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Invited Article

Some N.M.R. experiments using lyotropic nematic liquid crystals

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A series of lyotropic nematic liquid crystals based on aniso-dimensional micelles can be subdivided according to micelle shape and diamagnetic susceptibility anisotropy. The proton magnetic resonance spectra of benzene dissolved in dilute solution in several of these phases have been analysed. The signs of the partially averaged dipole–dipole coupling give information about the relative alignment of the six-fold symmetry axis of benzene, the director and the magnetic field. The system caesium perfluorooctanoate/water is unusual in two respects. The system forms a nematic phase with only a binary mixture and the disk micelles align in a perpendicular plane to the magnetic field. As a result the binary system has been studied previously in some detail (see N. Boden, S. A. Corne and K. W. Jolley, 1987, *J. phys. Chem.*, **91**, 4092). New measurements on the interesting phase diagram have been accomplished using caesium-133 and deuterium magnetic resonance measurements at various temperatures. Some dilatometric measurements have been made to complement the N.M.R. studies.

1. Introduction

The series of nematic phases formed when aniso-dimensional micelles become orientationally ordered in an aqueous matrix are now well recognized and have been studied by various groups [1-7]. These nematic phases have been used as solvents for relatively small molecule solutes and the study of the nuclear magnetic resonance of the solutes to elucidate molecular structure is widespread [8]. The classical study of Englert and Saupe [9] showed that in nematic liquid crystals the dipole–dipole coupling between nuclei on different molecules is averaged to zero while the coupling between nuclei on the same molecule is not. The earliest study of the spectra of the dissolved benzene molecule [10] in thermotropic liquid crystals was followed by a study in a lyotropic liquid crystal by Black *et al.* [11].

In the present work the study of benzene as a solute in thermotropic liquid crystals [9] is extended to a wide range of aqueous lyotropic nematic liquid crystals formed from finite micelles [1]. The proton magnetic resonance spectra of oriented benzene molecules contain the magnitude and sign of the ortho, meta and para dipole couplings. It is possible therefore to study the relative alignment of the nematic micelles and the benzene molecule [8]. These nematic systems can be subdivided into the shapes of the constituent micelles and the sign of the diamagnetic susceptibility anisotropy. We shall adopt a nomenclature for distinguishing the sub-types which was first proposed by Boden *et al.* [12] and not the more complex nomenclature of Marcondes Helene and Reeves [2].

The nematic phases formed by micellar systems in water can be distinguished from the positionally ordered lamellar bilayer phases L and the positionally ordered hexagonal phases M [13] by using the general symbol N for nematic [12]. Most of the micellar nematics can be sub-classified according to subscripts C and D for cylindrical and disc-like micelles respectively. The sign of the diamagnetic susceptibility anisotropy can also be used as a superscript to describe fully the behaviour of the mesophases in a magnetic field. The four principal sub-classifications are N_D^-, N_C^+, N_D^+ and N_C^-. For the most part the nematic phases occur in three or four chemical component phases. Usually there is a principal surfactant, water, and a neutral co-surfactant such as decanol, as well as added electrolyte to provide co-ions [14, 15]. If the principal surfactant has a normal hydrocarbon chain the disc nematic phase has a negative diamagnetic anisotropy, $\Delta\chi$, and the cylinder micellar phase has positive $\Delta\chi$.

Phase changes among the nematic types have attracted considerable attention as well as the phase change between N_D and L phases [6, 16]. The lamellar to nematic phase transition has been studied using low angle X-ray diffraction and found to be continuous under certain conditions [6]. It is the purpose of this present study to re-examine the $L \rightarrow N_D$ transition from the fundamental point of view of volume changes.

2. Experimental

2.1. *List of materials*

The components of the lyotropic mesophases prepared for this study are:

1. long chain detergents sodium decyl sulphate (SDS), potassium dodecanoate (KL), decylammonium chloride (DACl), disodiumchromoglycate (Intal) (DSCG), caesium perfluoroctanoate (CsPFO);
2. *n*-decanol;
3. electrolytes sodium sulphate (Na_2SO_4), potassium chloride (KCl), ammonium chloride (NH_4Cl);
4. D_2O and H_2O;
5. benzene.

