Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Elastic Constants and Electric Permittivities of Mixtures Containing Terminally Cyano Substituted Nematogens

M. J. Bradshaw [a] & E. P. Raynes [a]

[a] Royal Signals and Radar Establishment, Malvern, Worcs, WR14 3PS, UK

To cite this article: M. J. Bradshaw & E. P. Raynes (1983): The Elastic Constants and Electric Permittivities of Mixtures Containing Terminally Cyano Substituted Nematogens, Molecular Crystals and Liquid Crystals, 91:1-2, 145-155

To link to this article: http://dx.doi.org/10.1080/00268948308083082

Mol. Cryst. Liq. Cryst., 1983, Vol. 91, pp. 145–155
0026-8941/83/9102-0145$18.50/0

Printed in the United States of America

The Elastic Constants and Electric Permittivities of Mixtures Containing Terminally Cyano Substituted Nematogens

M. J. BRADSHAW and E. P. RAYNES
Royal Signals and Radar Establishment, Malvern, Worcs, WR14 3PS, UK

(*Received July 11, 1982*)

Measurements of electric permittivities and elastic constants for various terminally cyano substituted nematics and their mixtures with terminally dialkyl substituted nematogens are reported. The mixtures showed a considerably reduced ratio of the bend to splay elastic constants (k_{33}/k_{11}) compared with the pure *p*-cyano substituted nematics. Also the large diversity in k_{33}/k_{11} observed for the *p*-cyano substituted nematics was found to converge upon dilution. It is suggested that these results can be attributed to the reduced anti-parallel local ordering observed in the mixtures.

INTRODUCTION

The operation of liquid crystal display devices depends upon the modulation of ambient light by a liquid crystal layer which can be deformed by an electric field. This distortion and consequently the characteristics of the device are determined by the device construction and the physical properties of the liquid crystal. In particular, the elastic constants and the electric permittivities of the liquid crystal are important, and measurements of these are reported in this paper. Elastic constants and permittivities are also necessary for testing models and deriving empirical trends. These give an insight into the intermolecular interactions responsible for the anisotropic alignment and local molecular structure in the liquid crystal phase.

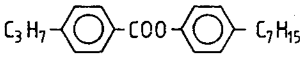
It is well known that nematogens with strong polar end groups tend to exhibit anti-parallel local ordering,[1,2,3] whereas nematogens without a polar end group do not show such an association. This anti-parallel local ordering is known to affect the permittivities and the X-ray scattering; we have now extended the range of observations to include elastic constants by studying mixtures of *p*-cyano substituted nematogens with *p*-dialkyl substituted nematogens.

MATERIALS

The liquid crystals used were of the general type:

where R and X are terminal groups of the central core of the molecule. R is a normal alkyl chain, and X can be CN (*p*-cyano nematic) or R (*p*-dialkyl nematic).

Table I shows the molecular structures of the *p*-cyano nematogens studied, and the *p*-dialkyl nematogens used were:


Me37

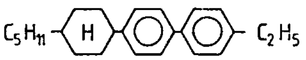
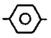
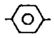
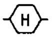
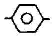
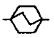
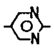
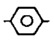
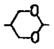
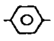
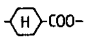
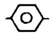

