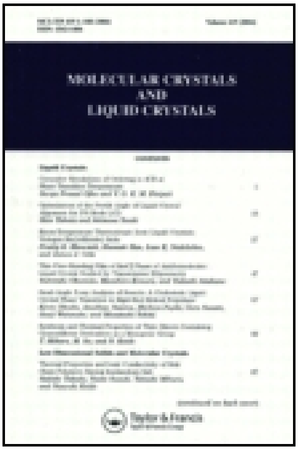


Molecular Crystals and Liquid Crystals

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

Molecular Properties of Pentyl-Cyano Mesogens Having Different Core Structures

D. A. Dunmur [a] & A. E. Tomes [a]

[a] Department of Chemistry, The University, Sheffield, S3 7HF, United Kingdom

To cite this article: D. A. Dunmur & A. E. Tomes (1983): Molecular Properties of Pentyl-Cyano Mesogens Having Different Core Structures, Molecular Crystals and Liquid Crystals, 97:1, 241-253

To link to this article: http://dx.doi.org/10.1080/00268948308073154

Mol. Cryst. Liq. Cryst., 1983, vol. 97, pp. 241–253
0026-8941/83/9704–0241/$18.50/0

Molecular Properties of Pentyl-Cyano Mesogens Having Different Core Structures*

D. A. DUNMUR and A. E. TOMES

Department of Chemistry, The University, Sheffield, S3 7HF, United Kingdom

(Received January 26, 1983)

The molecular properties of polarizability, polarizability anisotropy and dipole moment have been measured for a series of mesogenic molecules having a terminal cyano group and a terminal n-pentyl chain. Molecules investigated were of the form n-pentyl-X-cyano, where X was biphenyl, cyclohexyl-phenyl, phenyl-cyclohexyl, bicyclohexyl and bicyclo-octyl-phenyl. Measured polarizabilities were compared with bond additivity calculations for the molecules having different alkyl chain conformations. The relative nematic stabilities of the mesogens and their physical properties are discussed in terms of their measured molecular properties.

INTRODUCTION

In order for a molecule to exhibit a liquid crystalline phase, it must satisfy certain structural requirements, and much research effort has been directed toward correlating liquid crystalline behavior with molecular structure.[1,2] As a result of this work it has become clear that it is often very difficult to predict the effect of changes in molecular structure on the stability and properties of liquid crystals, and the relationships between structure and properties are very subtle. Such subtleties are not included in the existing theories of liquid crystals, which usually model the liquid crystal molecule by a rigid axially symmetric, impenetrable object. Some attempts have been made to include elements of flexibility[3] or biaxiality[4] into the models, but our real understanding of liquid crystalline behavior in terms of molecu-

---

*Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

lar structure is still very limited. In reality the situation is very complicated because, in addition to molecular structure and properties, many-body interactions between molecules must also be considered. Furthermore the observation of a liquid crystal phase at achievable temperatures and pressures may be obscured by the formation of a crystalline phase. Thus a complete theory of solid and fluid phases is necessary to understand the stability of liquid crystalline phases.

Within the context of existing theories of nematic liquid crystals and their physical properties, certain molecular parameters can be identified as being of particular significance. For example in the Maier-Saupe theory[5] of nematic stability, only attractive intermolecular forces are considered, and the nematic to isotropic transition temperature T_{NI} is predicted to vary as $I(\Delta\alpha)^2/V^2$, where I is the ionization potential, $\Delta\alpha$ is the polarizability anisotropy and V is the molecular volume. Hard particle theories[6] of nematic liquid crystals restrict attention to repulsive interactions and predict temperature independent order parameters which are much higher than normally measured. The only parameters in hard particle theories are the volume and length-width ratio of the molecules which are normally assumed to be sphero-cylinders; these theories predict that T_{NI} increases as the length-width ratio and density increases. Combining mean field and hard particle theories leads to a generalized van der Waals description of nematic order.[7,8] In this approach it is assumed that the attractive part of the intermolecular potential can be written as a sum of isotropic and anisotropic contributions, while the repulsive interactions are accounted for by an angle dependent excluded volume. The resulting single particle pseudopotential is of the form:

$$\varepsilon = -u_0\rho - u_2\rho P_2(\cos\theta)\langle P_2(\cos\theta)\rangle \tag{1}$$

where ρ is the number density, $P_2(\cos\theta)$ is the second Legendre polynomial and the angular brackets denote an ensemble average. The isotropic (u_0) and anisotropic (u_2) energy parameters in this expression both depend on the attractive and repulsive parts of the intermolecular potential, and in practice the major part of u_2 is determined by the *isotropic* attractive forces.[9]

