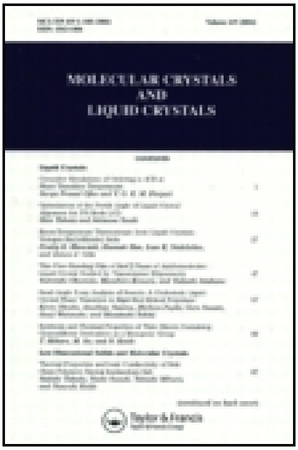

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Zvetkow Twist Viscosity Measurements of Some Nematic Liquid Crystals

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ZVETKOW TWIST VISCOSITY MEASUREMENTS OF SOME NEMATIC LIQUID CRYSTALS

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Zvetkow twist viscosity measurements are reported for a series of cyanobiphenyl liquid crystals and their eutectic mixtures in the nematic phase. The values obtained exhibit an odd–even variation. If the data are plotted against a reduced density, they divide into two groups, one corresponding to the odd and the other to the even series. This is attributed to effects of the configuration of the alkyl chain on the molecular packing density in the nematic phase. Using the Maier–Saupe theory, interaction energies are derived.

INTRODUCTION

The generation of long range orientational order is the principal difference between liquid crystalline and isotropic liquids. Recent studies by Gray[1] have shown that a wide variety of organic structures are capable of exhibiting liquid crystalline behavior. Although details of the intermolecular interactions necessary for the formation of a particular mesophase are far from well understood, it is clear that subtle changes in the aspect ratio of the molecule and the presence or absence of dipolar and weak electrostatic interactions can profoundly influence the range of stability of a particular mesophase, and the number of such phases which can exist. Recent reviews[2-4] of liquid crystals have indicated that many of their properties can be described by extensions to traditional

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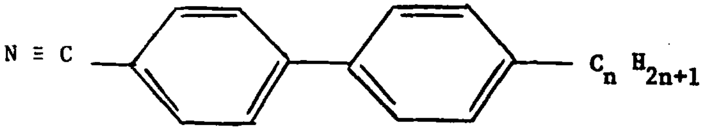
[a] Deceased.

statistical mechanical models for liquids. However, order in liquid crystals is macroscopically manifest in the anisotropy of quantities such as magnetic susceptibility, dielectric permittivity, and of course viscosity. A treatment of the hydrodynamic properties of nematic liquid crystals has been formulated using continuum theory by Ericksen[5] and Leslie.[6] This present study reports measurements of the Zvetkow twist viscosity coefficients for a series of liquid crystals which possess a common molecular structure, and also certain eutectic mixtures. Our aim is to investigate the way in which molecular interactions may influence the twist coefficient and improve our understanding of the factors influencing the formation of the nematic phase. Changes in the length of the hydrocarbon tail influence the ability of the molecules to pack together, but do not significantly influence the dipolar or van der Waals contributions to the intermolecular potential. These measurements therefore allow an investigation of the manner in which local molecular interactions may contribute towards the macroscopic behavior of these materials.

EXPERIMENTAL DETAILS

Materials

Two classes of liquid crystal are examined in this study; *N*-(4-methoxybenzylidene)-4′-*n*-butylaniline (MBBA) and a homologous series of cyanobiphenyls with the general structure



with *n* in the range 1 to 12. Gray[1] has suggested that these liquid crystals should be designated *n*CB, where *n* is the length of the alkyl chain. The cyanobiphenyls were obtained from BDH and are listed in Table I. Enantiotropic liquid crystalline properties first appear at $n = 5$ and persist up to $n = 12$. The lower members form the nematic phase, but a smectic phase (smectic A) also appears from $n = 8$ onwards, 10CB and 12CB exhibiting only this latter phase. The MBBA used in this study was synthesized and freshly distilled before being measured;[7] 4-butylaniline and 4-methyoxybenzaldehyde were condensed by heating under reflux for approximately thirty hours, a Dean–Stark trap being used to remove the water generated during the reaction. On completion of the

TABLE I

Transition temperatures for the liquid crystals studied

Code	Chain length n	Transition temperature (K) T_M	T_S	T_C
5CB	5	297.1	—	308.4
6CB	6	287.6	—	302.1
7CB	7	303.1	—	315.9
8CB	8	294.6	306.6	313.6
9CB	9	315.1	321.1	322.6
E7	—	263.1	—	333.6
E12	—	263.1	—	332.1
E18	—	263.1	—	333.1
MBBA	—	293	—	320

T_M is the solid-mesophase transition, T_S the smectic-nematic transition, and T_C the nematic-isotropic transition.

reaction the product was distilled at 441 K under a pressure of 66.7 Pa and recrystallized from dry hexane. The transition temperatures for the samples studied are listed in Table I.

