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The Dielectric Properties of Nematic 44′ *n*-pentylcyanobiphenyl

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The electric permittivity of nematic 44′ *n*-pentylcyanobiphenyl has been measured in the presence of electric and magnetic fields. Values of the permittivity components for the aligned state have been obtained and analysed in terms of the statistical theory of Maier and Meier. The behaviour of bulk samples of the material in electric and magnetic fields has been investigated, and yielded a mean permittivity for the non-aligned state. The macroscopic behaviour is discussed in terms of the continuum theory. Variable frequency measurements have shown the presence of a dispersion region in $\varepsilon_{\parallel}$ at about 5 MHz.

INTRODUCTION

The continuum theory of liquid crystals[1,2,3] has been relatively successful in describing the macroscopic properties of the nematic mesophase. This theory has been applied[4,5] to the description of a variety of electrical and optical effects in liquid crystals. The molecular understanding of the electric and electro-optic properties of liquid crystals is not as complete as that provided by the macroscopic approach, but there are a number of assumptions implicit in the macroscopic theory that have some molecular significance. The most important is that local anisotropy parameters such as $\Delta\varepsilon$, the permittivity anisotropy and $\Delta\chi$, the anisotropy in the diamagnetic susceptibility, are independent of the alignment of the liquid crystal, and depend only on the molecular properties and the molecular order parameter. Thus it is assumed that macroscopic alignment of liquid crystals by either electric or magnetic fields has no effect on the molecules or their environment.

A limitation of the continuum theory is that is provides no description of the properties of the non-aligned nematic state. The original theory of

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Frank[1] provides some understanding of this state in terms of director disinclinations, i.e. singularities in the director distribution, but the contribution of disinclinations to the macroscopic properties of the non-aligned nematic state has not yet been fully investigated.

Dielectric studies of nematic liquid crystals have proved to be a valuable source of information on the mesomorphic liquid crystalline phase.[6–12] Oriented samples of liquid crystals are dielectrically anisotropic, and both the real and imaginary parts of the permittivity tensor have two independent principal components. In this paper we report measurements of the anisotropic dielectric properties of nematic 44′ *n*-pentylcyanobiphenyl (PCB) in the presence of magnetic fields and both static and alternating electric fields. The primary objective of this work was to provide information on the dielectric properties of the non-aligned nematic state, and also to investigate the alignment of PCB by electric and magnetic fields.

EXPERIMENTAL

The material chosen for these studies was 44′ *n*-pentylcyanobiphenyl (PCB), which is one of a new series of nematogens recently reported.[13] The cyano-biphenyl compounds are potentially very valuable materials for many liquid crystal investigations and applications.[14] They possess a high degree of chemical stability, and they appear to be unchanged by exposure to air or static electric fields. In addition their relatively high dielectric anisotropy in the aligned state makes them particularly suitable for dielectric studies. Samples of PCB were prepared and purified in our laboratory. They had a nematic range of 22.5° → 35°C, although they readily supercooled below 22°C.

A variety of cells were used in the experiments. They were all parallel plate capacitors suitably thermostatted to 0.1°C, in which the separation of the electrodes could be set at different values in the range 0.1 cm → 0.6 cm. The electrode materials were either stainless steel or brass, and there was no evidence of chemical decomposition in the cells during the experiments. Cell volumes were between 1 cm^3 and 20 cm^3.

The capacitance of the cells was measured at 1592 Hz using a Wayne Kerr bridge (type B 331). For other frequencies in the range 200 Hz–20 kHz, or where variable bridge voltages were required, this was used in conjunction with an external variable frequency oscillator (Brookdeal type 471) and an external tunable detector (Brookdeal type 464). To convert measured capacitance to permittivity the cells were calibrated using liquids whose permittivities spanned the range of interest $\varepsilon = 6 \rightarrow 20$. All permittivities are quoted relative to the permittivity of free space. The permittivities of the chosen standard liquids were either obtained from the literature,[15] or measured in our laboratory. Dielectric measurements in the frequency range 100 kHz-10 MHz were made using a radiofrequency bridge (Wayne Kerr type B 201) together with an external source and detector (Wayne Kerr type SR 268).

Alignment of the liquid crystal by magnetic fields was achieved by placing a cell between the pole pieces of an electro-magnet (Mullard EE 1002). The magnetic field strength was measured using a calibrated Hall probe magnetometer (Scientifica and Cook type D 11), which was also used to establish the homogeneity of the magnetic field in the liquid crystal cells. Measurements of the permittivity parallel and perpendicular to the magnetic field were made by suitably orienting the cell between the magnet pole pieces.

In the presence of electric aligning fields it was only possible to measure the permittivity along the field direction. A variable static electric potential was provided by a 0 → 3 kV power supply (Hewlett Packard type 6515A), and this was connected to the measurement cell in the manner described in an earlier paper.[16] Measurements of the electric permittivity paralled to an alternating electric field were made by varying the bridge voltage applied to the sample cell.

RESULTS

All our results for the principal permittivity components of PCB are quoted with respect to laboratory fixed axes defined by the aligning field. Only the saturated values of the components, measured at high field strengths are comparable with values quoted by other workers.