2.2. *Purification of materials*

Sodium decyl sulphate was purified from the laboratory stock by repeated recrystallization from 90 per cent ethanol and then dried *in vacuo* for several days.

Potassium dodecanoate was prepared by reacting equimolar quantities of dodecanoic acid and potassium hydroxide in absolute ethanol followed by several recrystallizations from ethanol. Surfactant from laboratory stock was recrystallized from absolute ethanol and then dried in vacuum. The purity of the surfactant was checked from its ^1H N.M.R. spectra in D_2O.

Decyl ammonium chloride was prepared by neutralizing *n*-decylamine (Aldrich) with dilute HCl. After being dried, the crude product was recrystallized from a mixture of 1 : 3 (*v*/*v*) ethanol : petroleum ether.

Disodium chromoglycate was kindly provided by G. A. van Vlack from Fisons Pharmaceuticals as a crystalline solid hydrate. It was used without further purification.

Caesium perfluorooctanoate was used from the laboratory stock without further purification.

n-Decanol (Eastman) was refluxed for several hours over anhydrous magnesium sulphate (dried *in vacuo*) and then distilled in dry nitrogen gas. The middle fraction was collected. A ^{1}H N.M.R. spectrum and boiling point measurement confirmed the purity of the distillate (b.p. 230°C, literature value 231°C).

Sodium sulphate (99·9 per cent Baker), potassium chloride (99·9 per cent Baker) and ammonium chloride (100 per cent Baker) were air dried in an oven at 220°C.

D_2O was purchased from Merck, Sharp and Dohme Laboratories (99·7 per cent deuterated) and used without further purification.

Benzene and benzene-d_6 were purchased from Baker and Merk, Sharp and Dohme Laboratories, respectively, and were used without further purification.

2.3. *Preparation of mesophases*

Special care was taken to avoid D_2O–H_2O exchange with the moist air or glass surfaces to keep the ^{1}H resonance line of HOD as small as possible, in order to facilitate the observation of the benzene spectra. The lyomesophases were prepared in a similar manner as described in [3, 8, 11, 14]. Tables 1, 2, 3, 4 and 5 give the compositions in wt % of the SDS, KL, DACl, DSCG and CsPFO mesophases containing benzene as a solute. The components were placed in a glass tube which was sealed at one end; it was 100 mm long, with an internal diameter of approximately 10 mm and a constriction in the middle. The open end was sealed so that the material might be centrifuged forward and backward through the constriction until dissolution is completed. The procedure of warming up, inverting and centrifuging the sample was repeated until a homogeneous birefringent phase appeared, as observed through cross-polarizers.

The mesophases used to study the L → N_D^+ phase transitions were prepared from caesium perfluorooctanoate and D_2O, without benzene as a solute. Three compositions were used and these are listed in table 6. The three samples are subsequently indexed as 1, 2 and 3. The compositions may be referred to the phase diagram published earlier by Boden *et al.* [16]. By raising the temperature of phase 1 the system passes

Table 1. Composition and identification of mesophases used in the study of benzene solute N.M.R. spectra: weight per cent composition of sodium decylsulphate phases.

Mesophase identification	SDS	Decanol	Sodium sulphate	D_2O	C_6H_6	Phase type
SDS II	35·48	6·88	7·04	49·36	1·24	N_D^-
SDS I	39·19		4·49	54·99	1·33	N_C^+

Table 2. Composition and identification of mesophases used in the study of benzene solute N.M.R. spectra: weight per cent composition of potasium laurate phases.

Mesophase identification	KL	Decanol	Potassium chloride	D_2O	C_6H_6	Phase type
KL II	29·58	6·00	4·92	58·00	1·50	N_D^-
KL I	34·18		2·28	62·50	1·04	N_C^+

Table 3. Composition and identification of mesophases used in the study of benzene solute N.M.R. spectra: weight per cent composition of decylammonium chloride phases.

Mesophase identification	DACl	Ammonium chloride	D_2O	C_6H_6	Phase type
DACl 1	32·80	2·74	63·04	1·45	N_D^-
DACl 2	46·25	4·67	47·96	1·15	
DACl 3	45·05	4·45	49·50	1·00	
DACl 4	42·75	4·22	51·27	1·77	
DACl 5	40·89	4·13	53·36	1·61	
DACl 6	38·01	3·76	57·08	1·06	

Table 4. Composition and identification of mesophases used in the study of benzene solute N.M.R. spectra: weight per cent composition of disodiumchromoglycate phases.