Zvetkow Twist Viscosity Coefficient Measurement

The apparatus used is similar in design to that described by Zvetkow,[8,9] and the geometry of the experiment is indicated in Figure 1. A small

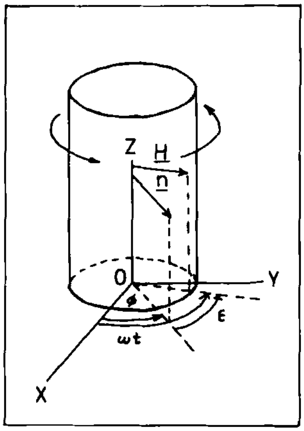


FIGURE 1 Geometry used in the Zvetkow Twist Viscosity Coefficient Measurement. H magnetic field vector, **n** director, z axis of rotation, ω rotational velocity, ϕ phase angle, ϵ phase lag angle.

circular tube filled with the sample of the nematic liquid crystal was suspended symmetrically by a torsion wire, the wire coinciding with the axis of rotation of a rotatable magnetic field. The torque developed as the field rotates was measured by the rotation of a mirror attached to the wire, and the twist viscosity follows from a plot of torque against the angular frequency of rotation of the magnetic field.

The glass tube containing the sample was 1 cm in length and had a total volume of about 0.7 ml. It was suspended inside a glass cylinder which was itself surrounded by a water jacket, with temperature control achieved by means of an external circulating bath. The temperature was measured using a thermo-couple placed within an oil filled glass insert protruding into the water jacket. The whole apparatus was placed on a heavy slate slab to eliminate effects of vibrations from the rotating magnet on the rest of the apparatus. The magnet was on a brass turntable and supported by thrust ball bearings. Rotation was achieved by a ¼ HP electric motor connected to the turntable via a 1/60 reduction gear box. The speed of the motor was controlled through an electric regulator and the angular velocity monitored using a series of photo-diodes positioned on the perimeter of the turntable. The torsion wire was constructed from Ni/Cr and had a diameter of 0.042 mm. If τ is the torque necessary to produce a twist of θ radians at the unclamped end of the wire, its torque elastic constant c is defined by

$$\tau = c\theta \tag{1}$$

and

$$c = \pi\mu r^4/2L \tag{2}$$

where μ denotes the elastic shear modulus, and r and L the radius and length of the wire, respectively. The characteristics of the wire were determined from measurement of the free oscillation frequency of the wire with various weights suspended.[10] The apparatus was calibrated as a function of temperature. Also possible effects due to magnetic impurities in the glass cell were investigated using a small quantity of a light oil as a damping liquid.

Density Measurements

Due to the high viscosity of the liquid crystals under investigation, it is not possible to measure the volume of the sample using a micropipette. Instead, therefore, the densities were measured using a digital densimeter DMA-60, thermostated by an external circulating bath. The specific volumes V_e were found to obey a Klement–Cohen relation[11,12]

$$V_e(T) = V_e^c + B(T_c - T)^{1/2} + C(T_c - T) \tag{3}$$

where V_e^c is the specific volume at the clearing temperature, B and C are constants, and T and T_c denote the temperature and clearing temperature in degrees Centigrade, respectively. The data obtained thus fit an equation of the form

$$V_e(T^*) = V_e^c + BT^{*1/2} + CT^* \tag{4}$$

where the reduced temperature $T^* = T_c - T$.

THEORY

Prost and Gasparoux[13] give an analysis of this experiment in terms of continuum theory on the basis that alignment is uniform throughout the sample, and further that no flow occurs. As Leslie[14] discusses, their assumptions ignore complications arising from the aligning influence of the container surface, but this appears to be reasonable at low rates of rotation on evidence found by Leslie, Luckhurst and Smith.[15] Since our measurements essentially employ lower rates of rotation, this existing theory is sufficient for our purposes.

