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VOLUMETRIC STUDIES OF THE HOMOLOGOUS SERIES OF ALKYL-CYANO-BIPHENYL LIQUID CRYSTALS

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Résumé. — Des mesures de densité en fonction de la température ont été rapportées pour les séries homologues de cristaux liquides d'alkyle-cyano-biphényle $C_nH_{2n+1}OOCN$ pour $n = 5$ à 9 . Des lignes cubiques B_{sp} ont été trouvées en accord avec les résultats expérimentaux et leurs dérivées ont donné les coefficients d'expansion thermique. Des changements de volume transitionnels ont été déterminés par extrapolation de la densité des phases de chaque côté d'une transition, et les variations de volume de nématique à isotrope montrent un effet pair-impair marqué. Les densités de phases nématique et isotrope en équilibre ont été utilisées avec une théorie de van der Waals des cristaux liquides pour fournir une information sur les paramètres d'un potentiel de champ moyen, les paramètres d'ordre transitionnel et les rapports longueur sur largeur moléculaire.

Abstract. — Measurements are reported of densities as a function of temperature for the homologous series of alkyl-cyano-biphenyl liquid crystals $C_nH_{2n+1}OOCN$ for $n = 5$ to 9 . Cubic B -splines have been fitted to the experimental results and their derivatives have given the coefficients of thermal expansivity. Transitional volume changes have been determined by extrapolation of the densities of phases each side of a transition, and the nematic to isotropic volume changes show a marked odd-even effect. The densities of the nematic and isotropic phases in equilibrium have been used in conjunction with a van der Waals theory of liquid crystals to provide information on mean field potential parameters, transitional order parameters and molecular length to breadth ratios.

1. Introduction. — The liquid crystalline state is characterised by the orientational ordering of its constituent molecules, and transitions between different mesophases are accompanied by changes in the local molecular order. These transitions are usually marked by changes in various anisotropic properties, but depending on the order of the transition they may also be accompanied by changes in scalar quantities such as enthalpy content or density. The alterations in density and thermal expansivity which accompany the nematic to isotropic phase transition have been the subjects of a number of investigations [1-6], and these have shown that there is a pretransitional anomaly in the thermal expansivity in both the nematic and isotropic phases close to the temperature at which they are in equilibrium. Although this anomaly is experimentally well-established, its theoretical description is less certain [7, 8], and the accurate determination of critical exponents for the divergence of the thermal expansivity is of considerable theoretical importance.

Recent observations by White, Cladis and Torza [9] have suggested a correspondence between a flow anomaly found in certain nematic liquid crystals and a discontinuous change in the thermal expansivity which occurs at the same temperature. The flow anomaly is attributed [10] to a change in sign of the

Leslie coefficient α_3 as a smectic A phase is approached, and the corresponding increase in molecular association is claimed to result in an abrupt decrease in the thermal expansivity. Although the theoretical link between these two effects remains to be established, measurements of the variation with temperature of the density of materials having smectic phases are likely to be of interest.

An important objective of any theory of the liquid crystalline state is the provision of an equation of state that describes the PVT surface of the mesophases and also accounts for discontinuities in the surface at mesophase transitions. This objective is still far from being realised, although the recent applications [11, 12, 13] of van der Waals theories to orientationally ordered phases is a considerable advance. The mean field theory of Maier and Saupe [14] predicts with reasonable accuracy the order parameter in the nematic phase and its variation with temperature: it does not however provide an equation of state, and the nematic to isotropic volume change is a parameter of the theory [1]. Hard particle theories [15, 16, 11] or van der Waals theories do give an equation of state, but the predictions of the order parameter at the transition and the transitional volume change are usually too high. The van der Waals theory requires potential parameters to describe

the mean field isotropic and anisotropic attractive forces, and both hard particle and van der Waals theories need some assumption of molecular size and shape. By introducing experimental transitional volume changes into these theories some constraints are placed on the parameters of the theories, and it is of interest to determine the consequences of these constraints on other predictions of the theories.