BiCH52

TABLE I

P-Cyano nematogens investigated

Material	–A–	–B–
nCB		
nPCH		
nBCO		
5/7*PYR		
3/5/7†PDX		
5CDe		

* 40 m% n = 5; 60 m% n = 7
† 30 m% n = 3; 40 m% n = 5; 30 m% n = 7

EXPERIMENTAL METHOD

The splay and bend elastic constants (k_{11} and k_{33}) and the two permittivity components ($\epsilon_\perp$, $\epsilon_\parallel$) were determined from the detailed analysis of the capacitance-voltage characteristics of a nematic layer with initial homogeneous alignment, and zero tilt and twist, distorted by an electric field applied normal to the layer.[4] The low voltage capacitance together with the empty capacitance gave $\epsilon_\perp$ repeatable to within 0.5%, and $\epsilon_\parallel$ was estimated from the high field data using a $1/V$ extrapolation.[5] The capacitance-voltage data, $\epsilon_\perp$ and the estimated $\epsilon_\parallel$ value were fitted to the continuum theory by a non-linear least squares fitting program to determine the "best fit" values of the three parameters $(k_{33} - k_{11})/k_{11}$, threshold voltage (V_c), and $\gamma = (\epsilon_\parallel - \epsilon_\perp)/\epsilon_\perp$. This gave k_{33}, k_{11} and $\epsilon_\parallel$ to within 5%, 2%, and 1%, respectively. To achieve this accuracy, an automatic system was used to measure the change in capacitance to within 0.01% and the voltage to 10^{-4} V. Equilibrium readings were ensured by stepping the voltage and having a sequence of pauses totalling 2 hours just above V_c. The quality of the alignment was checked by observation of the threshold sharpness of the capacitance/voltage curve and it was found that the increase in the reduced capacitance as the the bias voltage was increased to just below threshold $[C(V_c^{(-)}) - C_\perp/(C_\parallel - C_\perp)]$ was less than 0.03%. Thirty data points in the voltage range V_c to $2V_c$ were used and these gave residuals (the deviations between the fitted curve and experimental data points) of less than 10^{-4} V, which represents the resolution of the voltage measurements. The measurements were made in the temperature range from 0°C to 100°C with the temperature stabilized to within 0.1°C.

PERMITTIVITY RESULTS

For p-cyano nematics, measurements of $\bar{\epsilon} = (\epsilon_\parallel + 2\epsilon_\perp)/3$ show virtually zero temperature dependence near T_{NI} and a discontinuity $\delta\bar{\epsilon}$, of a few percent of $\bar{\epsilon}$, across the nematic to isotropic transition.[6,7,8] The same behavior was found for mixtures containing only p-cyano nematogens; this is illustrated in Figures 1 and 2 which show $\bar{\epsilon}$ and the isotropic permittivity (ϵ_{is}) of the cyanobiphenyl mixture E7, of 3PCH, and of a 3PCH/5CDe mixture. Conversely, for the p-dialkyl nematics, $\bar{\epsilon}$ is continuous with ϵ_{is} at T_{NI},[9] and both $\bar{\epsilon}$ and ϵ_{is} show a significant temperature dependence which approximates to the classical Debye $1/T$

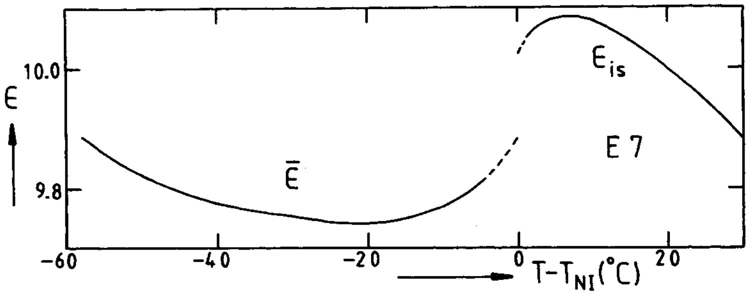


FIGURE 1 Permittivity of cyanobiphenyl mixture E7.