For a model of interacting triaxial ellipsoids in which attractive forces were neglected, Gelbart and Barboy[10] predicted that the transitional order parameter decreased as the ellipsoid deviated from axial symmetry, suggesting that the width-breadth ratio or biaxiality of a molecule might be an important factor in determining nematic stability. Other factors which may play a role in stabilizing liquid crystal phases are dipole-dipole interactions,[11] molecular shape and flexibility, although it is difficult to quantify the latter two contributions.

With regard to physical properties such as electric permittivity, refractive indices and magnetic susceptibilities, it is much easier to correlate the macroscopic properties with molecular parameters,[12] primarily because these properties are single particle properties, i.e. they are proportional to the number density. Elastic properties do not fall into this category and are a direct manifestation of intermolecular interactions; their dependence on molecular properties is therefore much more complicated. Most theoretical models for the elasticity of nematics[13-16] concentrate on the importance of molecular dimensions (i.e. length-width ratio); other calculations[17,18] using empirical intermolecular potentials also demonstrate the importance of the anisotropy of the potential. No systematic dependence of elastic constants on molecular properties such as polarizability and dipole moment has been observed,[19] but short range effects[20] resulting from dipole-dipole correlation or other sources may influence elastic properties.

To test the proposed relationships between liquid crystal properties and molecular properties, we have measured some molecular parameters for a series of mesogenic molecules having identical end groups but different core structures. The molecules have the basic structure C_5H_{11}—X—Y—CN, where X and Y may be phenyl, cyclohexyl or bicyclo-octyl. The properties measured for each molecule were dipole moment, mean polarizability, polarizability anisotropy and molecular volume. The orientation of the dipolar axis with respect to the principal axes of the polarizability tensor was calculated using a number of bond additivity schemes for the polarizabilities. Comparison of calculated and experimental values of the polarizabilities provided a test of the additivity schemes and also yielded information on the conformation of the terminal alkyl chain.

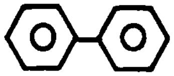
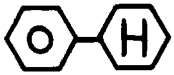
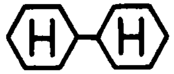
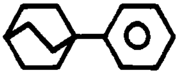
EXPERIMENTAL

The mesogens studied in this investigation are given in Table I. All measurements were carried out on dilute *p*-xylene solutions at concentrations up to 5% by weight of mesogen. The materials were used as supplied, but for the electro-optical experiments the solvent (*p*-xylene) was filtered through a 0.25 μm millipore filter before use.

Dipole moments and mean polarizabilities were obtained from electric permittivity and refractive index measurements on the solutions. Molar volumes were evaluated from accurate density measurements on the solutions over a range of concentrations. The molar Kerr constants of the solutions were measured for different solution compositions over a range of temperatures, and analysis of these measurements provides values for

TABLE I

Materials

Compound	Nematic range	Abbreviation
C_5H_{11}  CN	22.5–35.2°C	CB5
C_5H_{11}  CN	30.0–55.0°C	PCH5
C_5H_{11}  CN	$(T_{NI})_{virtual}$–25°C	reversed PCH5
C_5H_{11}  CN	65.0–88.0°C	CCH5
C_5H_{11}  CN	62.0–101.0°C	BCO5

the polarizability anisotropies. Our experimental techniques for making these measurements have been reported in an earlier paper[21] and will not be described here.

RESULTS

Values for various molecular parameters obtained for the mesogens studied are listed in Table II. Results for CB5 have been previously reported[21] by us, but the measurements were repeated in this work and are included in the table for completeness. In order to extract a value for the polarizability anisotropy from Kerr constant measurements, it is necessary to assume axial symmetry for the polarizability tensor and also to know the angle (θ) between the dipolar axis and the axis of maximum polarizability in the molecule. Neglecting hyperpolarizabilities, the molar Kerr constant at infinite dilution for a molecule with a spheroidal polarizability ellipsoid is:

$$ {}_mK_\infty = \frac{N}{405\varepsilon_0 kT}\left\{(\Delta\alpha)^2 + \frac{\Delta\alpha\mu^2}{2kT}(3\cos^2\theta - 1)\right\} \qquad (2)$$