In this paper we present the results of density measurements made as a function of temperature for the homologous series of alkyl-cyano-biphenyl liquid crystals. The results have been analysed to give thermal expansion coefficients and transitional volume changes, and the latter are used to give information on the parameters of the van der Waals theories and how they vary for different members of a homologous series of liquid crystals.

2. Experimental. — The measurements of density were made using an Anton Paar digital precision density meter (type DMA O2C). A hollow V-shaped glass tube of capacity 0.7 cm^3 is filled with the fluid under investigation and induced to vibrate by an electromagnetically excited magnet attached to the tip of the V. The glass tuning fork then vibrates at its natural frequency, with a period whose square is a linear function of the density of the fluid. By suitably calibrating the instrument it is possible to measure densities with an accuracy of $\pm 1.5 \times 10^{-6} \text{ g cm}^{-3}$, although to achieve this it is necessary to maintain the temperature of the sample constant to better than $\pm 0.01^\circ \text{C}$.

Our instrument was calibrated over the full range of the temperatures studied using air and deionised distilled water. Temperature control was achieved by a thermostatted circulation system whose measured stability was better than $\pm 0.02^\circ \text{C}$. The precision of our measurements is $\pm 5 \times 10^{-5} \text{ g cm}^{-3}$, but taking account of calibration uncertainties and irreproducibility between successive runs on different samples their accuracy is $\pm 2 \times 10^{-4} \text{ g cm}^{-3}$.

3. Results and analysis. — Our results for the densities of the homologous series of alkyl-cyano-biphenyl liquid crystals $\text{C}_n\text{H}_{2n+1}\cdot\text{O}\cdot\text{O}\cdot\text{CN}$ are presented in figures 1 to 5 for the series with $n = 5$ to 9. All these compounds have nematic phases, while the higher members with $n = 8$ and 9 also show smectic A phases. The nematic to isotropic transitions are all very sharp occurring over less than 0.1°C , but the smectic A to nematic transitions appear less sharp, and there is some evidence of pretransitional behaviour in the density below this transition.

In order to determine the volume changes at the nematic to isotropic and smectic to nematic transitions, the reciprocal of the density in each phase was fitted to a quadratic function of $|T - T_i|^{1/2}$, where T is the temperature and T_i is the appropriate transi-

tion temperature in $^\circ \text{C}$. This procedure is suggested by Klement and Cohen [17], except that we have allowed the coefficients of $|T - T_i|$ to assume different values in the two phases. A typical fitting of the reciprocal densities is shown in figure 6; the extrapolation necessary to obtain the transitional volume change was typically 0.04°C , and we

FIG. 1.

FIG. 2.

FIG. 3.

FIG. 5.

FIG. 4.

FIG. 1 to 5. — Densities (ρ) in g cm^{-3} and thermal expansivities (β : broken line) as a function of temperature for the alkylcyano-biphenyl liquid crystals.

FIG. 6. — Extrapolation of transitional volume change. ρ^{-1} ($\text{cm}^3 \text{g}^{-1}$) as a function of $|T - T_t|^{1/2}$ for 8 CB.

believe that the extrapolated volume changes are accurate to $\pm 0.0003 \text{ cm}^3 \text{g}^{-1}$. The determined volume changes are given in table I together with the

corresponding densities of the two phases in equilibrium. Transition temperatures obtained from the density measurements are also listed.