Mesophase identification	DSCG	D_2O	C_6H_6	Phase type
DSCG 1	15·96	81·98	2·06	N_C^-
DSCG 2	16·32	82·45	1·23	
DSCG 3	11·83	87·17	1·00	
DSCG 4	19·70	78·80	1·50	

Table 5. Composition and identification of mesophases used in the study of benzene solute N.M.R. spectra: weight per cent composition of caesium perfluoroctanoate.

Mesophase identification	CsPFO	D_2O	C_6H_6	Phase type
CsPFO 1	40·51	58·16	1·33	N_D^+

Table 6. Composition and identification of binary mixtures of caesium perfluoro-octanate and water which were used for studies of the nematic to lamellar transition.

Sample	CsPFO wt %	D_2O wt %
1	64	36
2	61	39
3	50	50

through the regions

$$L \rightarrow L + \text{isotropic} \rightarrow \text{isotropic}.$$

Mesophase 2 goes through the regions

$$L \rightarrow L + N_D^+ \rightarrow N_D^+ \rightarrow N_D^+ + \text{isotropic} \rightarrow \text{isotropic}.$$

Mesophase 3 goes through the stable phases

$$L \rightarrow N_D^+ \rightarrow N_D^+ + \text{isotropic} \rightarrow \text{isotropic}$$

as the temperature is raised.

2.4. *N.M.R. measurements*

Proton, deuterium and cesium-133 signals were registered on various Bruker spectrometers which included models WP80, CXP200, AM250 and WM400. The numbers of the model of spectrometer correspond to the proton resonance frequencies in MHz. These spectrometers are equipped with variable temperature units using heated or chilled air streams from a Bruker VT1000 temperature unit.

3. Results and discussion

3.1. *Proton magnetic resonance spectra of benzene as a solute in micellar nematic mesophases*

The spectrum of benzene in a liquid-crystalline solvent has 76 observable transitions and in most cases all of these were observed. The scalar coupling constants between ortho, meta and para protons have been determined previously from analysis of the carbon-13 satellites of benzene in an isotropic medium. The para coupling is less than 1 Hz and so far the sign of this coupling has not been determined though the J_{12} and J_{13} coupling constants are known to be absolutely positive. Reliable signs of the scalar couplings enable the determination of the signs of the corresponding dipolar couplings which give the best fit of the spectra. The larger the ordering of the benzene the larger the dipolar couplings are. The spectral analysis was achieved in three stages. Estimates of the dipolar couplings can be made from the transition frequency which can be expressed analytically in terms of the couplings [8, 17]. With these initial estimates of the dipolar couplings the computer code DIPEUA was used to fit iteratively all transitions of the experimental spectrum. The software code PANIC provided by Bruker was used to make the final experimental and theoretical plots of the spectrum for direct comparison. A typical result is illustrated for the SDS I mesophase listed in table 1. Table 7 is a list of the transitions of each half spectrum according to the numbering set out by Emsley and Lindon [17]. The experimental spectrum is best represented by the average deviation of the transition from the spectral centre. This experimental spectrum is compared with the best calculated spectrum obtained using the coupling constants $J_{12} = 7{\cdot}427\,\mathrm{Hz}$, $J_{13} = 1{\cdot}409\,\mathrm{Hz}$, $J_{14} = 0{\cdot}430\,\mathrm{Hz}$; $D_{12} = 138{\cdot}09\,\mathrm{Hz}$, $D_{13} = 26{\cdot}745\,\mathrm{Hz}$ and $D_{14} = 17{\cdot}433\,\mathrm{Hz}$. at 25°C in the nematic range. It is important to note that all couplings, both scalar and dipolar, are absolutely positive. The value of J_{14} is so small that we cannot definitely assert from this spectrum that the sign is positive but later experiments confirm this assertion. Figure 1 shows the experimental spectrum and the best fit computed spectrum below it. The legend to this figure gives the best estimate of probable error in the computed coupling constants. The spectrum of benzene in SDS I from table 1 is typical of all the other systems studied and the full results of the derived scalar and dipolar couplings in each case is presented as table 8. The experimental errors given full for the SDS I mesophase are all comparable and independent of the mesophase system. The dipolar couplings within the benzene ring are always positive, independent of the sub-type of the nematic mesophase which was used as solvent. Benzene has the highest degree of order in the mesophase CsPFO I and a very small ordering in DSCG II. This can be seen by comparing the values of D_{12} in both solvents. The sign of J_{14} can be said to be indeterminate in all mesophases except DSCG II. In this last mesophase the dipolar couplings are so small that a change in sign of the J_{14} of $-0{\cdot}882\,\mathrm{Hz}$ is sufficient to alter the computed spectrum. We conclude that for the first time J_{14} is correctly determined to have a positive sign.