Static permittivity measurements Our results for the principal components of the permittivity tensor, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, measured at various magnetic field strengths and temperatures are presented in Figure 1. These measurements were made at a frequency of 1592 Hz, an electrode separation of 0.5 cms, and a corresponding analysing field of 9 V cm^{-1}. Values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ measured for the magnetically aligned state are plotted as a function of temperature in Figure 2. Also plotted is the mean value of the permittivity $\bar{\varepsilon}_{\infty} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp})$ corresponding to the aligned state.

The variation of $\varepsilon_{\parallel}$ with analysing field (i.e. variable bridge voltage) in the absence of any other aligning field is given in Figure 3. Results are plotted for three electrode separations: all measurements were made at a temperature of 27°C. The measured electric permittivity approaches a limiting value for field strengths less than 10 V cm^{-1}, but the field necessary to produce alignment varies with electrode separation (d) from about 40 V cm^{-1} for

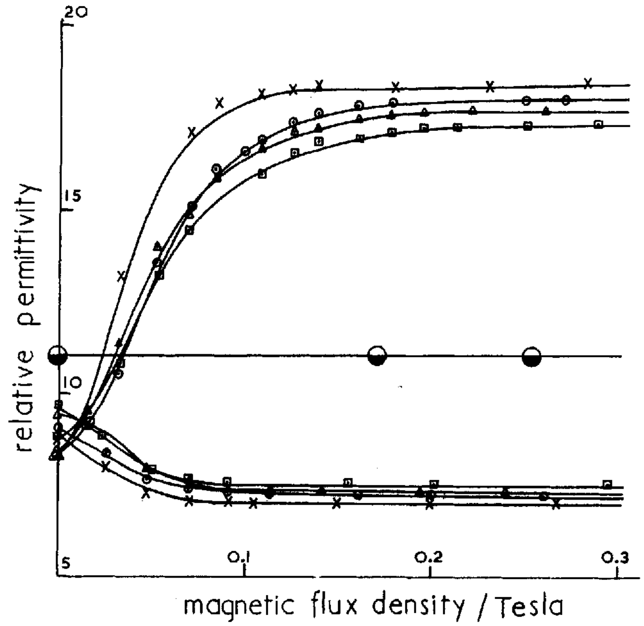

FIGURE 1 The permittivity of PCB as a function of magnetic field. The upper curves refer to $\varepsilon_{\parallel}$ and the lower curves to $\varepsilon_{\perp}$. Different temperatures are represented as follows: (×) 25°C; (⊙) 27.5°C; (△) 29°C; (⊡) 30.5°C; (◒) 36°C.

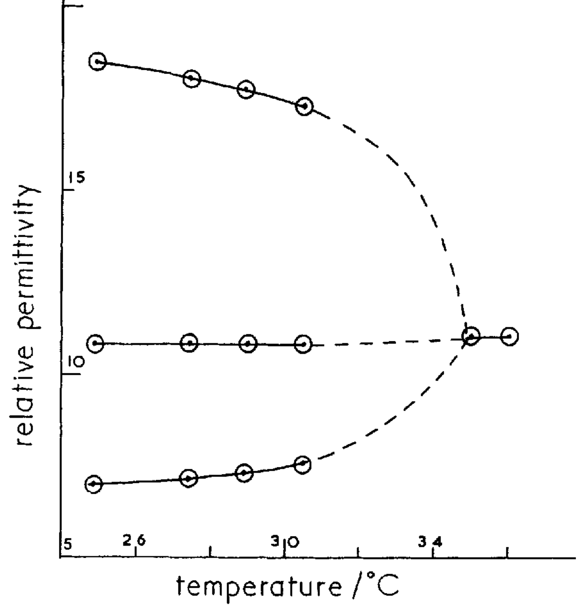

FIGURE 2 Saturated permittivity components at different temperatures; upper curve $\varepsilon_{\parallel}$, lower curve $\varepsilon_{\perp}$ and middle line $\bar{\varepsilon}_{\infty}$.

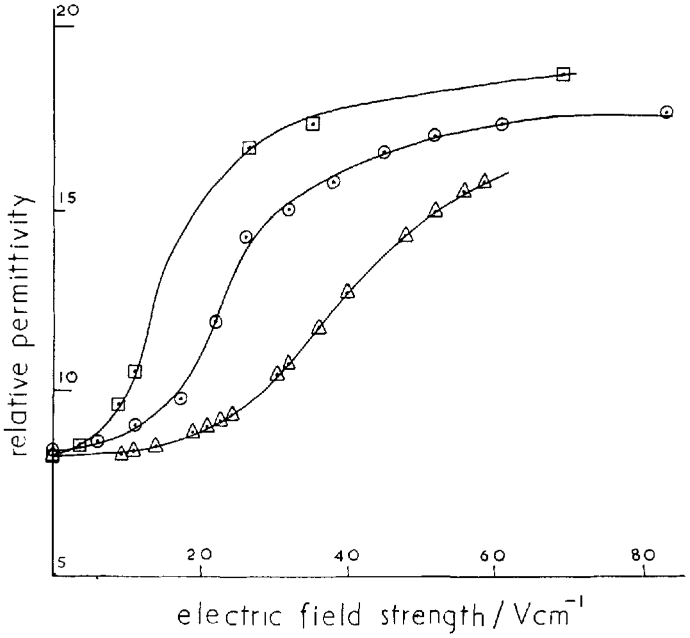

FIGURE 3 $\varepsilon_{\parallel}$ as a function of an alternating electric field at different electrode separations: (⊡) 0.17 cm, (⊙) 0.2 cm, (△) 0.56 cm.