In the absence of flow and with alignment uniform, the continuum equations[14] reduce to

$$\gamma_1 \mathbf{n} \times \frac{d}{dt}\mathbf{n} = \chi_a(\mathbf{n}\cdot\mathbf{H})\mathbf{n} \times \mathbf{H} \tag{5}$$

where the unit vector $\mathbf{n}$ is the director, $\mathbf{H}$ the magnetic field, γ_1 the twist viscosity coefficient, χ_a the diamagnetic susceptibility anisotropy, and t time. With an appropriate choice of Cartesian axes as in Figure 1, one considers solutions of the form

$$\begin{aligned} n_x &= \cos\phi(t), \quad n_y = \sin\phi(t), \quad n_z = 0, \\ H_x &= H\cos\omega t, \quad H_y = H\sin\omega t, \quad H_z = 0, \end{aligned} \tag{6}$$

with ω the angular frequency and H the constant strength of the magnetic field, and the above equation yields

$$2\gamma_1 \frac{d}{dt}\phi = \chi_a H^2 \sin 2(\omega t - \phi). \tag{7}$$

For sufficiently slow rotations such that

$$\omega \leqslant \omega_0 = \chi_a H^2/2\gamma_1, \tag{8}$$

this equation has a solution

$$\phi = \omega t - \epsilon, \quad \tan\epsilon = \omega_0/\omega - \sqrt{\omega_0^2/\omega^2 - 1}, \tag{9}$$

the director rotating with the field with a phase lag ϵ. For rotations greater than ω_0, one finds

$$\tan(\omega t - \phi) = \omega_0/\omega + (1 - \omega_0^2/\omega^2)^{1/2} \tan[(\omega^2 - \omega_0^2)^{1/2}(t - t_0)] \quad (10)$$

where t_0 is arbitrary.

The couple transmitted to the cylinder walls follows from the relationship for the surface stress vector **t**,

$$t_i = t_{ij}\nu_j, \quad t_{ij} = -p\delta_{ij} + \alpha_2 n_j \frac{d}{dt} n_i + \alpha_3 n_i \frac{d}{dt} n_j, \quad (11)$$

where Cartesian tensor notation is employed, **ν** denotes the unit surface normal, p is pressure, and α_2 and α_3 are viscosity coefficients related to γ_1 by

$$\gamma_1 = \alpha_3 - \alpha_2. \quad (12)$$

If R denotes the cylinder radius and h the depth of liquid crystal, a relatively straightforward calculation shows that the torque τ transmitted to the vessel wall and so to the torsion wire is given by

$$\tau = \pi R^2 h \gamma_1 \frac{d\phi}{dt} \quad (13)$$

this using the relationship Eq. (12). At slow rates of rotation therefore when Eq. (9) applies

$$\tau = V\gamma_1\omega, \quad (14)$$

V denoting the volume of liquid crystal. Hence a plot of torque τ against angular frequency ω at low rates of rotation determines γ_1, provided the volume V is known.

RESULTS

As shown above, the twist viscosity coefficient γ_1 may be obtained from a plot of the torque versus the angular frequency. However, this requires knowledge of the volume which is determined by weighing and use of the density measurements.

The results of our density measurements are summarized in Figure 2. The data can be fitted to a Klement–Cohen Eq. (4), the coefficients for which are listed in Table II.

To determine the twist coefficient a series of measurements of the torque τ were performed at different angular frequencies ω of the mag-

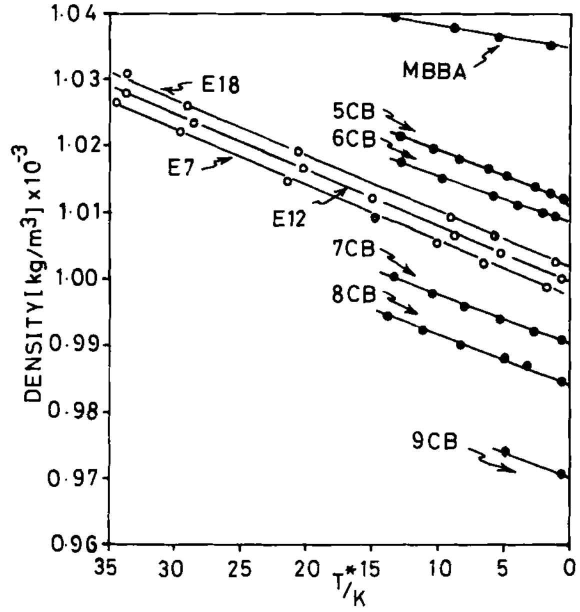


FIGURE 2 Density variation with reduced temperature for MBBA, cyanobiphenyls and their eutectics. Symbol indicates material.

