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Phase-transition studies of 5O.5 and 9O.4

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As part of our detailed comparative studies of groups of liquid-crystalline compounds that belong to a homologous series, we present phase-transition studies of the compounds *N*-(4-*n*-pentyloxybenzylidene)4′-*n*-pentylaniline (5O.5) and *N*-(4-*n*-nonyloxybenzylidene)4′-*n*-butylaniline (9O.4) using different experimental techniques. The compound 5O.5 is reported to exhibit a phase sequence N, S_A, S_C, S_B and S_G, while 90.4 shows the sequence S_A, S_F and S_G. The salient features of our work on 5O.5 are (i) a new smectic F phase is found in place of the reported smectic B phase, which is confirmed by both miscibility and X-ray studies; (ii) the formation of smectic-C-like short-range order in the nematic phase well above the S_A–N transition; and (iii) a large tilt-angle variation in the smectic C phase (0–23·5°C) in a small temperature range (4·1°C). The phase changes across the S_A–I transition, and for the first time across S_F–S_A transition, are carried out by volumetric studies. The detailed inferences of these are also presented.

1. Introduction

In recent years there has been increasing interest in the stable phases mediating the transition between different liquid-crystalline phases [1]. In particular, interest has focused on smectic liquid crystals in which the degree of order within the layers changes, quite often in a very subtle way, from one phase to another. In the smectic A, for example the director is parallel to the layer normal. However, as in the tilted smectic C phase, there are only short-range positional correlations within the layers. Upon cooling the smectic A or C phase, a smectic F phase is observed in some of the *N*-(4-*n*-alkoxybenzylidene)4′-*n*-alkylanilines, in which long-range bond orientational order is believed to set in [2–4], whereas the positional correlations remain short-range. A further reduction of temperature leads to the onset of long-range positional order in the smectic G phase, which is considered to be crystalline with molecular disorder and particular rotational degrees of freedom. Two such compounds *N*-(4-*n*-pentyloxybenzylidene)4′-*n*-pentylaniline (5O.5) and *N*-(4-*n*-nonyloxybenzylidene)4′-*n*-butylaniline (9O.4) of the *n*O.*m* homologous series exhibit the phase sequences N, S_A, S_C, S_F and S_G and S_A, S_F and S_G respectively. We present here studies of the phase transition for these compounds.

2. Experimental

The compounds 5O.5 and 9O.4 were prepared following the procedure described elsewhere [5]. Thermal microscopy was carried out using a Hertel and Reuss Superpan II polarizing microscope attached to a heating block. The details of the X-ray diffraction and density measurements have been reported earlier [5, 6].

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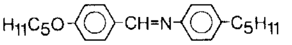
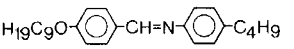
3. Results and discussion

The molecular formulae and transition temperatures of the compounds 5O.5 and 9O.4 are

5O.5


9O.4


5O.5 C 28°C S_G 47°C S_F 49°C S_C 53·1°C S_A 54·4°C N 77·8°C I;

9O.4 C 50°C S_G 66°C S_F 68·2°C S_A 80·9°C I.

The compound 5O.5 is reported to possess the phase sequence N, S_A, S_C, S_B and S_G. However, Smith and Gardlund reported the sequence N, S_A, S_C, S_3, S_G, and it is suggested that S_3 may be smectic F. We have carried out thermal microscopy, observing a chequerboard broken focal conic fan texture, and X-ray studies, indicating a tilted phase; thus confirming that the S_3 phase is smectic F rather than smectic B. The miscibility studies of 5O.5 with *N*-(4-*n*-heptyloxybenzylidene)4′-*n*-hexylaniline, 7O.6, *N*-(4-*n*-nonyloxybenzylidene)4′-*n*-butylaniline, 9O.4, and terephthalylidene bis(4-*n*-octylaniline) confirmed the existence of the smectic F phase [7]. Further confirmation of the smectic F phase was achieved by conoscopic study, which indicated a tilted and biaxial phase, while the X-ray study detected a tilt angle of 25°.

The X-ray diffraction photographs [6] of 5O.5 in the nematic phase, in which the nematic director $\hat{n}$ is perpendicular to the line joining the maxima of the outer diffuse reflections, indicated that the intensity of the inner maxima in the nematic phase grows continuously with decreasing temperature, which characterizes the formation of smectic-C-like short-range order in the nematic phase. Earlier reports [8] established that X-ray diffraction photographs of a classical nematic phase show that the outer and inner maxima possess almost identical intensities. However, in the cybotactic or nematic phase with short range translational order the intensity of the inner maxima is greater than the intensity of the outer maxima. The formation of short-range translational order, which was observed earlier in the nematic phase of 5O.8 and 5O.10, is reported as a pretransitional effect [9].