$d = 0.17$ cm to > 70 V cm^{-1} for $d = 0.6$ cm. For permittivities between the limiting values, measurements were subject to large regular fluctuations of approximately ± 0.7, however at both limits these fluctuations disappeared. The higher limiting value of the permittivity is equal to $\varepsilon_{\parallel}$ measured in the magnetically aligned sample, while the lower limiting value is the mean permittivity of the non-aligned state $\bar{\varepsilon}_0$. Taking account of experimental uncertainties $\bar{\varepsilon}_0 = 8.4 \pm 0.4$ at 27°C. This value was confirmed by an independent measurement using a permittivity cell (Wayne Kerr type D 121), which has no electrodes in contact with the material and an analysing field of less than 4 V cm^{-1}.

The results illustrated in Figure 1 for the variation of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ with magnetic field suggest that the perpendicular component of the permittivity saturates at a lower field strength than the parallel component. To investigate this further, measurements of the permittivity components parallel and perpendicular to a magnetic field were repeated with different electrode separations and different bridge voltages. The results of these measurements are illustrated in Figures 4(*a*) and 4(*b*), in which the dotted lines represent a limiting behaviour corresponding to an electrode separation of approximately 0.5 cm and an analysing field of 9 V cm^{-1}.

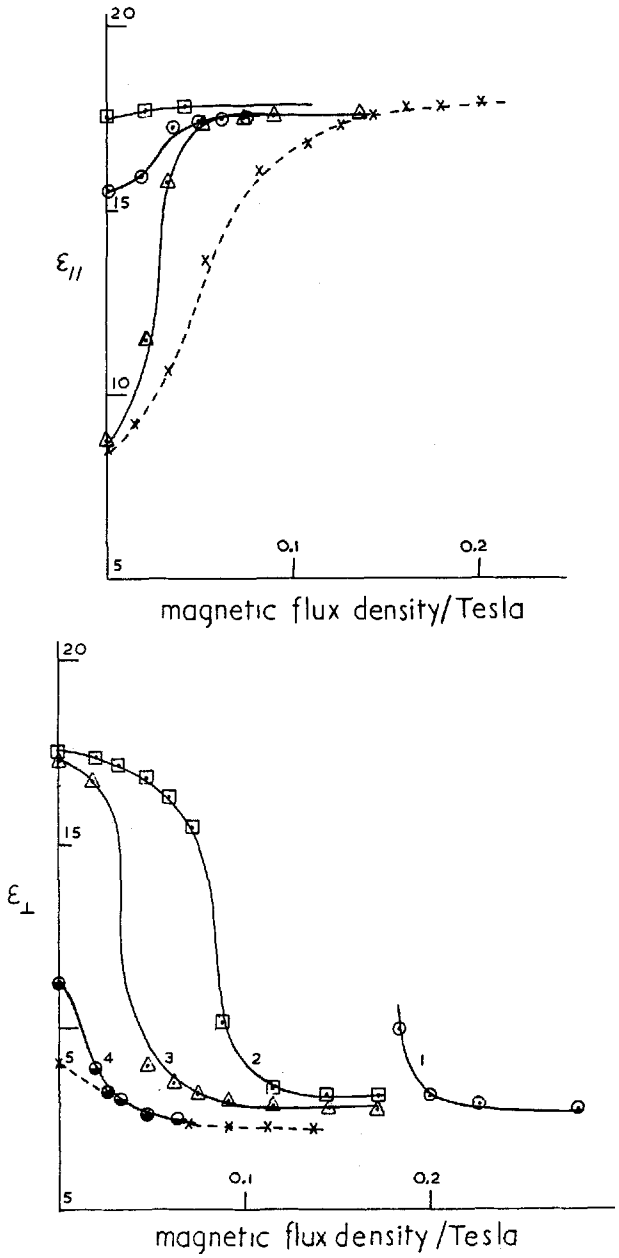

FIGURE 4(*a*) and (*b*) Permittivity components as a function of magnetic field at different electrode separations and different bridge voltages.
(*a*) parallel component ($\varepsilon_{\parallel}$); (□) $d = 0.2$ cm, $E = 57$ V cm^{-1}; (⊙) $d = 0.2$ cm, $E = 23$ V cm^{-1}; (△) $d = 0.2$ cm, $E = 5.8$ V cm^{-1}; (×) $d = 0{\cdot}56$ cm, $E = 8.2$ V cm^{-1}.
(*b*) perpendicular component ($\varepsilon_{\perp}$): (⊙) $d = 0.078$ cm, $E = 148$ V cm^{-1}; (□) $d = 0.078$ cm, $E = 59$ V cm^{-1}; (△) $d = 0.078$ cm, $E = 14.8$ V cm^{-1}; (◒) $d = 0.2$ cm, $E = 5.4$ V cm^{-1}; (×) $d = 0.5$ cm, $E = 9$ V cm^{-1}.