netic field. The actual torque on the glass container was the resultant of the viscous torque calculated above and other effects due to magnetic impurities present in the glass. The angular rate of rotation was calculated from five successive periods, and the torque from the angular displacement of the torsion wire. Half of the measurements were made with increasing angular velocities and the other half with decreasing

TABLE II

Coefficients for the Klement–Cohen equation

Material	V_e^c	$-B.10^4$ 10^{-3}kg/m^3	$-C.10^4$	ρ_c
5CB	0.98916	9.63	7.88	1.0110
6CB	0.9970	16.58	5.88	1.0030
7CB	1.0134	6.76	8.42	0.9867
8CB	1.0199	5.48	11.15	0.9805
E7	1.009	22.46	5.78	0.9911
E12	1.006	24.76	5.44	0.9940
E18	1.003	22.05	5.76	0.9970
MBBA	.9672	—	—	1.0339

ρ_c is the density at the clearing temperature.

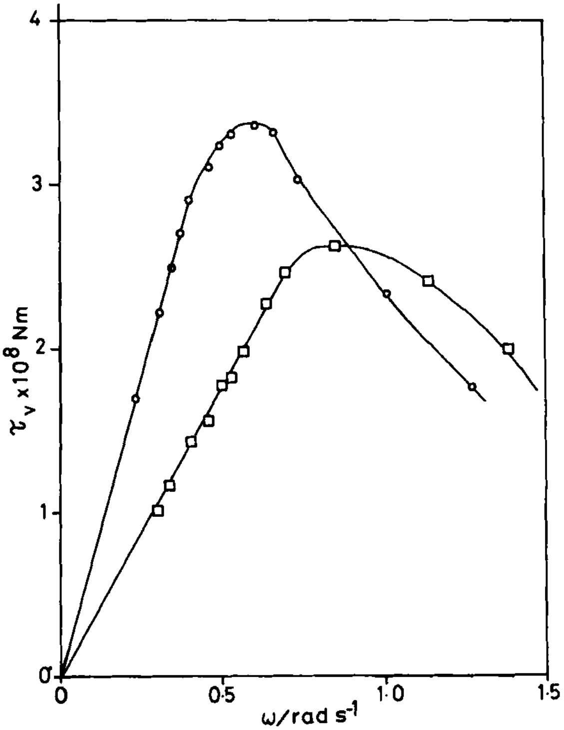


FIGURE 3 Plot of torque against rotation rate for 7CB. Temperature O—303K; □—307K.

rates of rotation. Identical values of the torque were observed in all cases indicating that no hysteresis effects were present in these measurements.

The values of γ_1 were determined from plots of torque τ against the rotation rate ω after deducting a contribution associated with the apparatus. The curves so obtained are shown in Figure 3, and are qualitatively similar in form to the predicted curve.[13] The torque increases rapidly to a maximum value and thereafter decreases. However, the predicted cusp is smoothed out suggesting that relaxation effects are operative before the critical angular velocity is reached. The gradient of the initial linear part of the curve divided by the volume of the sample gives the value of γ_1.

The variation of γ_1 with temperature is shown in Figure 4 in terms of the reduced temperature T^*. The coefficient decreases rapidly with temperature in the nematic phase becoming zero at the clearing temperature. No corresponding viscous torque was detectable in the