Table 7. Calculated and experimental transitions of the proton magnetic resonance spectrum of benzene oriented in the SDS I mesophase at 25°C. The transitions are numbered according the scheme set out in [17].

Transition	Low field/Hz	High field/Hz	Average/Hz	Calculated/Hz
1	519·83	520·53	520·18	520·18
2	18·91	19·05	18·98	18·86
3	148·74	149·12	148·93	149·46
4	382·42	383·09	382·76	383·05
5	439·67	440·34	440·01	440·11
6	8·80	8·99	8·91	9·31
7		294·99	294·99	294·73
8	468·33	468·91	468·62	468·82
9	294·34	294·99	294·34	294·58
10	114·29	114·81	114·55	114·23
11	115·69	116·13	115·97	116·79
12	204·55	204·55	204·55	204·83
13	519·83		519·85	520·07
14	51·84	52·05	51·97	52·46
15	372·66	373·34	373·00	373·48
16				687·81
17	479·04	479·72	479·70	480·35
18	158·40		158·40	159·30
19	154·81	155·03	154·92	155·06
20	281·57	282·32	281·95	282·43
21	138·24		140·55	138·59
22	286·24	286·69	286·47	286·70
23	386·51	387·99	387·33	387·91
24	25·62	25·76	25·69	26·11
25	385·54	385·35	385·45	385·19
26	241·95	242·57	242·26	242·49
27	277·21	277·90	277·56	277·80
28	81·22	81·40	81·31	81·49
29	61·18	61·42	61·30	61·70
30	342·39	343·03	342·71	343·45
31	104·02	104·27	104·15	104·26
32	25·64	25·74	25·69	25·60
33	168·58	169·01	168·80	169·25
34	69·56	69·85	69·71	69·94
35	199·24	199·72	199·48	199·93
36	11·22	10·89	11·06	10·85
37	249·44	249·98	249·71	250·08
38	379·54	380·00	379·77	380·15

We conclude that all scalar proton–proton couplings in the benzene ring are absolutely positive in sign as we have asserted earlier in this paper.

The fact that the dipole–dipole coupling constants between protons on the benzene ring are always positive for all nematic solvents studied here means that the order parameter, S_{ij}, for all axes in the plane of the benzene ring are negative. The degree of order of the six-fold axis perpendicular to the plane of the ring is therefore positive, indicating a parallel alignment to the applied magnetic field. This relationship between the benzene molecules and the magnetic field is independent of the shape of the micelles in the nematic phase and the sign of the diamagnetic anisotropy of the mesophase.