To determine the effect of a static electric field on the alignment of nematic PCB, measurements were made of the permittivity component parallel to such a field. The cell capacitance was measured by a small alternating (1592 Hz) analysing voltage across the electrodes, and measurements were made at three electrode separations. The results are given in Figure 5, and it is apparent that they show the same qualitative behaviour as the magnetic field measurements in Figure 4(*a*). Comparing Figure 5 with Figure 3 it is also apparent that an alternating electric field of frequency 1.6 kHz causes alignment much more rapidly than a static electric field. Measurements at other frequencies[17] suggest that the rate of alignment increases with increasing frequency up to the limit of our measurements (8 kHz).

Dielectric dispersion of $\varepsilon_{\parallel}$ The frequency dependence of the real and imaginary permittivity components $\varepsilon'_{\parallel}$ and $\varepsilon''_{\parallel}$ was measured at different temperatures for a sample of PCB magnetically aligned by a field of 0.4 Tesla. Our results are given in Figures 6(*a*) and 6(*b*). Measurements were made in the temperature range 14°C → 30°C: below 22°C the material was in a

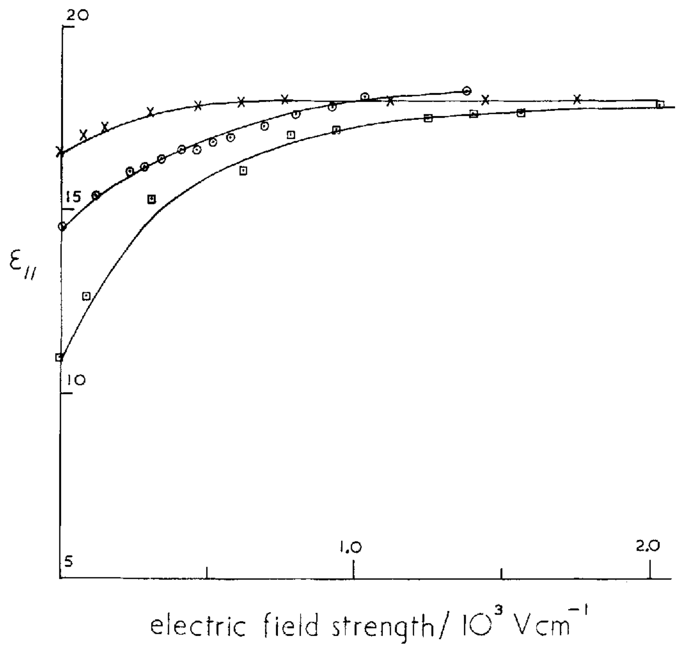

FIGURE 5 $\varepsilon_{\parallel}$ as a function of a static electric field at different electrode separations: (×) $d = 0.065$ cm, $E_{ac} = 71$ V cm^{-1}; (⊙) $d = 0.27$ cm, $E_{ac} = 17.1$ V cm^{-1}; (□) $d = 0.64$ cm, $E_{ac} = 7.2$ V cm^{-1}.