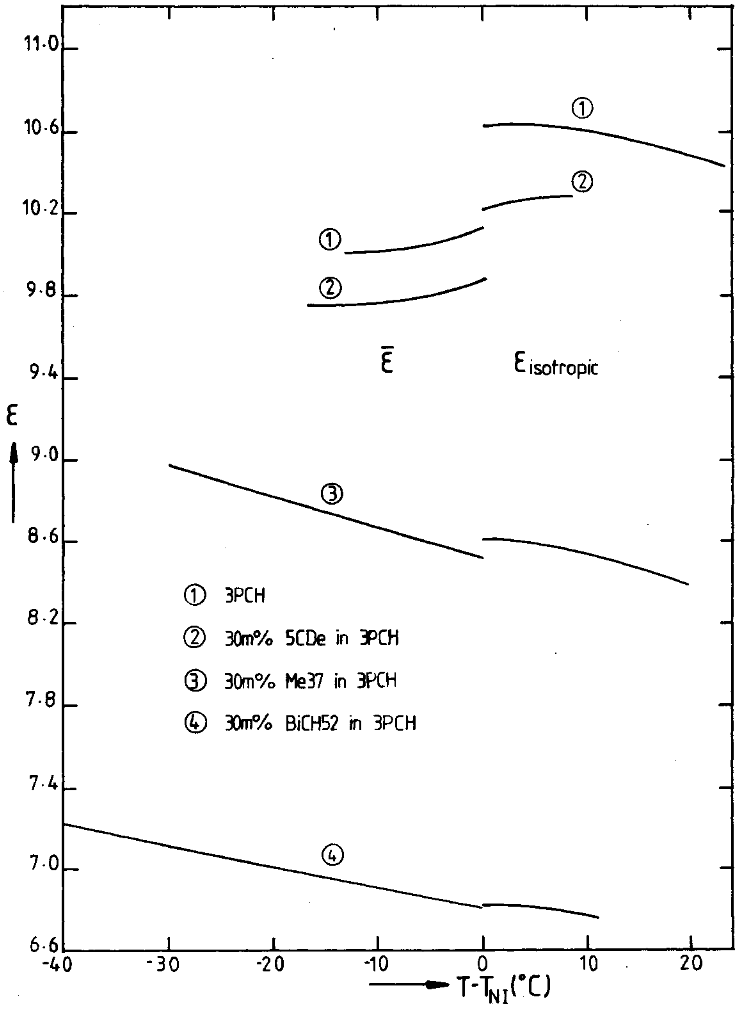


FIGURE 2 Permittivities of 3PCH and its mixtures.

value[10]; this is illustrated in Figure 3 which shows the isotropic permittivity of Me37.

When a *p*-dialkyl nematogen was added to a *p*-cyano nematic, it was found that the magnitude of the discontinuity $\delta\bar{\epsilon}$ at T_{NI} decreased rapidly and the temperature dependence of $\bar{\epsilon}$ increased and approached the classical $1/T$ dependence. This is illustrated in the plot of $\bar{\epsilon}$ and ϵ_{is} as a function of reduced temperature for various 3BCO/Me37 mixtures (Figure 4), which shows that $\delta\bar{\epsilon}$ decreased from ~4% $\bar{\epsilon}$ for pure 3BCO to 0.5% $\bar{\epsilon}$ at 30 molar % Me37 concentration. Similar effects have been found when other *p*-dialkyl nematogens are added to *p*-cyano nematics. Figure 2 shows that $\delta\bar{\epsilon}$ is significantly smaller and $d\bar{\epsilon}/dT$ is larger for the 3PCH/BiCH52 and 3PCH/Me37 mixtures compared with the pure 3PCH and the 3PCH/5CDe mixture.

ELASTIC CONSTANT RESULTS

Elastic constant measurements of mixtures containing only *p*-cyano nematogens showed an approximately additive variation in k_{33}/k_{11}; this is illustrated in Figure 5 which shows k_{33}/k_{11} for mixtures of 7CB and 3BCO. However, when *p*-dialkyl nematogens were added to *p*-cyano nematics, k_{33}/k_{11} was found to decrease rapidly. This can be seen in Figure 5 which shows k_{33}/k_{11} as a function of Me37 concentration for 3BCO and 3PCH, illustrating that small amounts of Me37 significantly decrease k_{33}/k_{11}. The large decreases in k_{33}/k_{11} produced by the addition of 30 molar % Me37 to various *p*-cyano nematics are presented in Table II, and the results show that in these mixtures the diversity in k_{33}/k_{11} between the various *p*-cyano nematics is much reduced; also k_{33}/k_{11} for an homologous series converge. Similar trends

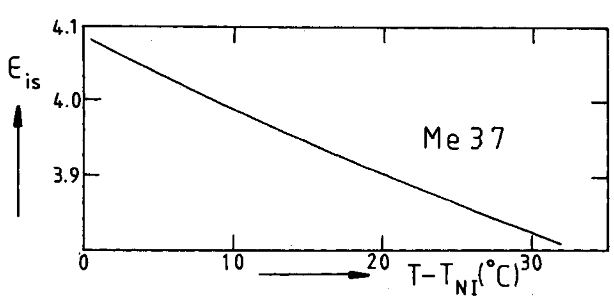


FIGURE 3 Isotropic Permittivity of Me37.