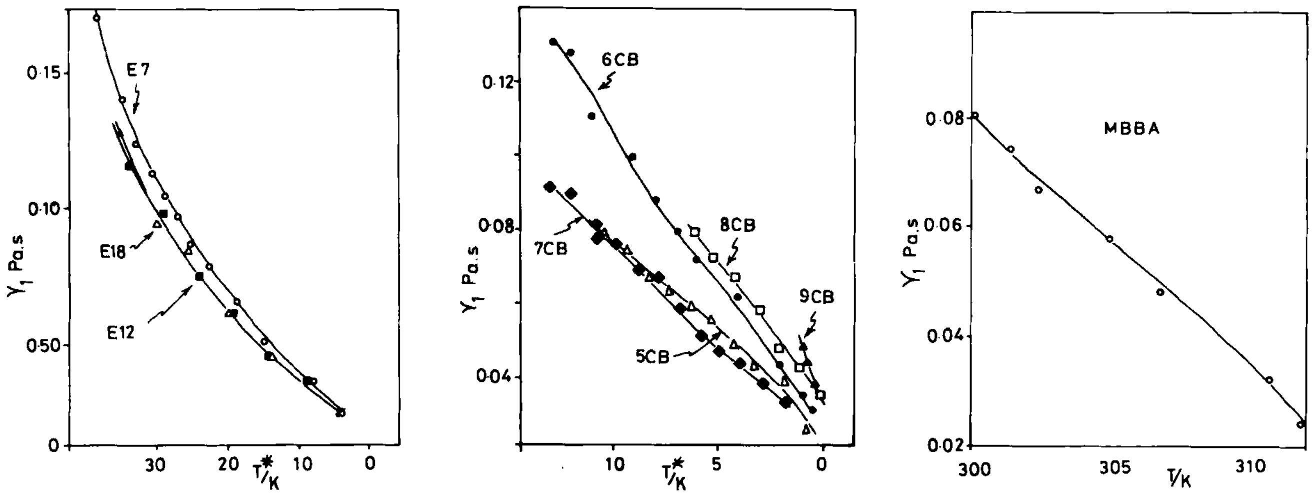


FIGURE 4 Plot of the twist coefficient versus temperature for MBBA, the cyanobiphenyls and their eutectics.

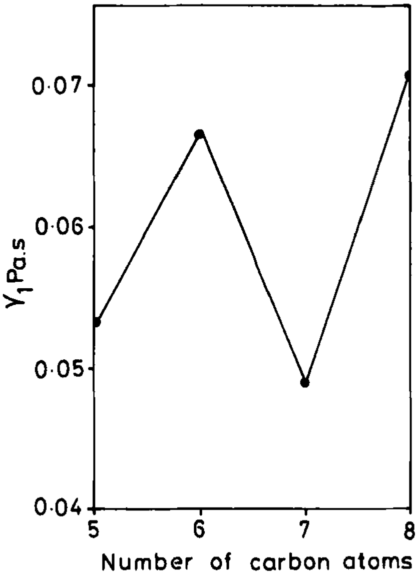


FIGURE 5 Plot of the twist coefficient versus the number of carbon atoms in the alkyl chain in the cyanobiphenyls, $T^* = 5$K.

isotropic phase in all of the materials studied. The data for MBBA are included in Figure 4 and are similar to results reported in the literature.[16-18] Figure 5 gives plots for the cyanobiphenyls of the coefficient γ_1 against the length of the alkyl chain at a reduced temperature of 5K, and shows a periodic variation with maxima at 6CB and 8CB. It was not possible to consider 9CB in this comparison due to its rather short nematic range (1.5K) but extrapolation of the data obtained would seem to indicate a higher value for γ_1, than that observed for 8CB.

DISCUSSION

Densities

In the cyanobiphenyls, the density in the nematic phase is greater than that in the isotropic phase, and in 8CB and 9CB it is greater in the smectic phase than in the nematic. This suggests that the molecular packing density increases with an increase in the molecular order. At a given relative temperature T^*, the density is lower for members of the homologous series with longer alkyl chain; the plot of density against alkyl chain length exhibits ripples with "maxima" at $n = 6$ and 8, Figure 6. Other properties such as the dielectric anisotropy and birefrin-

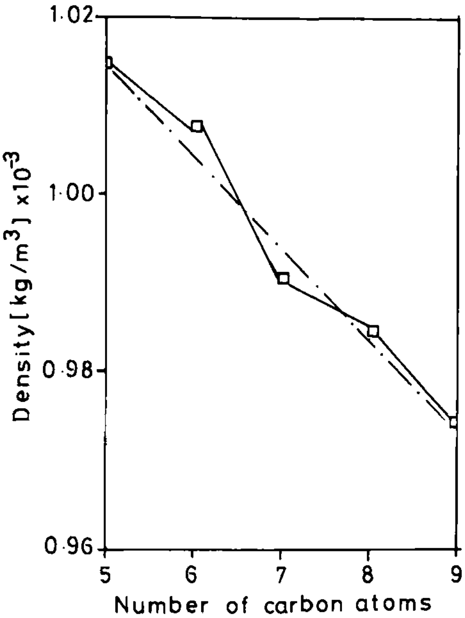


FIGURE 6 Density against the number of carbon atoms in the alkyl chain in the cyanobiphenyls, $T^* = 3$K.