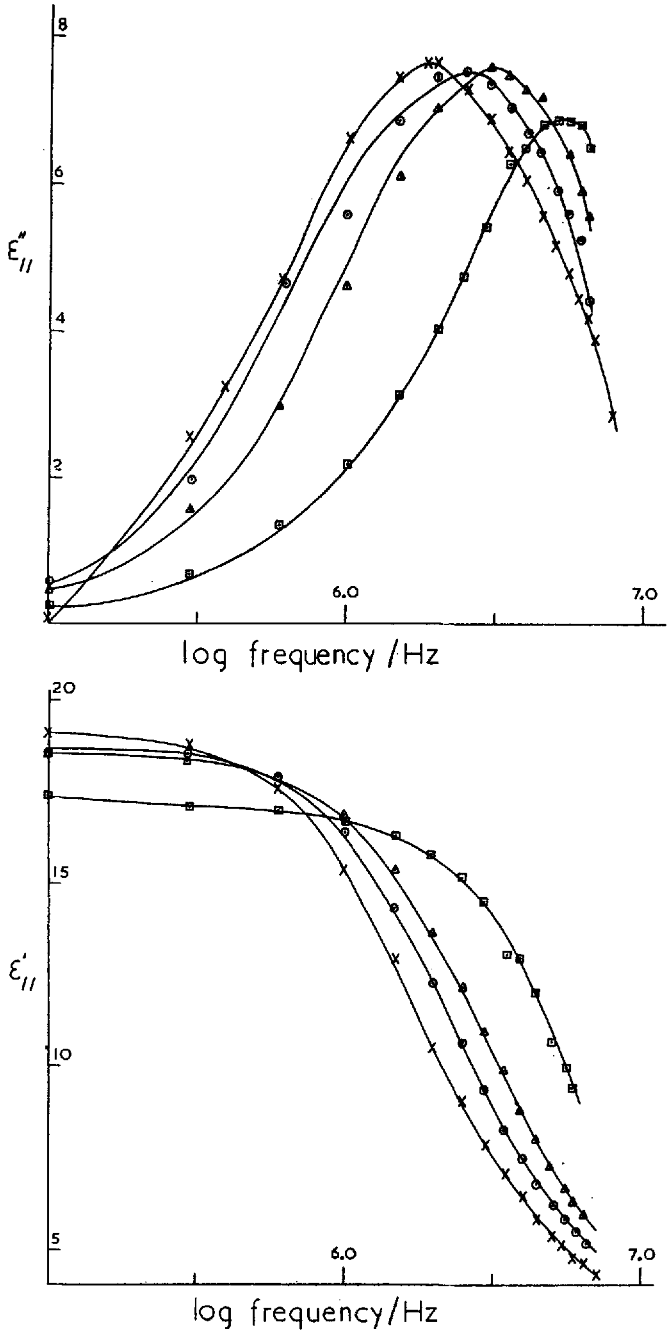

FIGURE 6 (*a*) and (*b*) Dispersion in $\varepsilon_{\parallel}$ for PCB at various temperatures.
(*a*) imaginary component ($\varepsilon''_{\parallel}$)
(*b*) real component ($\varepsilon'_{\parallel}$); (×) $T = 14°C$; (⊙) $T = 17°C$; (△) $T = 19°C$; (⊡) $T = 28°C$.

supercooled nematic state, although this does not affect the interpretation of the results.

Measurements of $\varepsilon'_{\parallel}$ and $\varepsilon''_{\parallel}$ could be precisely fitted to a semi-circular Cole-Cole plot at each temperature; the corresponding relaxation times are given in Table I. Further discussion of these results will be given in the next section.

TABLE I

Relaxation times for nematic PCB

Temperature °C	relaxation time (secs)
14	$8{\cdot}5 \times 10^{-8}$
17	6.7×10^{-8}
19	5.4×10^{-8}
22·5	4.2×10^{-8}
28	2.7×10^{-8}

DISCUSSION

Macroscopic behaviour of the static permittivity The results of dielectric measurements on bulk samples of nematic PCB suggest that the alignment of nematic liquid crystals by electric or magnetic fields is a complicated process.

We have attempted to establish that the mean permittivity ($\bar{\varepsilon}_0$) of the macroscopically isotropic non-aligned nematic state differs from that of the aligned state ($\bar{\varepsilon}_{\infty}$). The permittivity in laboratory fixed axes may be related to the local permittivity tensor $\boldsymbol{\varepsilon}_d$ defined with respect to the director as follows:

$$\varepsilon_{\parallel} = \bar{\varepsilon}_d + \Delta\varepsilon_d(\langle\cos^2\phi\rangle - \tfrac{1}{3})$$

$$\varepsilon_{\perp} = \bar{\varepsilon}_d - \frac{\Delta\varepsilon_d}{2}(\langle\cos^2\phi\rangle - \tfrac{1}{3}) \qquad (1)$$

The angular brackets indicate an average over the angular distribution of the director, and ϕ is the angle between the director and the parallel direction. Evidently the mean permittivity $\bar{\varepsilon}$ should be independent of director distribution, and so should be independent of the aligning field. Our measurements for PCB and other materials[17] indicate that $\bar{\varepsilon}$ is a function of aligning field, and in Figure 7 $\bar{\varepsilon}$ and $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ are plotted as a function of magnetic field. Partial alignment at electrode surfaces would affect the measured values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, and the results in Figure 1 suggest that there may be some such residual alignment under zero field conditions. However this should not contribute to the mean permittivity $\bar{\varepsilon}_0$, unless the local order parameter near the surface of the electrodes differs from that in the bulk material.

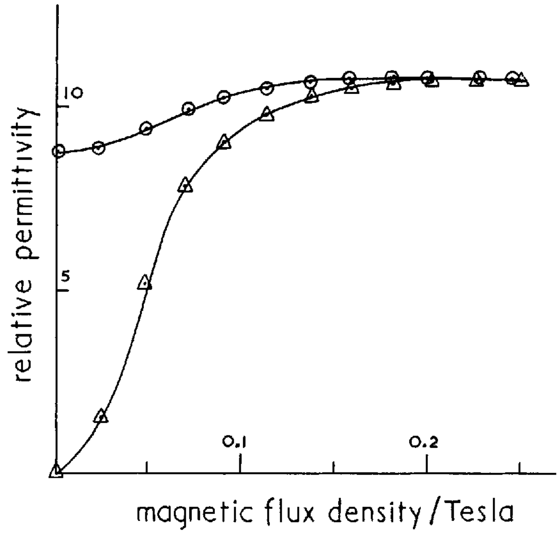

FIGURE 7 Mean permittivity (○) and permittivity anisotropy (△) as a function of magnetic field for PCB at $T = 27.5°C$.