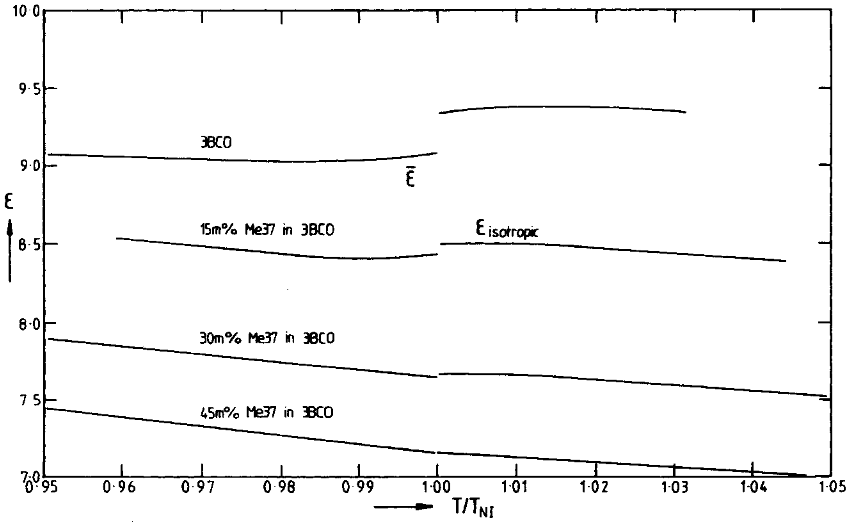


FIGURE 4 Permittivities of 3BCO and mixtures with Me37.

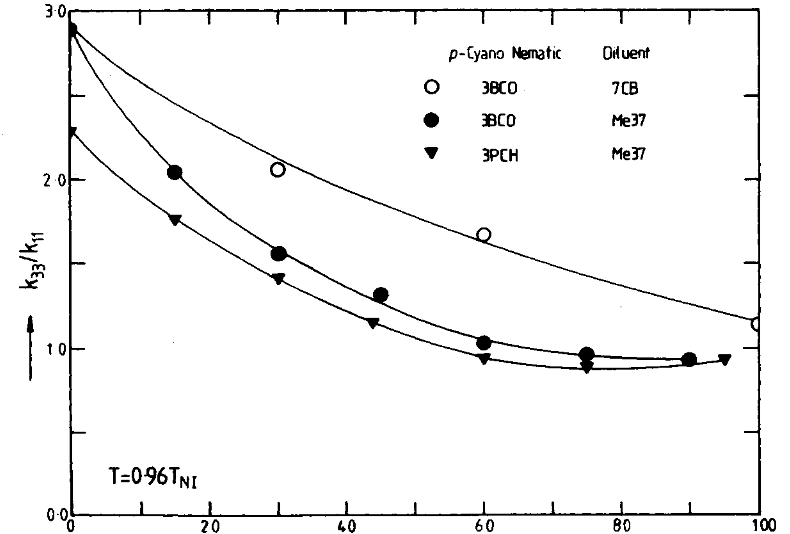


FIGURE 5 k_{33}/k_{11} of various mixtures.

TABLE II

k_{33}/k_{11} for P-Cyano nematics and their mixtures with 30 molar % Me37.

p-Cyano nematic (CN)	k_{33}/k_{11} 100% CN	 70 m% CN 30 m% Me37
2/4 CB (1:1)	—	0.94
5 CB	1.46	0.93
6 CB	1.30	0.81
7 CB	1.14	0.84
8 CB	—	0.78
9 CB	—	0.82
5/7 CB*	1.38	0.90
3 PCH	2.20	1.42
5 PCH	1.77	1.20
7 PCH	1.50	1.13
3 BCO	2.89	1.54
5 BCO	2.35	1.45
7 BCO	1.71	1.38
3/5/7 PDX	1.35	0.96
5/7 PYR	1.03	0.89
5 CDe	1.47	1.16

* Eutectic Mixture E1
Reduced temperature (T/T_{NI}) = 0.96

were found when other *p*-dialkyl nematogens, with or without the ester linkage, were added to *p*-cyano nematics; Figure 6 shows that k_{33}/k_{11} for the mixtures of 3PCH/Me37 and 3PCH/BiCH52 are comparable, and are much less than the ratios found for 3PCH and for the 3PCH/5CDe mixture.