In principle θ can be determined by fitting the variable temperature measurements, but for small θ the precision of our results is not sufficient to allow this. The angle θ has therefore been obtained by calculation; the consequent small uncertainty attached to the angle will not significantly affect the derived values for the polarizability anisotropy. Table III lists our

TABLE II

Molecular properties

Compound	Mean polarizability (10^{-40} $J^{-1}C^2m^2$)	Polarizability anisotropy (10^{-40} $J^{-1}C^2m^2$)	Dipole moment (10^{-30} Cm)	Ionisation potential (10^{-19} J)	Molar volume (10^{-6} m^3)
CB5	37.5 ±0.2	19.4 ±0.9	15.9 ±0.2	7.0	247
PCH5	36.2 ±0.2	16.0 ±0.8	13.8 ±0.2	8.5	265
Reversed PCH5	36.2 ±0.2	12.2 ±0.6	12.1 ±0.2	8.5	265
CCH5	35.5 ±0.2	12.6 ±0.6	12.0 ±0.2	8.5	282
BCO5	38.8 ±0.2	16.6 ±0.8	13.6 ±0.2	8.4	278

TABLE III

Calculated and experimental molar Kerr constants

	Molar Kerr constants (10^{-24} $C^2J^{-2}m^5$)							
	PCH5		Rev-PCH5		CCH5		BCO5	
Temperature (°C)	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.
10	3.45	3.34	2.01	2.05	1.99	1.95	3.55	3.49
20	3.23	3.19	1.88	1.90	1.86	1.86	3.31	3.29
30	2.92	3.03	1.76	1.78	1.74	1.77	3.10	3.10
40	2.83	2.87	1.65	1.62	1.63	1.67	2.91	2.92
50	2.57	2.72	1.55	1.51	1.53	1.59	2.74	2.76

measured values of ${}_{m}K_{\infty}$ together with those calculated using Eq. (2) and the derived molecular parameters from Table II. The agreement at all temperatures is good, indicating that the molecular parameters obtained are fully consistent with our Kerr effect measurements.

CALCULATIONS

The prediction of molecular properties from bond or group properties has frequently been used[22,23] for mesogenic molecules because of the lack of experimental data on the free molecule properties. While the simple bond additivity scheme is probably satisfactory for dipole moments, at least of nonconjugated molecules, there are difficulties in predicting the components of the polarizability tensor from assumed bond polarizabilities. For flexible molecules, the contributions of different conformations to the average measured polarizability must be considered, and this is of particular significance in mesogenic molecules with long alkyl chains. In this section we report calculations of the molecular polarizability tensor for the various molecules listed in Table I. We have used three different bond additivity schemes and have also calculated the effect of chain flexibility on the results.

The method of calculation is to assume a particular geometry for the molecule, sum the bond polarizability components in an arbitrary fixed axis system and then diagonalize the resultant tensor to obtain the principal polarizabilities and the orientation of the principal axes with respect to the molecular frame. Results for different conformations can be obtained and an average calculated using the appropriate statistical weights.

All-*trans*-conformations

For these calculations the conformations of the molecules were assumed to be as illustrated in Figure 1. Chain positions 1 and 2 were considered to be equally probable for CB5, reversed PCH5 and BCO5, but for PCH5 and CCH5 the relative probabilities of 1 and 2 were assumed to be 0.845 and 0.155 respectively. These values were obtained from the relative energies of the $tg^{\pm}t$ and ttt conformations of the all-*trans*-alkyl chain with respect to the chair cyclohexane ring (see below).

Using values for the bond polarizabilities from the literature[24] and reproduced in Table IV, the principal polarizabilities and angles between the major axis and the dipolar axis (assumed to be along the CN bond) were calculated, and the results are given in Table V. In these calculations, no allowance was made for conjugation between the aromatic rings and the cyano-group and the aromatic ring. Including the effects of conjugation[25] produced a second set of bond polarizabilities also listed in Table IV. These enhanced bond polarizabilities were obtained empirically by requiring good agreement to be maintained between the calculated and measured mean polarizabilities. Revised values for the molecular polarizability components using the enhanced bond polarizabilities are also given in Table V.