Measurements made under conditions of variable alternating electric field (Figure 3) at different electrode separations all extrapolate to the same value of the relative permittivity. If residual alignment at electrode surfaces made a significant contribution to the measured permittivity, one would expect the limiting value of the permittivity $\bar{\varepsilon}_0$ to depend on the electrode separation. In particular for a parallel alignment at the electrode surface and a positive material, the limiting value of $\bar{\varepsilon}_0$ should approach $\varepsilon_{\perp}^{\infty}$ as the electrode separation decreased; we found no evidence of such an effect. Furthermore the agreement between our extrapolated $\bar{\varepsilon}_0$ and the value measured in a cylindrical glass cell with no metal surfaces in contact with the liquid crystal provides additional evidence that the contribution of residual alignment to the mean permittivity is not important in our measurements.

The field dependence of $\bar{\varepsilon}$ could be explained by a field dependent molecular order parameter S. No measurements have been reported of S in other than fully aligned samples, but it is unlikely that any detected field dependence of S would be sufficient to explain our results. An alternative explanation is that the disinclinations which are present in the non-aligned nematic phase contribute to the measured permittivity of the material. This would imply that the singularity which exists in the director distribution at a disinclination influences the local molecular environment and hence the polarization of the medium.

Our results for the alignment of nematic PCB by static and alternating electric fields indicate that the static field necessary to cause complete alignment is substantially greater than the corresponding alternating field of frequency 1.6 kHz. It is well known that electric field-induced flow in nematic liquid crystals can cause instabilities,[24,25] and hence affect their alignment. PCB is a dielectrically positive material having a positive conductivity anisotropy, and so it is to be expected that hydrodynamic flow will augment the orienting torques of applied fields.

Measurements of $\varepsilon_\perp$ in the presence of a magnetic field and a variable a.c. electric field are illustrated in Figure 4(*b*). The curves have the same shape as those obtained by Carr[7] for measurements of the microwave permittivity in the presence of low frequency electric fields perpendicular to an applied magnetic field. They correspond to the reorientation of the director from a direction parallel to the a.c. electric field to a direction parallel to the magnetic field. This type of reorientation is known as a Fréedericksz transition, and is well described by continuum theory which predicts[18] that:

$$V_c^2 = \left(k_{11}\pi^2 + d^2\frac{\Delta\chi B^2}{\mu_0}\right)\Big/\varepsilon_0\Delta\varepsilon \tag{2}$$

V_c and B are the voltage and magnetic field at which reorientation of director occurs, k_{11} is the splay elastic constant, $\Delta\varepsilon$ and $\Delta\chi$ are the anisotropies in the electric permittivity and diamagnetic susceptibility, and d is the thickness of the sample.

In Figure 8 the results of Figure 4(*b*) are plotted according to Eq. (2). The points are numbered to correspond to the curves in Figure 4(*b*). The points 1, 2, 3 and 4 lie approximately on a straight line in accord with theory, and from the slope of this line we have obtained a value for the diamagnetic susceptibility anisotropy of $0.83 \pm 0.15 \times 10^{-6}$ ($0.67 \pm 0.12 \times 10^{-7}$ emu cgs) for PCB at 27°C. Our measurements are not sufficiently accurate to provide a value for the elastic constant k_{11}. Assuming that it is of the order of 3×10^{-12} Jm^{-1} (3×10^{-7} dynes) the value of $k_{11}\pi^2/\varepsilon_0\Delta\varepsilon$ is estimated to be 0.35 V^2, giving an effectively zero intercept in Figure 8. Measurements made with a sample thickness of 0.5 cms (point 5) do not lie on the line, presumably because reorientation of partially aligned liquid crystals is not adequately described by Eq. (2).

Microscopic theory of the saturated static permittivity The statistical theory of Maier and Meier[19] relates the saturated permittivity components to the molecular dipole moment μ, mean polarizability $\bar{\alpha}$ and polarizability anisotropy $\Delta\alpha$ of a nematogen. For an axially symmetric molecule the relations are:

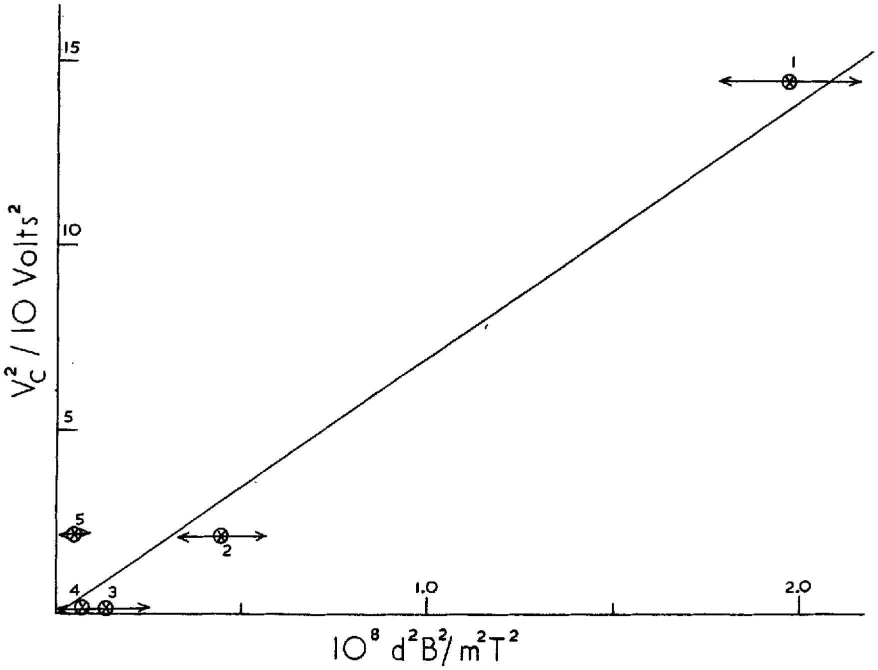

FIGURE 8

$$\varepsilon_{\parallel}^{\infty} = 1 + NLF\varepsilon_0^{-1}\left\{\bar{\alpha} + \frac{2\Delta\alpha S}{3} + \frac{F\mu^2}{3kT}[1 + 2S]\right\}$$