DISCUSSION

Permittivity[1,7] and X-ray[2,3] studies indicate that there is a structural difference between *p*-cyano and *p*-dialkyl nematics. X-ray measurements of the layer spacings of *p*-dialkyl materials show a repeat distance approximately equal to a molecular length. However, for *p*-cyano materials, the repeat distance tends to be greater than the molecular length, and is typically equal to one molecular length plus one tail length; this has been attributed to anti-parallel ordering of the molecules such that their cores and *p*-cyano groups overlap. Further evidence for the anti-parallel local ordering of the molecules of *p*-cyano nematics is found in

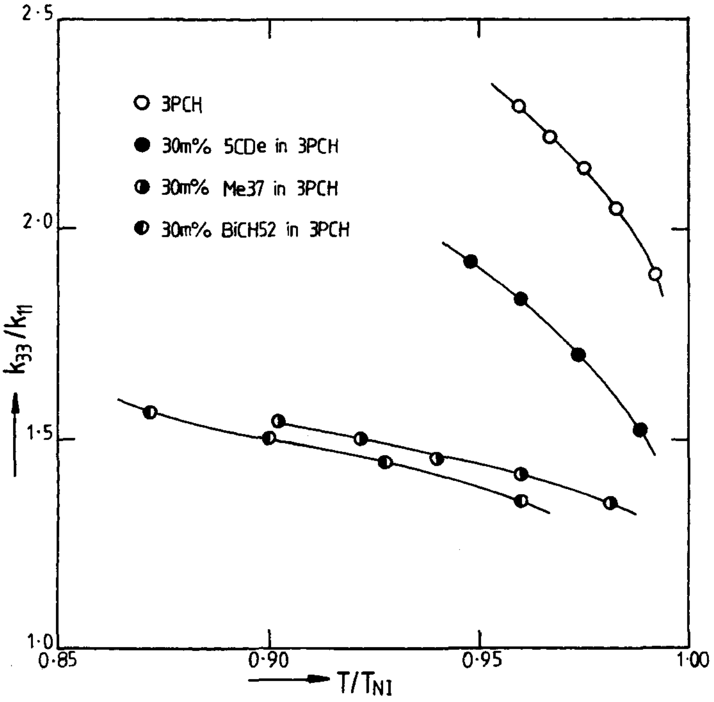


FIGURE 6 k_{33}/k_{11} of 3PCH and its mixtures.

permittivity measurements. Chandrasekhar calculated that the discontinuity $\delta\bar{\epsilon}$ at T_{NI} observed in *p*-cyano nematics could be explained if the molecules were anti-parallel aligned.[1] Also the small temperature dependence of $\bar{\epsilon}$ and ϵ_{is} found near T_{NI} in *p*-cyano nematics can be attributed to the anti-parallel local ordering of the molecules changing close to T_{NI} and compensating for the Debye $1/T$ dependence.[11] Measurements of the anisotropic and isotropic Kirkwood dipole correlation factors,[12] calculated from the molecular polarizabilities, dipole moments, and permittivities of *p*-cyano nematogens yield values less than one,[13,14,15] which are also indicative of considerable anti-parallel local ordering.

X-ray studies of mixtures containing only *p*-cyano nematogens indicate that an interdigitated structure exists at all concentrations.[16] These results, together with the permittivity measurements described previously, suggest that the anti-parallel local ordering is maintained in these mixtures, whereas, there is evidence of a structural change occurring when *p*-dialkyl nematogens are added to *p*-cyano nematics. These mixtures often exhibit unusual phase diagrams[17] as illustrated in Figure 7 which shows the presence of an "injected" smectic A phase in the mixtures of 7CB, 7PCH, and 7BCO with Me37, even though the pure materials themselves do not exhibit smectic phases. X-ray studies of "layer spacings" show that the repeat distance changes rapidly when a *p*-dialkyl nematogen is added to a *p*-cyano nematogen;[3,18] this is illustrated in Figure 8 which shows the "layer spacings" for 9CB as a function of Me37 concentration. The results indicate that the molecular structure changes from bilayer to monolayer with the addition of 30 to 40 molar % of Me37. The permittivity results described previously show that the *p*-cyano nematic characteristics of a discontinuity of $\bar{\epsilon}$ of a few percent and a low $d\bar{\epsilon}/dT$ near T_{NI} are rapidly lost when a *p*-dialkyl nematogen is added. In fact, mixtures with *p*-dialkyl nematogen concentrations greater than 40 molar % exhibit the more classical permittivity properties of the *p*-dialkyl nematic. Thus both the X-ray and the permittivity results imply that the addition of the *p*-dialkyl nematogen reduces the anti-parallel local ordering of the *p*-cyano nematic.