Recently Jernigan has suggested[26] that induced-dipole-induced-dipole interactions in all-*trans*-alkyl chains can increase the effective polarizability anisotropy of each segment by a factor of two. Incorporating this effect into the calculations gives a new set of molecular polarizability anisotropies which are listed in Table V. Since the Jernigan scheme does not calculate the influence of dipolar interactions on the individual components of the bond polarizability tensor, we have not calculated the separate components of the molecular polarizabilities.

Statistically averaged conformations

Different molecular conformations result from internal rotations about the carbon-carbon bonds in the alkyl chain. For simplicity we adopt the three

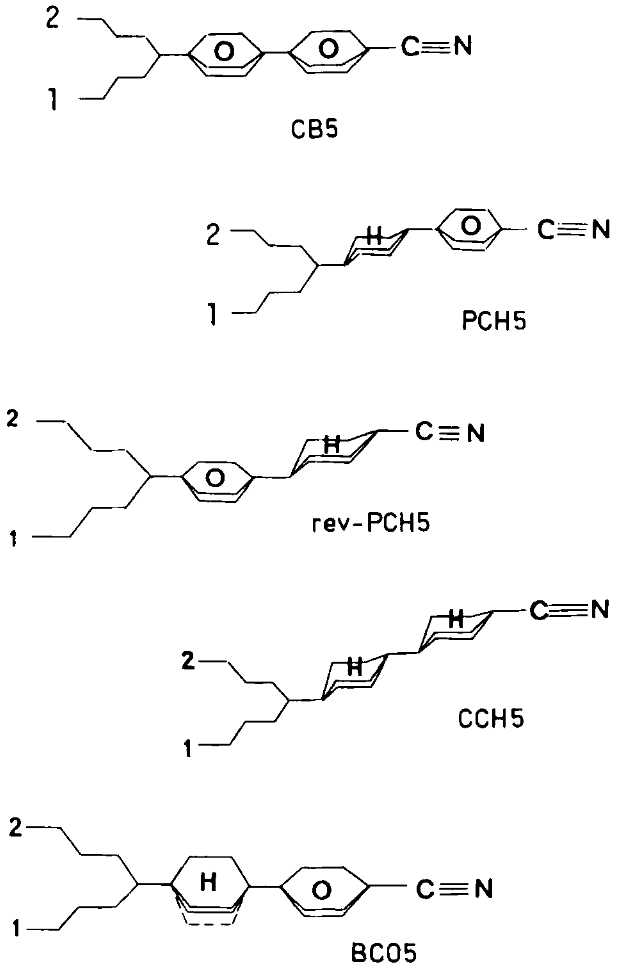


Figure 1 Molecular structures

rotational isomeric state model developed by Flory[27] in which the dihedral angle between two carbon-carbon bonds separated by a third can be 60°(g^+), 180°(t) or 300°(g^-). The energy of the all-*trans*-conformation is taken as zero, and the relative energies (E_i) of the other conformations of the pentyl chain may be calculated from the isomeric state energies of $E_{tg}{}^{\pm} = E_{g}{}^{\pm}{}_{g}{}^{\pm} = 2.1$ kJ mol^{-1} and $E_{g}{}^{\mp}{}_{g}{}^{\pm} = 12.5$ kJ mol^{-1}.[27] The polarizability tensor was evaluated for each conformation and an average calculated by attributing a statistical weight to each conformation of $\exp(-E_i/RT)$. Conformations involving $g^{\mp}g^{\pm}$ contributed less than 1% of

TABLE IV

Bond polarizabilities in units of $10^{-40}\ J^{-1}C^2m^2$

Bond	$\alpha_\parallel$	$\alpha_\parallel^*$	$\alpha_\perp$
$C_{sat}—C_{sat}$	1.091	1.091	0.300
$C_{ar}—C_{ar}$	2.582	2.582	0.490
$C_{sat}—C_{ar}$	1.091	1.091	0.300
$C_\phi—C_\phi$		3.061	0.490
C_{sat}—CN		2.471	0.300
C_{ar}—CN		4.675	0.300
C—N	3.450	3.450	1.558
C—H	0.712	0.712	0.712

*Enhanced bond polarizabilities resulting from conjugation.

The subscripts sat and ar refer to bonds between saturated and aromatic carbon atoms, and ϕ indicates a bond within biphenyl rings.

the total because of their high energy, and they were excluded from the analysis.