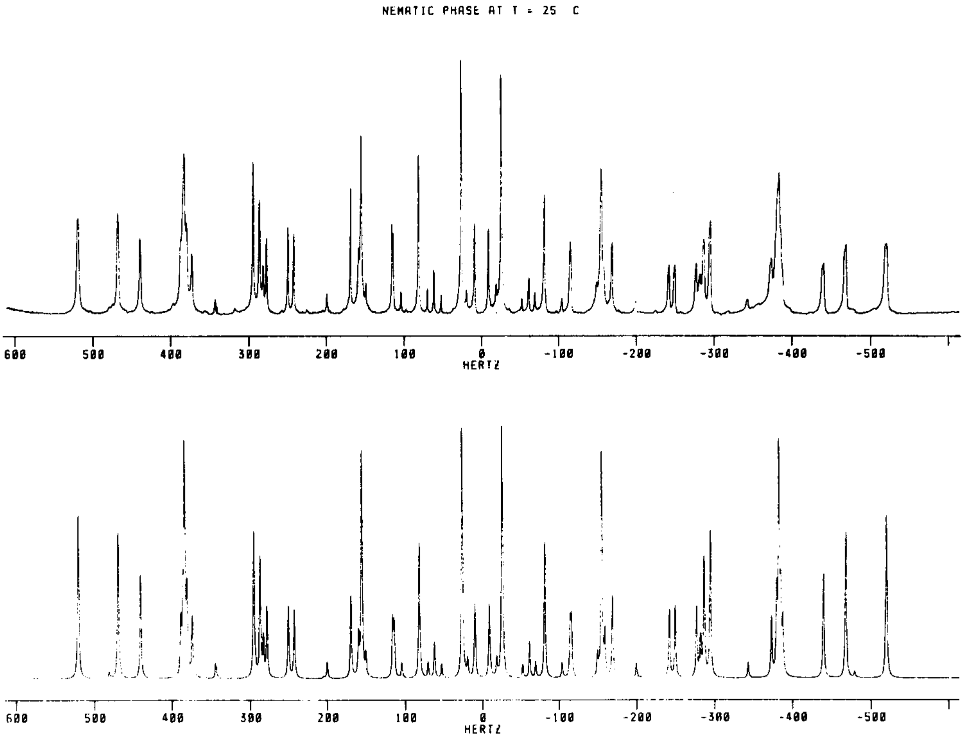

Figure 1. ^{1}H spectra of benzene in mesophase SDS I listed in table 1. Solute concentration, 1·33 wt %; probe temperature, 25° C; number of FIDS 500; average linewidth, 1·32 Hz; R.M.S. error, 0·461 Hz; maximum error of any line position, 1·114 Hz; probable error D_{12}, 0·035 Hz; probable error D_{13}, 0·043 Hz; probable error D_{14}, 0·045 Hz; probable error J_{12}, 0·092 Hz; probable error J_{13}, 0·094 Hz; probable error J_{14}, 0·100 Hz. The upper spectrum is the experimental one and the lower spectrum is calculated.

Table 8. Scalar and dipolar coupling constants for benzene aligned in lyotropic nematic phases at 25° C.

Nematic sub-type	N_D^-	N_C^+	N_C^+
Phase identification from tables 1–6	SDS II	SDS I	KL I
J_{12}/Hz	7·519	7·427	7·427
J_{13}/Hz	1·366	1·409	1·351
J_{14}/Hz	0·770	0·430	0·913
D_{12}/Hz	168·0	138·09	96·11
D_{13}/Hz	32·76	26·745	18·72
D_{14}/Hz	21·396	17·443	12·187
Nematic sub-type	N_D^-	N_C^-	N_D^+
Phase identification from tables 1–6	DACl II	DSCG II	CsPFO I
J_{12}/Hz	7·501	7·546	6·608
J_{13}/Hz	1·433	1·620	1·898
J_{14}/Hz	0·500	0·882	1·166
D_{12}/Hz	273·68	24·52	882·33
D_{13}/Hz	52·64	4·760	170·48
D_{14}/Hz	35·18	3·263	111·07