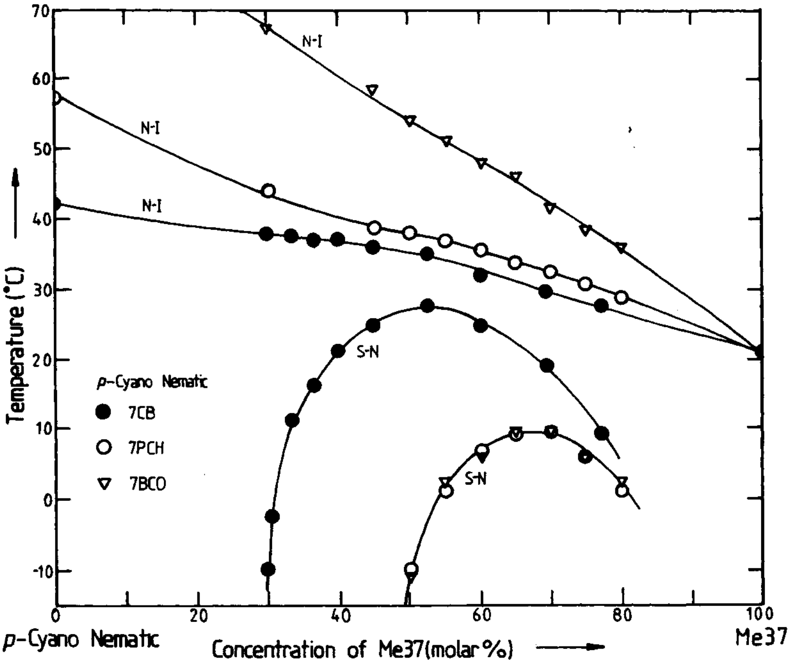


FIGURE 7 Phase diagram of 7CB, 7PCH, and 7BCO in Me37.

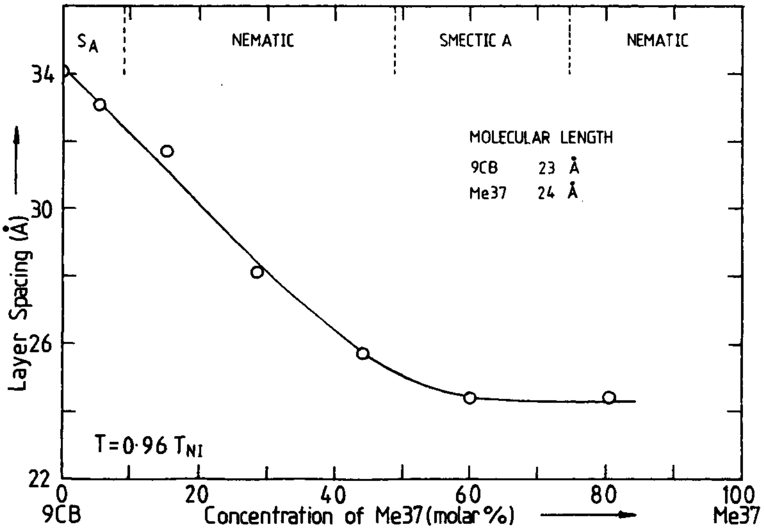


FIGURE 8 X-ray "layer spacings" of 9CB/Me37 mixtures.