For CB5, reversed PCH5 and BCO5, interactions between the chain and the core were excluded; however, for PCH5 and CCH5 the statistical weight of a particular conformation depended on the conformation of the chain segment attached to the cyclohexyl ring. Finally it should be pointed out that conformations corresponding to $tg^{\pm}t$ and *ttt* contributed equally to the molecular polarizability anisotropy.

The results of our calculations of the polarizability components including all possible conformations are given in Table VI. The differences between the values in Tables V and VI are fairly small; this reflects the fact that most of the polarizability of these molecules comes from the core and cyano group, and also that the *ttt* and $tg^{\pm}t$ states account for about 40% of the conformations.

DISCUSSION

The most satisfactory agreement between the calculated and measured polarizabilities is obtained if the enhanced bond polarizabilities are assumed and induced-dipole-induced-dipole effects are included. Furthermore, our calculations indicate that the chain conformation is likely to be ttt or $tg^{\pm}t$. This result is in agreement with results obtained from light scattering measurements on the homologous series of alkyl cyanobiphenyls,[28,29] where it was concluded that for less than six carbon atoms in the chain, only the all-trans-conformations contributed significantly to the polarizability anisotropy.

TABLE V

Calculated principal polarizabilities for *ttt* and $tg^{\pm}t$ conformations

Compound	Simple bond polarizabilities (10^{-40} $J^{-1}C^2m^2$)							Enhanced bond polarizabilities							Including induced-dipole effects
	$\alpha_\parallel$	$\alpha_\perp$	$\alpha'_\perp$	$\bar{\alpha}$	γ	$\overline{\Delta\alpha}$	θ^0	$\alpha_\parallel$	$\alpha_\perp$	$\alpha'_\perp$	$\bar{\alpha}$	γ	$\overline{\Delta\alpha}$	θ^0	$\overline{\Delta\alpha}$
CB5	41.6	25.1	34.9	33.9	14.3	11.6	0.0	48.1	25.1	37.7	36.9	20.6	16.7	0.0	18.4
PCH5	40.5	28.3	34.6	34.5	10.5	9.1	4.0	44.0	28.3	34.6	35.7	13.7	12.6	3.1	15.1
rev-PCH5	40.5	28.3	34.6	34.5	10.5	9.1	4.0	41.8	28.3	34.6	34.9	11.7	10.3	4.0	11.7
CCH5	39.2	32.1	33.5	35.0	6.5	6.4	10.3	40.6	32.1	33.5	35.4	7.9	7.8	8.8	12.0
BCO5	43.7	32.0	36.9	36.5	11.0	11.0	0.0	47.3	32.0	36.9	38.7	13.5	12.8	0.0	15.3

$$\overline{\Delta\alpha} = \alpha_\parallel - (\alpha_\perp + \alpha'_\perp)/2$$

$$\gamma = ((\alpha_\parallel - \alpha_\perp)^2 + (\alpha_\parallel - \alpha'_\perp)^2 + (\alpha_\perp - \alpha'_\perp)^2)^{1/2}/2^{1/2}$$

For strongly dipolar molecules $\overline{\Delta\alpha}$ is the quantity measured by the static Kerr effect, but the optical Kerr effect and depolarized light scattering measures γ^2.

TABLE VI

Calculated principal polarizabilities for statistically-averaged conformations

		Simple bond polarizabilities						Enhanced bond polarizabilities					Including induced-dipole effects
Compound	$\alpha^{\parallel}$	$\alpha_{\perp}$	$\alpha'_{\perp}$	γ	$\overline{\Delta\alpha}$	θ^0	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\alpha'_{\perp}$	γ	$\overline{\Delta\alpha}$	θ^0	$\overline{\Delta\alpha}$
CB5	41.2	25.4	35.7	13.9	10.6	0.0	48.1	24.7	39.3	20.1	15.7	0.0	16.3
PCH5	40.0	28.6	35.4	10.0	8.1	3.8	43.6	28.6	35.4	13.1	11.7	2.9	13.0
rev-PCH5	40.0	28.6	35.4	10.0	8.1	3.8	41.4	28.6	35.4	11.1	9.5	3.9	10.7
CCH5	38.8	32.4	34.4	5.7	5.4	10.0	40.2	32.4	34.4	7.0	6.8	8.5	10.0
BCO5	43.3	32.3	37.7	9.5	8.3	0.0	46.9	32.3	37.7	12.8	11.9	0.0	13.3

Magnetic resonance measurements[30] of the ordering matrices of chain segments in nematic CB5 suggest that there is considerable chain flexibility even in the ordered liquid crystalline state, and the order parameter averaged over all conformations[31] is substantially less than the order parameter resulting from the all-trans-conformation. Our conclusions on chain conformation are based on the assumption of a particular bond anisotropy for the chain segments. The work of Jernigan[26] suggests that the segment polarizability depends on the chain conformation, but we have not included this effect in our calculations.