gence[19] exhibit similar variations, and it is possible that the higher homologues are less ordered than the lower members of the series. The even-odd effect observed in many of the properties of these nematic phases[20,21] can be explained by the variation in the geometric compatibility to the alkyl chains. X-ray diffraction studies[22] show that there is pronounced local ordering in 5CB and 7CB with a repeat distance of about 1.4 molecular lengths along the main axis and extending for about 100 molecules. This has been interpreted in terms of the molecules overlapping in a head to tail fashion in a quasi-layer structure, resembling on a local scale a smectic A phase. A detailed study[23] of 8CB indicates that short range smectic A structure is observable in the nematic phase, the two rings of the cyanobiphenyl overlapping and the "tail" occupying a volume which is determined by the angle between the chain axis and the ring. This effect due to differences in the molecular axis of the two component parts would be more pronounced in the even numbered alkyl chains. Lastly, we remark that the density data presented here are in good agreement with other values in the literature.[24–26]

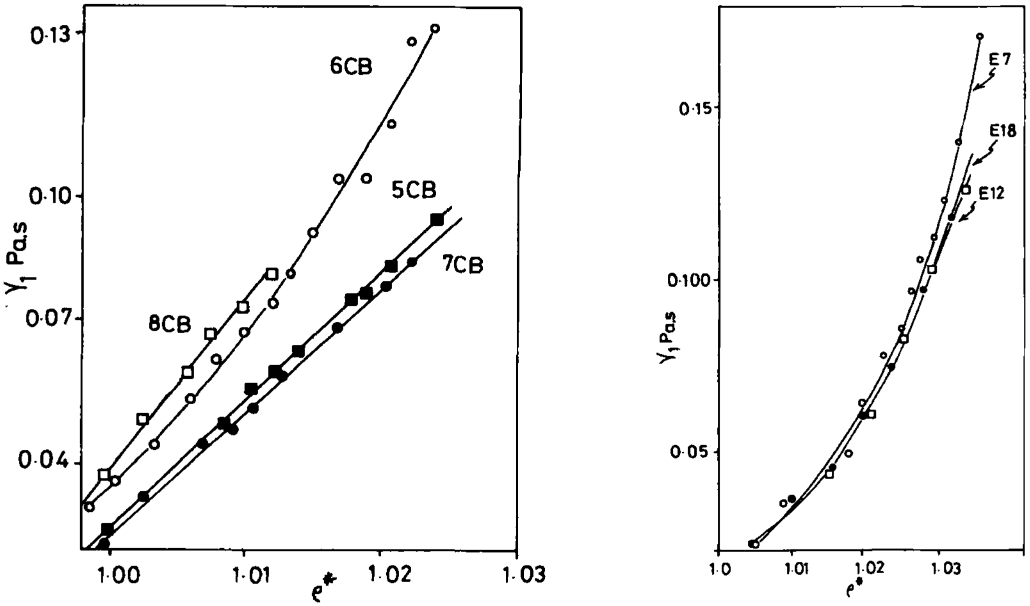


FIGURE 7 Plot of the twist coefficient against the reduced density.

Twist Viscosity Coefficients

The variation of the twist coefficient with alkyl chain length shown in Figure 5 exhibits maxima at 6CB and 8CB. Alternatively, if one plots the values of γ_1 against a reduced density ρ^* defined by the ratio ρ/ρ_c, two straight lines of similar gradient are obtained, one group corresponding to the odd and the other to the even series of molecules. This is shown in Figure 7. One can explain this effect in terms of the compatibility of the alkyl chains leading to a strained or less strained ordered structure. In the case of the even molecules, the non-coincidence of the two axes causes the molecules to have greater difficulty in packing than in the corresponding odd series.

Martins[27] has predicted the variation of the coefficient γ_1 with temperature in terms of a molecular orientational motion, this taking place against a potential barrier of height E given by

$$E = D(\theta)_{\max} - D(\theta)_{\min} = 3AS/2mV^2 = \epsilon S \tag{15}$$

where $D(\theta)$ is the mean field potential of the Maier–Saupe theory[28,29] for nematics, S the order parameter, A a molecular constant, m the cluster parameter, and V the nematic volume. In particular, Martins predicts that

$$\gamma_1 = cS^2 \exp(\epsilon S/kT) \tag{16}$$

where c is a constant roughly independent of temperature. This is an Eyring type of rate expression in which ϵ is an energy term related to an interaction energy in ordered phases. A graph of ln (γ_1/S^2) against the ratio S/T should yield a straight line from which the interaction energy can be derived.