These results suggest that the large reduction in k_{33}/k_{11} observed when *p*-dialkyl nematogens are added to *p*-cyano nematics can be attributed to a reduction in the anti-parallel local ordering. This explains why similar large changes in k_{33}/k_{11} are not found in mixtures containing only *p*-cyano nematogens in which the anti-parallel local ordering tends to be preserved. However, it has recently been suggested[15] that increased anti-parallel correlation decreases k_{33}/k_{11}. The evidence for this suggestion was the observation of a connection between k_{33}/k_{11} and the Kirkwood correlation factors of the isotropic phase of *p*-cyano nematogens obtained using calculated molecular dipole moments. Contrary to this conclusion, recent molecular dipole moment measurements[19] have enabled a comparison to be made between isotropic Kirkwood correlation factors and k_{33}/k_{11} for most of the compounds in Table II, and no systematic trend was observed. Also, as these measurements were made using the isotropic phase, they are not necessarily relevant to properties of the nematic phase.

CONCLUSIONS

X-ray studies and permittivity measurements indicate that the anti-parallel local ordering characteristic of *p*-cyano nematics can be significantly reduced by the addition of *p*-dialkyl nematogens. Measurements of the elastic constants of such mixtures show a much reduced k_{33}/k_{11} compared with the pure *p*-cyano nematics and this suggests that the effect of the anti-parallel local ordering is to increase k_{33}/k_{11}. These results are important for device applications since the low k_{33}/k_{11} of these *p*-cyano/*p*-dialkyl nematic mixtures makes them useful materials for multiplexed twisted nematic displays.

Acknowledgments

We wish to thank BDH Chemicals Ltd, Mr. S. M. Kelly of Hull University, E. Merck and F. Hoffman-La Roche & Co Ltd for supplying the liquid crystals. We also thank Dr. D. G. McDonnell, Dr. R. J. A. Tough, and Professor A. J. Leadbetter for valuable discussions, and Dr. G. J. Brownsey and Miss M. A. Mayo for assistance with some of the experiments.

References

1. N. V. Madhusudana and S. Chandrasekhar, *Proceedings of the International Liquid Crystals Conference, Bangalore,* December 1973, *Pramana Supplement I,* p 57.
2. A. J. Leadbetter, R. M. Richardson and C. N. Colling, *J. Phys. (Paris)*, **36,** 37 (1975).
3. J. E. Lydon and C. J. Coakley, *J. Phys. (Paris)*, **36,** 45 (1975).
4. R. J. A. Tough and E. P. Raynes, *Mol. Cryst. Liq. Cryst. Lett.,* **56,** 19 (1979).
5. M. G. Clark, E. P. Raynes, R. A. Smith and R. J. A. Tough, *J. Phys. D: Appl. Phys.,* **13,** 2151 (1980).
6. M. Schadt, *J. Chem. Phys.,* **56,** 1494 (1972).

7(a) B. R. Ratna, M. S. Vijaya, R. Shashidhar and B. K. Sadashiva, *Proceedings of the International Liquid Crystals Conference, Bangalore,* December 1973, *Pramana Supplement I,* p 69.

7(b) B. Ratna and R. Shashidhar, *Pramana,* **6,** 278 (1976).

8. Hp. Schad, G. Baur and G. Meier, *J. Chem. Phys.,* **71,** 3174 (1979).
9. W. H. de Jeu and Th. W. Lathouwers, *Z. Naturforsch.,* **29a,** 905 (1974).
10. W. Maier and G. Maier, *Z. Naturforsch.,* **16a,** 262 (1961).
11. M. J. Bradshaw and E. P. Raynes, *Mol. Cryst. Liq. Cryst. Lett.,* **72,** 73 (1981).
12. P. Bordewijk, *Physica,* **75,** 146 (1974).
13. D. A. Dunmur, M. R. Manterfield, W. H. Miller and J. K. Dunleavy, *Mol. Cryst. Liq. Cryst.,* **45,** 127 (1978).
14. C. Druon and J. M. Wracnevier, *Ann. Phys.,* **3,** 199 (1978).
15. Hp. Schad and M. A. Osman, *J. Chem. Phys.,* **75,** 880 (1981).
16. A. J. Leadbetter and A. Mehta, private communication.
17. C. S. Oh, *Mol. Cryst. Liq. Cryst.,* **42,** 1 (1977).
18. B. Engelen, G. Heppke, R. Hopf and F. Schneider, *Mol. Cryst. Liq. Cryst.,* **49,** 193 (1979).
19. D. A. Dunmur, private communication.