TABLE I

Transitional densities and volume changes for the alkyl-cyano-biphenyl liquid crystals R.O.O.CN

Liquid crystal (R)	Transition temperatures (°C)		Transitional densities (g cm ⁻³)			Transitional volume change $\Delta V/V_{\text{nem}}$
	T_s	T_N	smectic A	nematic	isotropic	
C ₅ H ₁₁ (5 CB)	—	35.0	—	1.011 35	1.009 33	0.002 00
C ₆ H ₁₃ (6 CB)	—	29.4	—	1.003 36	1.002 40	0.000 96
C ₇ H ₁₅ (7 CB)	—	42.7	—	0.986 21	0.984 06	0.002 2
C ₈ H ₁₇ (8 CB)	33.6	40.6	0.989 55	0.989 22	—	0.000 3
				0.979 96	0.978 31	0.001 7
C ₉ H ₁₉ (9 CB)	47.7	49.5	0.972 62	0.972 24	—	0.000 4
				0.967 90	0.964 34	0.003 7

The measurements of density were fitted to a series of cubic B-splines [18], and coefficients of thermal expansivity β were obtained by differentiation of the appropriate spline functions. Our results for

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P$$

are given in figures 1 to 5 for the materials studied.

4. Discussion of results. — The density of the smectic phase is greater than that of the nematic phase, which in turn is greater than the density of the isotropic liquid, so as the degree of molecular order decreases the molecular packing density also decreases. Within the homologous series the densities of both the nematic and isotropic phases in equilibrium at the transition decrease with increasing chain length, which suggests that the higher homologues are less ordered than the lower members of the series. This behaviour is paralleled by the anisotropic properties such as dielectric anisotropy or birefringence of these compounds [19].

The volume changes $\Delta V/V_{\text{nem}}$ are plotted as a function of alkyl chain length in figure 7, and a significant odd-even effect is apparent, with the odd members of the series having larger proportional volume changes than the even members. This odd-even effect is observed with many properties of liquid crystals [20], most noticeably with the nematic to isotropic transition temperatures. It is explained [21] by the alternation of interactions between the alkyl chains: those having an odd number of carbon atoms are more extended than those with an even number, and have a higher order parameter. Thus the relatively higher order of the odd members of the series results in a larger volume change at the nematic to isotropic transition.

At the smectic A to nematic transition the volume change is much smaller than that at the nematic to isotropic transition, and in view of the pretransitional behaviour noted in the smectic A phase, it may in fact tend to zero as suggested by the measurements of Armitage and Price on CBOOA [6].

Although the derivatives of the cubic B-spline functions through the measured densities vary smooth-

FIG. 7. — Fractional volume changes (nematic to isotropic) as a function of alkyl chain length for the homologous series of alkyl-cyano-biphenyls ($n = 5 \rightarrow 9$).

ly over most of the temperature ranges, the corresponding thermal expansion coefficients are probably only accurate to ten percent. In view of this we have not attempted to obtain the critical exponents for the pre-translational divergence of β . The thermal expansion coefficients increase with temperature through the nematic phase, and then decrease discontinuously at the nematic to isotropic transition, which is in agreement with the observations of other workers [2, 3, 4]. However our measurements are not precise enough to detect a discontinuity in the nematic phases of 8 CB and 9 CB which also possess smectic A phases.

5. Theoretical analysis. — A van der Waals theory of nematic liquid crystals has been developed, which combines a hard sphero-cylinder repulsion with a

mean field attractive potential containing both isotropic and anisotropic terms of the form :

$$\bar{u} = -v_0 \rho - v_2 \rho S P_2(\cos \theta) \quad (1)$$

where ρ is now the number density and S is the usual order parameter. Two versions of the theory have been developed by Cotter [11] and Gelbart and coworkers [12, 13, 22], and their approaches differ

in that the latter allows for coupling between the isotropic attractions and the angle-dependent hard core repulsions. In our analysis we use the theory developed by Cotter, although our results suggest that the coupling included by Gelbart is important.