For the materials studied here, one obtains a linear relationship for a large portion of the temperature range, but deviations occur near the clearing point. This is shown in Figure 8 for the cyanobiphenyls. The values of S used were calculated from the indices of refraction and polarization given by Karat and Madnusudana[25] from the formulae

$$S = (n_e^2 - n_o^2)\bar{\alpha}/(\bar{n}^2 - 1)\Delta\alpha, \quad \bar{n}^2 = 1/3(n_e^2 + 2n_o^2) \tag{17}$$

where n_o and n_e are respectively the ordinary and extraordinary indices of refraction, and $\bar{\alpha}$ and $\Delta\alpha$ respectively the mean and anisotropic polarizabilities. A least squares fit of Eq. (16) to the data summarized by Figure 8 allows one to determine the activation energy ϵ, and the values obtained are given in Table III. According to Martins and Diogo,[30] the product ϵS should be roughly twice the nematic–isotropic transition enthalpy, this assuming a pair wise interaction potential. With the

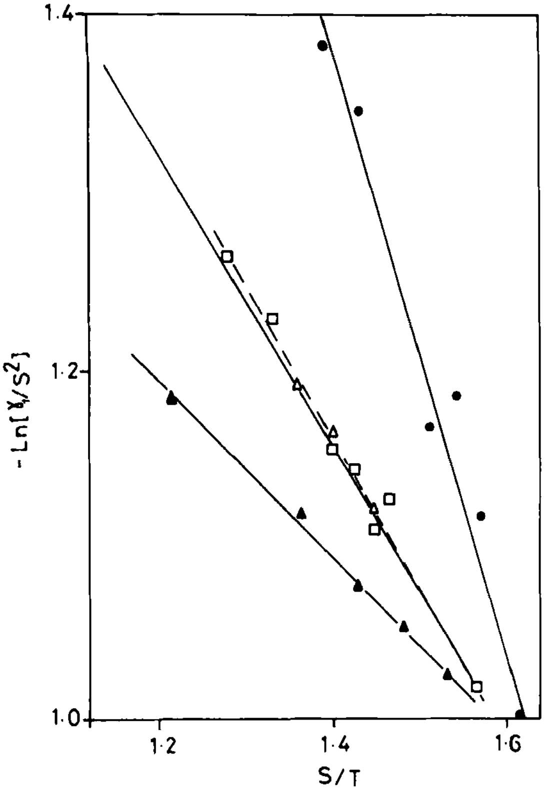


FIGURE 8 Plot of ln (γ_1/S^2) against S/T for the cyanobiphenyls. Key □ 5CB; △ 6CB; ● 7CB; ▲ 8CB.

available data for 8CB,[23,31] the values found are much smaller than the transition heat, which has the value 2.92 kJ/mol.

Leadbetter[22] has pointed out, however, that this material exhibits a short range smectic order, and this suggests that the theory should not be applicable in this case. No reliable transition heat data exists at present for the other compounds studied. Gray[32] has remarked that the

TABLE III

Activation energies and coefficients of Eq. (16)

Material	c(MPa.s)	ϵ(kJ/mol)	ϵS(kJ/mol)
5CB	91.2	7.3	2.75
6CB	147.5	6.8	2.28
7CB	24.6	13.7	5.05
8CB	138.9	5.2	1.80

nematic–isotropic transition enthalpy of the homologous series is between 0.42 and 1.25 kJ/mol in agreement with Martins' prediction but different from the value cited for 8CB.[23]

The behavior observed for the eutectic systems is very different from that for the pure compounds, and is probably a reflection of the differences in molecular packing in a mixed system compared with that in a pure compound. Since there is considerable uncertainty as to the nature of the molecular interactions in these eutectic systems, no detailed discussion is attempted of the data obtained for these mixtures.

