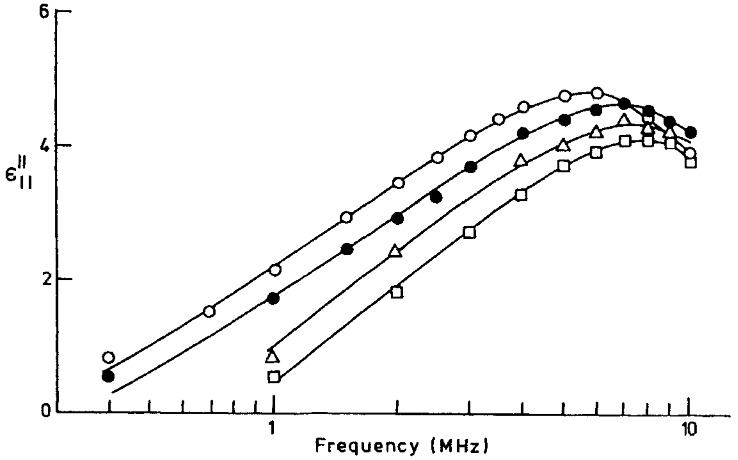

FIGURE 4 $\epsilon''_{\parallel}$ as a function of frequency for 8CB at 33.5°C (○), 34.6°C (●), 35.6°C (△) and 36.5°C (□).

energy *W* has a greater value for the higher homologues which have a smectic C phase in addition to the nematic phase than for the lower ones which have only the nematic phase. They have ascribed this increase to the influence of short range smectic-like order in the nematic phase. We do not get any such increase from 7CB to 8CB although the latter exhibits a smectic A phase at lower temperatures. Interestingly the behaviour of the ratio of

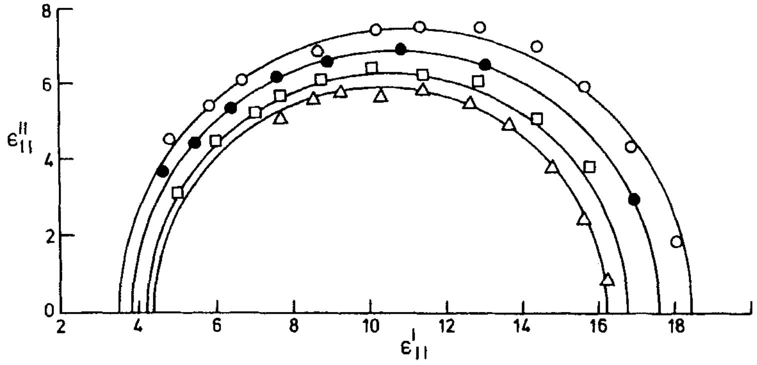

FIGURE 5 The Cole–Cole plot for 5CB at different temperatures (see Figure 1).

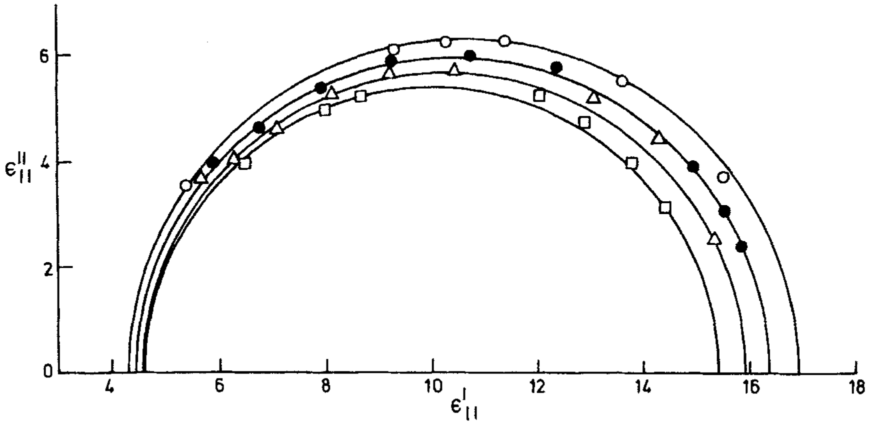

FIGURE 6 The Cole–Cole plot for 6CB at different temperatures (see Figure 2).

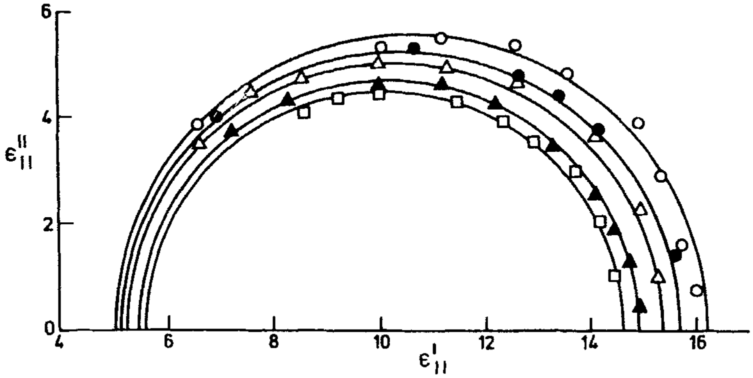

FIGURE 7 The Cole–Cole plot for 7CB at different temperatures (see Figure 3).