The smectic C thermal range is short (only 4·1 K) and its structural investigation presents an interesting feature. The smectic C phase possesses a finite tilt angle between the layer normal and the director. If the molecule is linear then there is a single tilt angle, but for mesogens like 5O.5 with their zig-zag molecular structure there are at least three tilt angles, one associated with the core region and the other two with the alkyl-chain regions of the smectic layer [10]. Independent molar volume and X-ray studies [11] revealed that the end chains are inclined in the smectic A phase, making a small angle to the layer normal. Hence we present here the temperature dependence of the tilt angle in 5O.5 determined from the X-ray measurements, assuming that the rigid central part makes the tilt angle with the layer normal.

The determination of the tilt angle by X-ray diffraction requires a monodomain sample of the smectic C phase, which is readily obtained when it is preceded by both nematic and smectic A mesophases as in 5O.5. The sample is first heated into the nematic phase and the director is aligned parallel to the magnetic field. The temperature is then lowered until the smectic A phase is formed and so the smectic layers are arranged orthogonal to the field. The temperature is further decreased until the transition to the smectic C phase occurs, at which temperature the director tilts with respect to the layer normal, which remains parallel to the magnetic field. In this configuration all of the tilt directions are equivalent. The tilt angle was obtained from

$$\theta_t = \cos^{-1}(d_C/d_A),$$

where d_C and d_A are the layer thicknesses in the smectic C and smectic A phases respectively. Since the molecular conformation (in particular, the chain conformation) in the smectic phase is unknown and furthermore thermal fluctuations will reduce the effective molecular length, this is taken as the layer spacing d_A of the smectic A phase. The tilt angle, which is assumed to be zero in the smectic A phase, grows continuously with decreasing temperature in the smectic C phase. The tilt angles determined in this way are plotted as a function of temperature in figure 1; the experimental error is ± 1°. The tilt angle is seen to grow rapidly from its value of zero at $T_{S_CS_A}$, the smectic C–smectic A transition temperature, as expected for a continuous transition, and reaches its maximum value of 23·6° prior to the formation of the smectic F phase, at which the tilt angle suddenly increases to 25°. Even though a large tilt-angle variation has been observed [12, 13] for other homologous series, viz terephthalylidene bis(4-*n*-alkylanilines) and 5-*n*-alkyl-2-(4-*n*-alkyloxyphenyl)-pyrimidines, these are not as large as that found for 5O.5 over a small temperature range of 4·1 K. Previous reports [14] have indicated the difficulty of measuring the temperature dependence of the tilt angle in compounds exhibiting a small S_C thermal range.

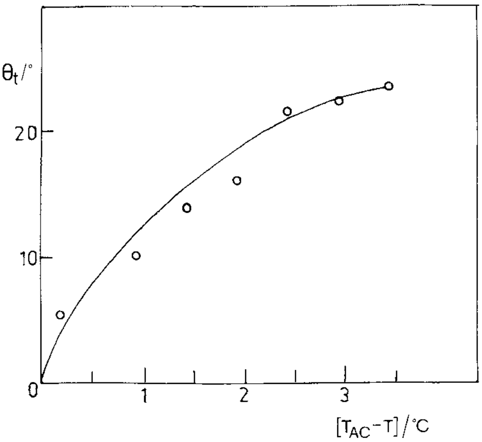


Figure 1. Variation of the tilt angle with temperature for 5O.5.

The temperature dependence of the tilt angle is fitted to the expression

$$\theta = A(T_{AC} - T)^{\nu},$$

proposed by de Gennes [1], to quantify the difference in the measured tilt angles.

The quality of the fit for 5O.5 is sensitive to the choice of $T_{S_CS_A}$ because the smectic range is so small. The best fit, which is in good agreement with experiment, was obtained wth $T_{S_CS_A} = 326{\cdot}1$ K, which is just 0·15 K below than the transition temperature measured optically. The exponent ν was determined to be 0·41 ± 0·04, which agrees well with the values of 0·39 ± 0·03 for 7O.4 [15] and 0·31 ± 0·02 for

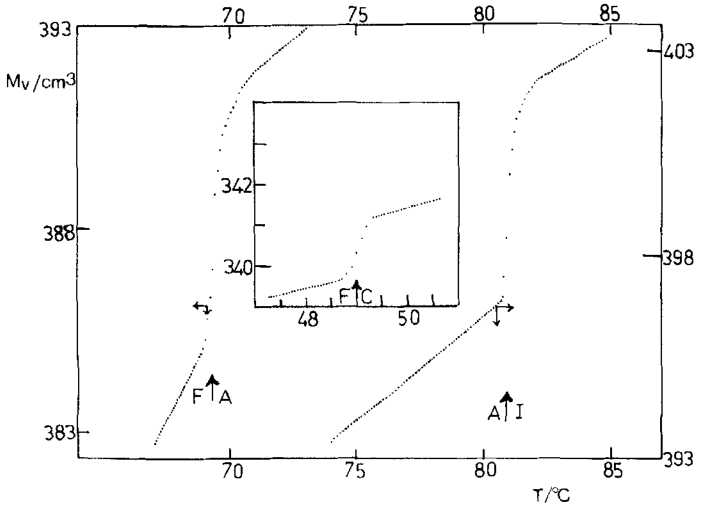


Figure 2. Variation of the molar volume with temperature for 9O.4. The inset shows the results for 5O.5 across the smectic F–smectic C transition.