A scaled particle approximation to the free energy of a system of hard spherocylinders together with the mean field attractive potential yields an equation of state [11] :

$$\frac{Pv_0}{kT} = \Pi - \frac{1}{2}(v_0 + v_2 S^2) v_0 \rho^2 / kT$$

where

$$\Pi = \frac{v_0 \rho}{(1 - v_0 \rho)^3} \left\{ 1 + v_0 \rho + \frac{2(3x^2 - 1)}{(3x - 1)^2} v_0^2 \rho^2 + \frac{3(x - 1)^2}{(3x - 1)} \left[1 + \frac{(x + 1)}{(3x - 1)} v_0 \rho \right] 1 - \frac{5S^2}{8} v_0 \times \rho \right\}. \quad (2)$$

The parameters of this equation of state are the isotropic and anisotropic potential parameters v_0 and v_2 , the molecular volume v_0 and the length to breadth ratio x of a molecular spherocylinder. By equating the pressures of two phases in equilibrium at the nematic to isotropic transition, and using the self-consistency relation for the order parameter :

$$S = \frac{\int_0^\pi P_2(\cos \theta) [\exp \Phi S P_2(\cos \theta)] \sin \theta d\theta}{\int_0^\pi \exp \Phi S P_2(\cos \theta) \sin \theta d\theta} \quad (3)$$

it is possible to obtain the value of S at the transition. In equation (3) the reduced energy Φ is given by

$$\Phi = \frac{15(x - 1)^2 v_0 \rho}{4(3x - 1)(1 - v_0 \rho)^2} \left[1 - \frac{(x - 1) v_0 \rho}{(3x - 1)} \right] + \frac{1}{2} \frac{\rho}{kT}. \quad (4)$$

These equations (2) and (3), and similar ones including hard core repulsive-isotropic attractive coupling have been solved [11, 13, 22] for a variety of molecular parameters to yield values for S at the transition together with the corresponding equilibrium nematic and isotropic densities. We have solved these equations for the homologous series of alkyl-cyano-biphenyls, but have fixed the isotropic and nematic densities at their experimental values, and have allowed the parameters v_0 and v_2 to vary. The molecular volume was evaluated for each molecule from appropriate van der Waals radii [23], and v_0 and v_2 were adjusted to give calculated transition temperatures within a degree of the experimental values. This procedure enabled self-consistent values of S and x to be determined, which reproduced

the experimental transitional volume change and the nematic to isotropic transition temperature. We found that v_0 and v_2 could only be varied over limited ranges to give consistent values for the order parameter.

Our results are summarised in table II, and it is clear that realistic length to breadth ratios result from very small values for the ratio v_2/v_0 . The values of x increase as the alkyl chain length increases, while the order parameter shows an odd-even effect, which reflects the transitional volume changes. Unfortunately experimental measurements of S at the nematic to isotropic transition have not been made for the liquid crystals studied, but values between 0.2 and 0.3 are probably reasonable. The ratios of the anisotropic to isotropic potential parameters are unrealistically small, and presumably reflect inadequa-

TABLE II

Mean field potential parameters, order parameters and length : breadth ratios for the alkyl-cyano-biphenyl liquid crystals

Liquid crystal ($v_0/\text{\AA}^3$)	Potential parameters				
	$v_0/v_0 \text{ kK}$	$v_2/v_0 \text{ kK}$	S	x	x_{calc}^*
5 CB (258)	40 000 50 000	2 050 450	0.39 0.25	1.22 2.13	2.50
6 CB (275)	40 000 50 000	1 900 350	0.25 0.17	1.32 2.20	2.67
7 CB (291)	40 000 50 000	1 950 325	0.35 0.25	1.36 2.23	2.86
8 CB (308)	40 000 50 000	1 900 300	0.31 0.22	1.38 2.26	3.04
9 CB (325)	40 000 50 000	1 900 225	0.42 0.31	1.45 2.32	3.23

(*) Calculated from bond lengths and bond angles.

cies in the theory such as neglect of molecular flexibility and short range correlation. In spite of this the variations of v_0 and v_2 with alkyl chain length do reflect the trends in the isotropic and anisotropic parts of the polarizabilities [19], the former being approximately constant down the series, while the latter decrease with increasing chain length. Inclusion of coupling between the isotropic attraction and hard core repulsion would increase the ratio v_2/v_0 with a

consequent increase in the order parameter, and might give more realistic values for the potential parameters.

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