From our measurements of polarizability, ionization potential and molar volume there is no correlation between the Maier-Saupe predictions of the nematic to isotropic transition temperatures and observed values. Neither do the results for the mean polarizability give any support to the generalized van der Waals theory which suggested that isotropic dispersion forces might be a dominant factor in stabilizing the nematic phase since the mean polarizabilities for the mesogens studied are approximately equal. The overall length of the molecules is very nearly constant, and variations in the length-width ratio are relatively small. Values for the ring sizes calculated from bond lengths and van der Waals radii are given in Table VII. T_{NI} appears to increase as the length-width ratio decreases, but the more symmetric molecules do have higher transition temperatures than the lath-like CB5. There is some theoretical basis for this observation from the work of Gelbart and Barboy[10] who calculated that nematic stability was overestimated by the assumption of cylindrical symmetry.

In this discussion of nematic stability the role of core flexibility has been neglected. No theoretical models have attempted to include this as a stabilizing influence, but it has been suggested[32] as a possible explanation for the relative stabilization of some nematogens when a rigid aromatic ring is replaced by a more flexible cyclohexyl ring. The case of reversed PCH5 is interesting in this respect, since its physical properties are almost identical with CCH5, but it does not form a stable nematic phase. One explanation is that the lack of flexibility in the aromatic ring attached to the alkyl chain prevents the adoption of linear conformations, which would enhance the

TABLE VII

Ring sizes and width-breadth ratios

Ring	Width (Å)	Breadth (Å)	Ratio
Phenyl	3.4	6.7	2.0
Cyclohexyl	5.3	6.7	1.3
Bicyclooctyl	6.3	6.3	1.0

TABLE VIII

Physical properties of mesogens at a reduced temperature of 0.96

Compound	Dielectric anisotropy	Birefringence	Bend-splay elastic constant ratio
CB5	12.5	0.20	1.46
PCH5	11.0	0.125	1.77
CCH5	4.0	0.05	1.59
BCO5	10.0	0.14	2.35

anisotropy of intermolecular interactions. Further evidence for this is provided by the molecule reversed BCO5, which although it does not have a stable nematic phase, has a virtual T_{NI} at 50°C.[33]

Values for the physical properties of the nematic phases of the compounds studied are listed in Table VIII. The birefringence and dielectric anisotropy of the mesophases increase as the molecular polarizability anisotropy and the square of the dipole moment increase. There is significant dipole-dipole correlation in the more polar nematogens which complicates the simple interpretation of dielectric properties.[34] It is difficult to correlate the elastic constants with any molecular property, and the only molecular feature that has emerged so far as being significant is the length-width ratio.[17] However this cannot explain the increase in the ratio of bend-splay elastic constants in going from CB5 to BCO5. One possible explanation is based on the strong intermolecular correlation that exists in the nematic phases of cyano-phenyl liquid crystals.[35] The effective length-width ratio then refers to associated pairs rather than individual molecules, and while this might explain the variation in elastic constant ratios for CB5, PCH5 and BCO5, the mesogen CCH5 is anomalous.

In conclusion, the prediction of liquid crystalline properties from molecular parameters is still far from being possible. Even the nematic to isotropic transition temperatures cannot be correlated in any simple way with the molecular properties that are thought to determine them. The absence of reliable empirical relationships between liquid crystalline behavior and molecular structure suggests that simple theories are unlikely to be successful in explaining the properties of liquid crystals, and features such as molecular flexibility and short range order will have to be included.

Acknowledgments

The authors wish to thank B. D. H. Chemicals Ltd. and Professor George Gray of Hull University for providing us with the materials used in this investigation. We are grateful to the United Kingdom Science and Engineering Research Council for financial support and for the award of a Research Studentship to one of us (A.E.T.).