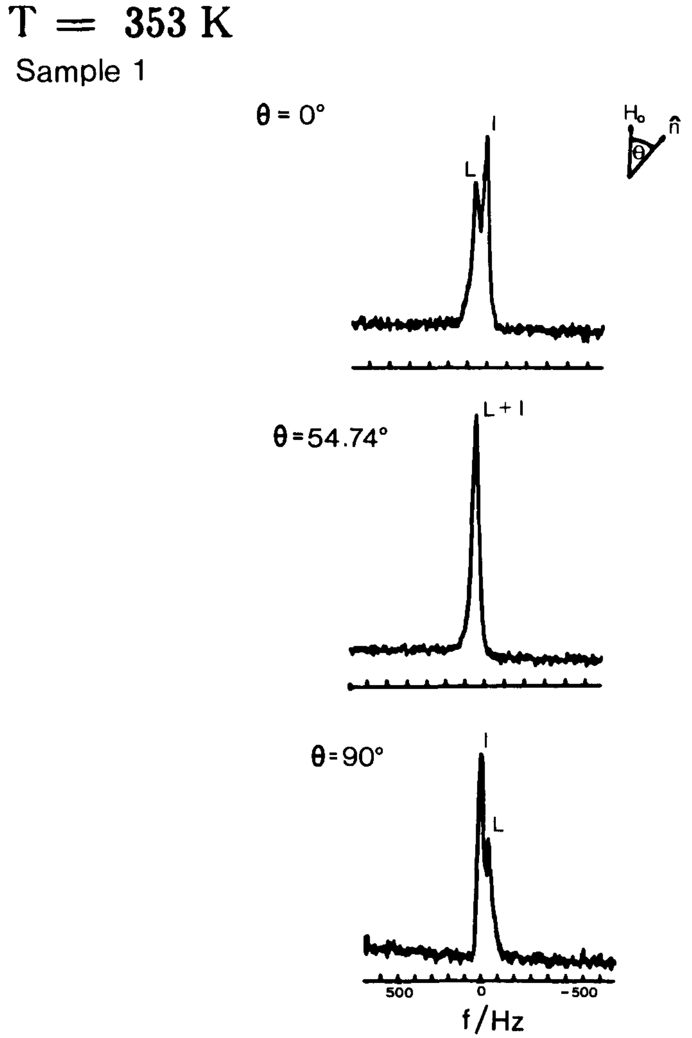

Figure 2. Caesium-133 N.M.R. spectrum of sample 1 described in table 6. The spectra show the central transition of the aligned lamellar phase (L) and the single transition of the isotropic micellar phase (I) in equilibrium. In the upper spectrum the lamellar phase director is in parallel to the applied field, in the centre spectrum at the magic angle of 54° 44′ and in the lower spectrum perpendicular to the applied magnetic field.

3.2. *Studies of caesium perfluorooctanoate/water*

The phase diagram earlier published by Boden *et al.* [16] was investigated using the three compositions listed in table 6 by both deuterium and caesium-133 magnetic resonance studies. Sample 1 at room temperature exists in a lamellar phase, L, but on raising the temperature a two-phase region occurs; one of the phases is lamellar and the other isotropic. At the highest temperatures only the isotropic micellar phase remains. On first raising the temperatures the lamellar phase is not aligned and the deuterium N.M.R. spectrum of the D_2O in the phase shows the classical randomly aligned Pake doublet. The caesium-133 magnetic resonance spectrum is a seven transition, first order quadrupole splitting for the spin quantum number 7/2. The centre

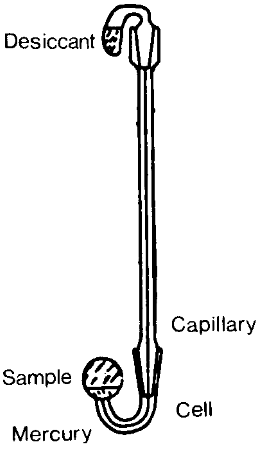

Figure 3. The capillary dilatometer.

transition manifests the random alignment of the directors by a typical powder pattern originating from the chemical shift ansotropy. When the sample is cooled slowly in the magnetic field from the isotropic micellar region the nematic phase appears, uniformly aligned with the director parallel to the field direction. At lower temperatures the nematic phase undergoes a transition to an aligned lamellar phase with the director also along the field direction. In aligned samples the central sharp transition of the caesium N.M.R. spectrum is apparently chemically shifted between isotropic and lamellar phases in equilibrium (see figure 2). The central transition of the caesium-133 spectrum for the lamellar phase appears at lower field. This is shown in figure 2 in the uppermost spectrum. Rotation of the sample in an iron magnet geometry allows the director for the lamellar phase to be set at any desired value to the magnetic field because on rotation of the sample no reorientation of the director of the lamellar phase occurs. Figure 2 shows the variation of the spectrum of the central caesium-133 transition with the angle between the magnetic field and the lamellar phase director. The central spectrum shows that at the magic angle the caesium-133 signal from the isotropic micellar phase is co-incident with that of the lamellar phase. There is therefore no real chemical shift between the two phases and we conclude that the caesium ion is in the same environment in both isotropic and lamellar phases in equilibrium. When the lamellar phase director is perpendicular to the magnetic field the central caesium-133 signal appears at high field with half the apparent shift of the uppermost spectrum in figure 2.