CONCLUSIONS

Examination of the temperature dependence of the density and twist viscosity coefficient indicates that the effectiveness of molecular packing has a marked effect on the liquid crystalline properties of these materials. The conformation of the alkyl chain and the effective coincidence of its axis with that of the phenyl rings depends upon whether it is an odd or even hydrocarbon. The observed properties do in fact exhibit an odd–even type of behavior consistent with effects associated with the geometric compatibility of the packing of the alkyl chains. Since the packing is not strictly nematic at a molecular level, it is perhaps not surprising that predictions of molecular theories for nematic phases are not particularly accurate.

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References

1. G. W. Gray, *"The Molecular Physics of Liquid Crystals,"* Ed. G. R. Luckhurst and G. W. Gray, Academic Press, Chpt. 1 (1979).
2. G. R. Luckhurst, *"The Molecular Physics of Liquid Crystals,"* Ed. G. R. Luckhurst and G. W. Gray, Academic Press, Chpt. 4 (1979).
3. F. Dowell and D. E. Matire, *J. Chem. Phys.*, **68**, 1088, 1094 (1978).
4. P. G. de Gennes, *"The Physics of Liquid Crystals,"* Oxford University Press (1974).
5. J. L. Ericksen, *Trans. Soc. Rheol.*, **5**, 23 (1961).
6. F. M. Leslie, *Arch. Rat. Mech. Anal.*, **28**, 265 (1968).
7. N. N. V. Raghavan and L. A. Paddoek, *OPP I Briefs*, **7**, 311 (1975).
8. W. M. Zvetkow and G. M. Michailow, *Acta Physicochim, USSR*, **8**, 77 (1938).
9. W. M. Zvetkow, *Acta Physicochim, USSR*, **10**, 555 (1939).
10. P. J. Flanders, *Mol. Cryst. Liq. Cryst.*, **29**, 19 (1974).

11. W. Klement and L. H. Cohen, *Mol. Cryst. Liq. Cryst.*, **27**, 359 (1974).
12. R. M. Stimpfle, R. A. Orwell and M. E. Schott, *J. Phys. Chem.*, **83**, 613 (1979).
13. H. Gasparoux and J. Prost, *J. Phys. (Paris)*, **32**, 953 (1971).
14. F. M. Leslie, *Adv. Liq. Cryst.*, **4**, 1 (1979).
15. F. M. Leslie, G. R. Luckhurst and H. J. Smith, *Chem. Phys. Lett.*, **13**, 368 (1972).
16. W. H. de Jeu, *Phys. Lett.*, **69A**, 122 (1978).
17. C. Gähwiller, *Mol. Cryst. Liq. Cryst.*, **20**, 301 (1973).
18. J. Prost and H. Gasparoux, *Phys. Lett.*, **36A**, 245 (1971).
19. D. A. Dunmur, M. R. Manterfield, W. H. Miller and J. K. Dunleavy, *Mol. Cryst. Liq. Cryst.*, **45**, 127 (1978).
20. G. W. Gray, *"Liquid Crystals and Plastic Crystals,"* Ed. G. W. Gray and P. A. Windsor, Ellis Horwood, Vol. 1, 103 (1974).
21. S. J. Marcelja, *J. Chem. Phys.*, **60**, 3599 (1974).
22. A. J. Leadbetter, R. M. Richardson and C. N. Colling, *J. Phys. (Paris)*, **36**, C1, 37 (1975).
23. A. J. Leadbetter, J. L. A. Durrant and M. Rugman, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 231 (1977).
24. D. A. Dunmur and W. H. Miller, *J. Phys. (Paris)*, **40**, C3, 141 (1979).
25. P. P. Karat and N. V. Madnusudana, *Mol. Cryst. Liq. Cryst.*, **36**, 51 (1976).
26. L. Leger and A. J. Martinet, *J. Phys. (Paris)*, **37**, C3, 89 (1976).
27. A. F. Martins, *Port. Phys.*, **9**, 1 (1974).
28. W. Maier and A. Saupe, *Z. Naturf.* **A**, **14**, 882 (1959).
29. W. Maier and A. Saupe, *Z. Naturf.* **A**, **15**, 287 (1960).
30. A. F. Martins and A. C. Diogo, *Port. Phys.*, **9**, 129 (1975).
31. P. L. Sherrel and D. A. Crellin, *J. Phys. (Paris)*, **40**, C3, 211 (1979).
32. G. W. Gray, K. J. Harrison and J. A. Nash, *Pramana Suppl.*, **1**, 381 (1975).