References

1. G. W. Gray, Proceedings of the Eighth International Liquid Crystal Conference, *Mol. Cryst. Liq. Cryst.*, **63**, 3 (1981).
2. W. H. de Jeu, Proceedings of the Eighth International Liquid Crystal Conference, *Mol. Cryst. Liq. Cryst.*, **63**, 83 (1981).
3. A. Wulf and A. G. De Rocco, *J. Chem. Phys.*, **55**, 12 (1971).
4. G. R. Luckhurst, C. Zannoni, P. L. Nordio and U. Segre, *Mol. Phys.*, **30**, 1345 (1975).
5. W. Maier and A. Saupe, *Z. Naturforsch.*, **14a**, 882 (1959).
6. M. A. Cotter, *Molecular Physics of Liquid Crystals* (Eds. G. R. Luckhurst and G. W. Gray), Academic Press, London, 1979, p. 169.
7. W. M. Gelbart and B. A. Baron, *J. Chem. Phys.*, **66**, 207 (1977).
8. M. A. Cotter, *J. Chem. Phys.*, **66**, 4710 (1977).
9. W. M. Gelbart and A. Gelbart, *Mol. Phys.*, **33**, 1387 (1977).
10. W. M. Gelbart and B. Barboy, *Mol. Cryst. Liq. Cryst.*, **55**, 209 (1979).
11. S. Chandrasekhar and N. V. Madhusudana, *Pramana, Suppl.* **No. 1**, 1975, p. 57.
12. W. H. de Jeu, *Physical Properties of Liquid Crystalline Materials*, Gordon and Breach, New York, 1980.
13. R. G. Priest, *Phys. Rev.*, **A7**, 720 (1973).
14. A. Poniewierski and J. Stecki, *Mol. Phys.*, **38**, 1931 (1979).
15. W. H. Gelbart and A. Ben Shaul, *J. Chem. Phys.*, **77**, 96 (1982).
16. B. W. van der Meer, F. Postma, A. J. Dekker and W. H. de Jeu, *Mol. Phys.*, **11**, 1 (1982).
17. T. W. Ruijgrok and K. Sokalski, *Physica*, **111A**, 45 (1982).
18. D. A. Dunmur and W. H. Miller, *Chem. Phys. Lett.*, **86**, 353 (1982).
19. F. Leenhouts and A. J. Dekker, *J. Chem. Phys.*,**74**, 1956 (1981).
20. Hp. Schad and M. A. Osman, *J. Chem. Phys.*, **75**, 880 (1981).
21. D. A. Dunmur, M. R. Manterfield, W. H. Miller and J. K. Dunleavy, *Mol. Cryst. Liq. Cryst.*, **45**, 127 (1978).
22. P. P. Karat and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **36**, 51 (1976).
23. P. L. Sherrell and D. A. Crellin, *J. Phys. (Paris)*, **40**, 211 (1979).
24. C. G. Le Fevre and R. J. W. Fevre, *Rev. Pure and Appl. Chem.*, **5**, 261 (1955).
25. R. J. W. Le Fevre, *Adv. Phys. Org. Chem.*, **3**, 1, (1965).
26. R. L. Jernigan and S. Miyazawa, *Molecular Electro-optics* (Ed. S. Krause), Plenum Press, New York, 1981, p. 163.
27. P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley, New York, 1969, p. 55.
28. J. R. Lalanne, B. Lamaire, J. Rouch, C. Vaucamps and A. Proutiere, *J. Chem. Phys.*, **73**, 1927 (1980).
29. J. R. Lalanne, B. Lemaire, J. Rouch, C. Vaucamps and A. Proutiere, *Mol. Cryst. Liq. Cryst.*, **66**, 1 (1981).
30. J. W. Emsley, G. R. Luckhurst and C. P. Stockley, *Mol. Phys.*, **44**, 565 (1981).
31. J. W. Emsley, G. R. Luckhurst and C. P. Stockley, *Proc. Roy. Soc.*, **A381**, 117 (1982).
32. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **53**, 147 (1979).
33. G. W. Gray, N. Carr and D. G. McDonnell, Proceedings of the Ninth International Liquid Crystal Conference.
34. D. A. Dunmur and W. H. Miller, *Mol. Cryst. Liq. Cryst.*, **60**, 281 (1980).
35. A. J. Leadbetter and A. I. Mehta, *Mol. Cryst. Liq. Cryst. Lett.*, **75**, 51 (1981).