3.3. *The phase transition* $N_D^+ \rightarrow L$

The phase transition between disk nematic phases and lamellar phases involves the appearance or disappearance of translational order along one dimension perpendicular to the bilayer lamellae [6, 16]. It has been suggested that this phase transition can be continuous rather than first order [6, 16]. The order of the phase transition has been based on indirect evidence, such as N.M.R. studies and/or X-ray scattering from the samples [6]. The definition of a first order phase transition derives from the behaviour of the thermodynamic functions of state at the transition. The thermodynamic state function most easily accessible is volume and yet no measurements have yet been made of this quantity at the phase transition. A capillary dilatometer

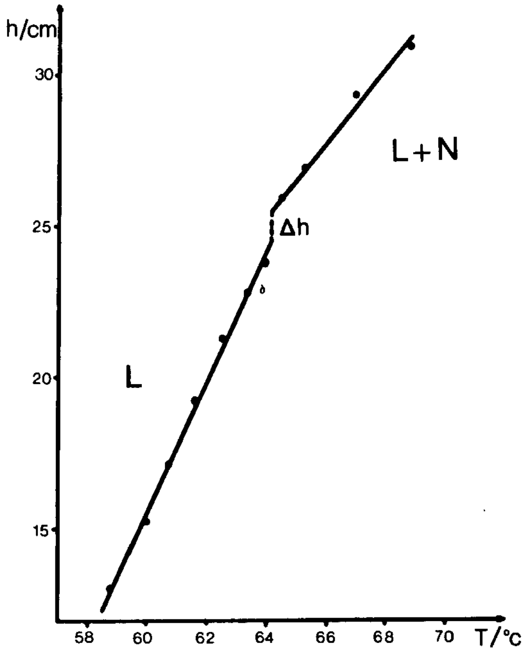

Figure 4. A plot of the temperature dependence of the mercury height, *h*, for sample 2. The solid line shows the best fit.

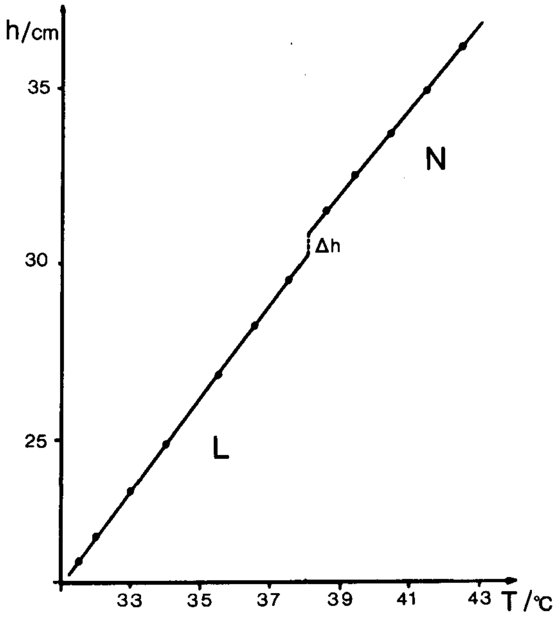

Figure 5. The temperature dependence of the mercury height, *h*, for sample 3. The best fit is shown as the solid line.

was constructed with the design shown in figure 3. The sample bulk about 8 ml in volume and the capillary diameter was 0·5 mm. In all three samples (listed in table 6) there was discontinuities in density at the phase transition showing that the transition may be first order. The cathetometer readings of the mercury level in the capillary dilatometer is given for sample 2 and sample 3 as figures 4 and 5. The expansion of the sample with temperature is accurately linear except at the phase transition. The discontinuity at the phase transition was measured as 1·01 cm for sample 1, 1·14 cm for sample 2 and 0·65 cm for sample 3. We concluded that, according to definition, the phase transition lamellar to nematic disk may be first order for these three samples. The expansion coefficient with temperature in the ND_D^+ and lamellar phases are equal in figure 5.

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