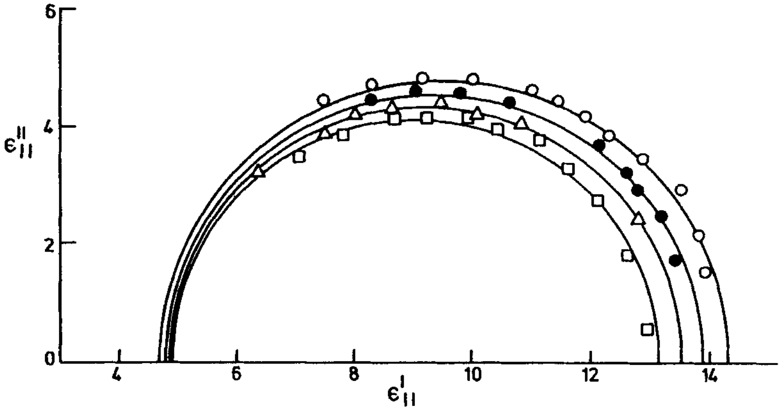

FIGURE 8 The Cole–Cole plot for 8CB at different temperatures (see Figure 4).

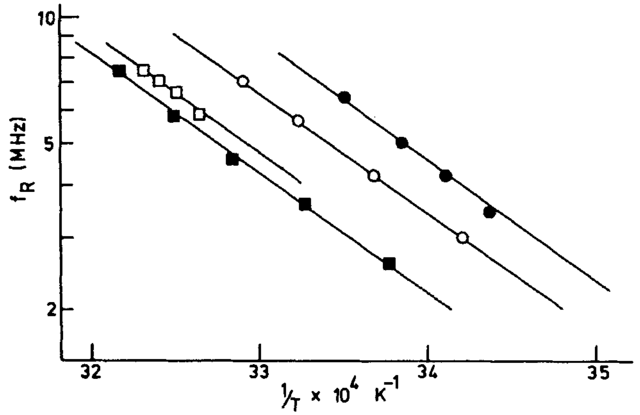

FIGURE 9 f_R vs. $1/T$ for 5CB (○), 6CB (●), 7CB (■) and 8CB (□).

TABLE I

Nematic–isotropic transition temperatures (T_{NI}) and activation energies (W) of 4'-*n*-alkyl-4-cyanobiphenyls

Compound	T_{NI} (K)	W (eV)
5CB	308	0.56
6CB	301.8	0.57
7CB	315	0.56
8CB	313.4	0.56

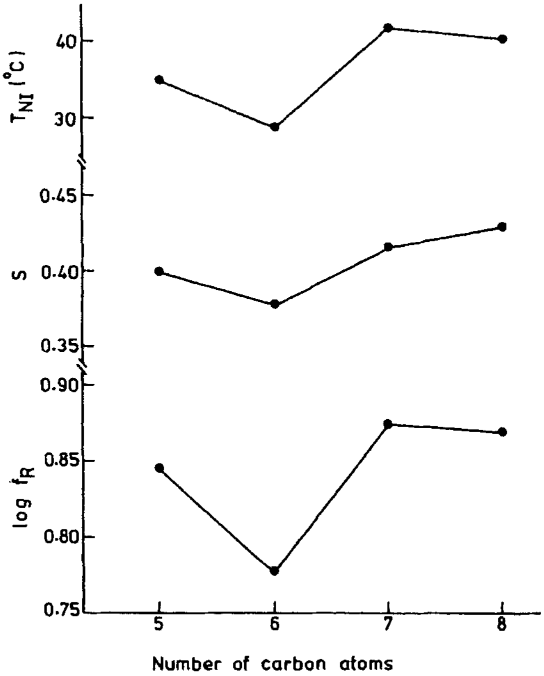

FIGURE 10 Nematic–isotropic transition temperature (T_{NI}), order parameter (S) and $\log f_R$ at $(T_{NI} - 4)°$ as functions of the number of carbon atoms in the alkyl chain.

the electrical conductivity ($\sigma_{\parallel}/\sigma_{\perp}$) is also markedly different for 8CB[15] and the higher homologues of alkoxy azoxy benzenes.[14]

There have been a few other studies[1,8,11] on the relaxation frequencies for different members of a homologous series. In all cases it was found that the relaxation frequency of the higher member is less than that of the lower one and it was suggested that this may be due to the difference in the alkyl chain length. This is found to be the case with our own data for 5CB and 7CB at any given temperature, but not for 6CB which has a higher f_R than either 5CB or 7CB at the same temperature (see Figure 9). However, an entirely different picture emerges when we compare the relaxation frequencies of these compounds at a common relative temperature ($T_{NI} - T$). Log f_R now shows an alternation with increasing chain length very similar to that of T_{NI}[16] or the orientational order parameter[17,18] (Figure 10). As far as we are aware, this is the first observation of such an alternation in successive members of a homologous series. The result is not surprising as the low frequency relaxation is evidently related to the orientational order in the nematic phase.

Acknowledgements

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