$$\varepsilon_{\perp}^{\infty} = 1 + NLF\varepsilon_0^{-1}\left\{\bar{\alpha} - \frac{\Delta\alpha S}{3} + \frac{F\mu^2}{3kT}(1 - S)\right\} \qquad (3)$$

where $L = 3\bar{\varepsilon}/(2\bar{\varepsilon} + 1)$; $F = 1/(1 - \bar{\alpha}f)$; $f = (2\bar{\varepsilon} - 2)/4\pi\varepsilon_0 a^3(2\bar{\varepsilon} + 1)$; S is the molecular order parameter. The factors L and F were introduced by Onsager[20] to account for the cavity field and reaction field in an isotropic dielectric; a is the molecular radius. In Maier and Meier's extension of Onsager's theory to anisotropic media it was assumed that these factors remain equal to their isotropic values. However it is to be expected that the long range anisotropy of an aligned nematic liquid crystal will influence the local electric field experienced by a molecule. We may introduce anisotropic cavity field and reaction field factors defined by:

$$L_{\parallel} = 3\varepsilon_{\parallel}/(2\varepsilon_{\parallel} + 1); \quad F_{\parallel} = 1/(1 - \bar{\alpha}f_{\parallel}); \quad f_{\parallel} = (2\varepsilon_{\parallel} - 2)/4\pi\varepsilon_0 a^3(2\varepsilon_{\parallel} + 1)$$

and similar expressions for the perpendicular factors. The use of $\bar{\alpha}$ in the equation for F recognises that even in the aligned state the molecules have considerable rotational freedom.

Using our measured values for the saturated permittivity components together with unpublished values for the principal refractive indices (Table II),

TABLE II

Principal permittivities and refractive indices for aligned nematic PCB at 25°C, and derived molecular parameters.

$\varepsilon_{\parallel} = 18.5$ $n_{\parallel} = 1.71$†

$\varepsilon_{\perp} = 7.0$ $n_{\perp} = 1.53$‡

	isotropic local field	anisotropic local field
dipole moment μ	1.1×10^{-29} Cm	1.09×10^{-29} Cm
mean polarizability $\bar{\alpha}$	3.62×10^{-39} $C^2m^2J^{-1}$	3.62×10^{-39} $C^2m^2J^{-1}$
polarizability anisotropy $\Delta\alpha$	3.02×10^{-39} $C^2m^2J^{-1}$	2.75×10^{-39} $C^2m^2J^{-1}$
molecular order parameter S	0.46	0.40

† derived from $n_{\text{isotropic}}^{37.5°C} = 1.59 \cong \frac{1}{3}(n_{\parallel} + 2n_{\perp})$
‡ measured at $\lambda = 546$ *nm*

we have calculated μ, $\bar{\alpha}$, and $\Delta\alpha$ for PCB via Eqs. (3). These values are given in Table II. Both isotropic and anisotropic cavity field and reaction field factors were used. The inclusion of the anisotropic L and F factors has little effect on the molecular parameters, although they do have a significant effect on the derived order parameter. There are unfortunately no values in the literature for the free molecule dipole moment, polarizability and polarizability anisotropy of PCB, although these results should be shortly available from our laboratory. The derived dipole moment of PCB in the nematic state may be compared with a value[21] of 1.4×10^{-29} Cm for cyanobiphenyl. The difference of approximately one Debye can scarcely be accounted for by the presence of an *n*-pentyl group, and so clearly local interactions are important in nematic PCB.

The very small effect of an anisotropic local field is surprising. The local field correction factors in equations (3) are strictly only correct for a macroscopic spherical sample in a continuous medium.[22] Since in the isotropic case contributions to the local field from molecules within the spherical sample can be shown[22] to be zero, Onsager replaced the macroscopic spherical sample by one of molecular dimensions. In an anisotropic liquid crystal contributions to the local field from molecules within a spherical sample will not vanish, and the use of a molecular sized cavity in the Maier and Meier theory will neglect the major contributions to the anisotropic local field.