n-hexyl-4′-n-decyloxybiphenyl-4-carboxylate (HDBC) [16] obtained from tilt-angle data obtained using E.S.R. spectroscopy. These results support de Gennes's prediction for the exponent of 0·35 but not the mean-field value of 0·50. Unlike ν, the coefficient A, which may be identified as the tilt angle when $T_{AC} - T$ is 1 K, are quite different for the three mesogens. Thus for 5O.5 this coefficient is 13·3° $K^{-0\cdot41}$ whereas for 7O.4 and HDBC the values are smaller, being 11·4° $K^{-0\cdot39}$ and 6·5° $K^{-0\cdot31}$ respectively. Our values are in good agreement with the reported results of Heeks and Luckhurst [17]. The molecular origins of this relatively large difference in the A coefficients for these mesogens are not apparent—indeed their interpretation presents another problem to elucidate the structural details.

The smectic F–smectic C and smectic F–smectic A transitions in 5O.5 and 9O.4 respectively are examples of transitions from disordered tilted or orthogonal structure to ordered tilted structure, are revealed by large density jumps. The transition from the S_C phase, with its one-dimensional translational order of tilted molecules with disordered centres of mass positions and fluid layers, to the S_F phase, where the moleculars are packed in layers with a pseudo-hexagonal arrangement with a two-dimensional structure of the positional order and long axes tilted (tilt towards an edge

Table 1. The transitional properties of the nO.ms.

Compound	Smectic–smectic transition	($\Delta v/v$) per cent	(dT_t/dP)/K kbar^{-1}	References
5O.5	C–F	0·39	43	[6]
9O.4	A–F	1·42	48	Present work
8O.4	A–B	0·42	15	[18]
5O.8	A–B	0·79	49	[19]
5O.10	A–B	0·76	42	[20]
TBOA	C–F	1·01	43	[21]
TBDA	C–I	0·55	43	[22]
7O.5	C–B	0.76	36	[23]
7O.8	C–B	0·84	42	[24]

Table 2. The transition temperatures and associated changes in density and enthalpy together with the estimated pressure-dependent S_A–I transition temperatures.

Compound	T_{S_AI}/°C	($\Delta v/v$)/per cent	ΔH/J mol^{-1}	(dT_t/dP)/K kbar^{-1}
Di-*n*-hexadecyl 4,4′-azoxycinnamate	135·0	0·40	4764	26·7
Di-*n*-undecyl 4,4′-azoxycinnamate	160·2	0·35	5555	34·9
Di-*n*-undecyl 4,4′-azoxy-α-methylcinnamate	85·7	1·21	8565	18·9
n-Amyl 4-(4-*n*-dodecyloxybenzylideneamino)cinnamate	137·2	1·28	8414	33·7
Diethyl 4,4′-azoxydibenzoate	123·0	1·98	5442	43·0
Terephthalylidene bis(4-*n*-octylaniline)	202·4	0·96	5670	42·0
Terephthalylidene bis(4-*n*-nonylaniline)	199·0	1·00	6680	41·5
Terephthalylidene bis(4-*n*-decylaniline)	190·2	1·82	7080	72·2
N-(4-*n*-Heptyloxybenzylidene)4′-*n*-octylaniline	83·0	1·04	5870	27·3
N-(4-*n*-Octyloxybenzylidene)4′-*n*-octylaniline	86·2	0·73	–	–
N-(4-*n*-Octyloxybenzylidene)4′-*n*-butylaniline	81·2	1·11	5680	26·5
N-(4-*n*-Nonyloxy benzylidene)4′-*n*-butylaniline	80·9	1·22	6320	39·5

of hexagon) with respect to the layer planes (i.e. with uncorrelated layers but long-range bond orientational order), is expected to be a first-order transition. The S_F–S_A transition (see figure 2) is found only in 9O.4, and we are unaware of any other report of volume or density studies across this transition. The volume jumps across the smectic–smectic transitions are given in table 1. The volume jump across the S_F–S_A transition is found to be much higher than the corresponding S_B–S_A, S_F–S_C, C–I or C–S_B transitions. The smectic A–isotropic transition in 9O.4 (see figure 2) is accompanied by a significant volume jump of 1·22 per cent, indicating the first-order nature of the S_A–I transition. The growth of the orientational order as well as the translational order from the isotropic liquid predicts a larger volume change. The volume jump across this transition in 9O.4 falls on the higher side of the values reported across this transition in other compounds; these are illustrated in table 2. The transition temperatures, volume jumps and enthalpies of transition for different compounds are presented in table 2 for completeness.

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