Dispersion in $\varepsilon_{\parallel}$ A characteristic of dipolar nematic materials is the existence of a low frequency dispersion region between 1 kHz and 10 MHz, which vanishes in the isotropic liquid phase. This dispersion is normally ascribed to the restricted rotation of molecules about an axis perpendicular to the director, since in an aligned sample the dispersion is only found in the parallel component of the permittivity. Our measurements of the frequency dependence of $\varepsilon_{\parallel}$ in PCB aligned by a magnetic field are given in Figures 6(*a*) and 6(*b*). The corresponding relaxation times at different temperatures may be plotted according to an empirical Arrhenius equation, with an energy parameter of $W = 53$ kJ mol^{-1}. To obtain the height of the barrier to Debye rotation from this energy it is necessary to know[23,9,11] the temperature dependence of the anisotropic viscosity of PCB. Unfortunately this information is not available from the literature; we may note that our value of W is similar to that obtained by other workers[9,11,12] for other nematic materials.

The decrease in the real part of $\varepsilon_{\parallel}$ which accompanies the dispersion is greater than the dielectric anisotropy. Hence assuming no dispersion in $\varepsilon_{\perp}$ between 1 kHz and 10 MHz the dielectric anisotropy of PCB changes sign in the MHz region. This behaviour has been observed[11] for other nematic materials having smaller dielectric anisotropies. A molecular explanation of the change of sign of $\Delta\varepsilon$ in PCB is difficult, since a negative dielectric anisotropy would imply that the average molecular polarizability in a plane perpendicular to the molecular symmetry axis was greater than that along the axis.

CONCLUSIONS

In this paper we have presented a series of measurements of the electric permittivity of nematic PCB under a variety of external influences. We have attempted to establish that the non-aligned nematic state has a mean permittivity significantly different from that of the aligned state. It is tentatively proposed that this difference may be due to disinclinations in the non-aligned state.

The static permittivity components measured in the aligned state have been analysed in terms of the statistical theory of Maier and Meier, and have yielded values for the dipole moment, mean polarizability and polarizability anisotropy of PCB. It was found that inclusion of anisotropic local field corrections did not significantly affect the results, although it was pointed out that the major contribution to the local field anisotropy in liquid crystals is implicitly omitted in the Maier and Meier theory.

Dispersion measurements of the parallel component of the permittivity revealed a dielectric loss in the region of 5 MHz. This could be analysed in terms of a single relaxation time, and temperature studies yielded an activation energy for the dipole reorientation. The dielectric increment associated with the dispersion in $\varepsilon_{\|}$ suggests that above about 10 MHz PCB may have a negative dielectric anisotropy.

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References

1. F. C. Frank, *Disc. Faraday Soc.*, **25**, 19 (1958).
2. J. L. Erickson, *Arch. Rat. Mech. Anal.*, **9**, 371 (1962).
3. F. M. Leslie, *Arch. Rat. Mech. Anal.*, **28**, 265 (1968).
4. E. Dubois-Violette, P. G. de Gennes and O. Parodi, *J. de Phys.*, **32**, 305 (1971).
5. W. Helfrich, *J. Chem. Phys.*, **51**, 4092 (1969).
6. For early references see A. Saupe, *Angew. Chem. Int. Ed.*, **7**, 97 (1968).
7. E. F. Carr, *Mol. Cryst. Liquid Cryst.*, **7**, 253 (1969).
8. D. P. McLemore and E. F. Carr, *J. Chem. Phys.*, **57**, 3245 (1972).
9. M. Schadt, *J. Chem. Phys.*, **56**, 1494 (1972).
10. F. Rondelez, D. Diguet, and G. Durand, *Mol. Cryst., Liquid Cryst.*, **15**, 183 (1971).
11. W. H. De Jeu and Th. W. Lathowers, Fourth Int. Liq. Cryst. Conf., Kent, U.S.A., (1972), *Mol. Cryst., Liquid Cryst.* (in press).
12. V. K. Agarwal and A. H. Price, *J. Chem. Soc. Faraday Trans.* II, **70**, 188 (1974).
13. G. W. Gray, K. J. Harrison and J. A. Nash, *Electron. Lett.*, **9**, 130 (1973).
14. A. Ashford, J. Constant, J. Kirton and E. P. Raynes, *Electron. Lett.*, **9**, 118 (1973).
15. F. Buckley and A. Maryott, Nat. Bur. Standards Circular No. 589, Washington (1958).
16. P. G. Cummins, D. A. Dunmur and N. E. Jessup, Liquid Crystals and Ordered Fluids (Ed. Johnson, J. F. & Porter, R. S.), Vol. 2, Plenum Press, New York 1974, p. 341.
17. P. G. Cummins, Thesis, University of Sheffield (1974).
18. W. H. De Jeu, C. L. Gerritsma and Th. W. Lathowers, *Chem. Phys. Lett.*, **14**, 503 (1972).
19. W. Maier and G. Meier, *Zeit. Naturforschg.*, **16a**, 262 (1961).
20. L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1936).
21. A. L. McClellan, Tables of Experimental Dipole Moments, W. H. Freeman & Co., San Francisco 1963, p. 436.
22. H. Frohlich, Theory of Dielectrics, Clarendon Press, Oxford 1958, pp. 24–25.
23. W. Maier and A. Saupe, *Mol. Cryst.*, **1**, 515 (1966).
24. W. Helfrich, *J. Chem. Phys.*, **51**, 4092 (1969).
25. W. H. De Jeu and C. J. Gerritsma, *J. Chem. Phys.*, **56**, 4752 (1972).