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Interdigitated smectic A and B mesophases in higher homologues of the 5O.*m* series

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We report the synthesis, characterization and structural studies of the higher homologues of *N*(4-*n*-pentyloxybenzylidene)4-*n*-alkylaniline compounds, viz. 5O.12, 5O.14 and 5O.16 by thermal microscopy, differential scanning calorimetry and X-ray diffraction. The compounds exhibit N–S_A–S_B, N–S_A–S_B and N–S_A phase sequence variants, respectively. The X-ray results reveal the existence of an interdigitated smectic A phase in 5O.16 and smectic B phase in 5O.14. Results are discussed in light of the available data on the *n*O.*m* series

1. Introduction

The *N*(4-*n*-pentyloxybenzylidene)4-*n*-alkylaniline compounds (5O.*m*s) [1–3] in the *n*O.*m* homologous series occupy a unique place in liquid crystal science since the increase of the alkyl chain number in these materials shows interesting phase sequence variants, N–S_C ($m=2$), N–S_A–S_C–S_F–S_G ($m=5$), N–S_A–S_C–S_B–S_F–S_G, ($m=6$ the most extensive polymorphism reported in the *n*O.*m* series) and N–S_A–S_B or N–S_A for the higher homologues with varying thermal ranges. Systematic studies [4] of the nature of the N–S_A transition in the *n*O.*m*s as functions of alkyl and alkoxy chain lengths reveal (i) a second order N–S_A transition in the compounds with $n<5$ and weak first order transitions with $n>5$, (ii) a possible existence of a tricritical point (TCP) in 5O.*m* compounds, (iii) the predominant role played by the alkoxy chain (n) rather than the alkyl chain (m) in deciding the nature of the N–S_A transition, and (iv) that the McMillan parameter M, T_{NS_A}/T_{NI} is not useful in comparing different homologous series of liquid crystals [5–10].

M depends sensitively on the magnitude of various molecular interactions that govern the order of the N–S_A transition. These molecular interactions in lower homologous series are primarily dipolar or of a dispersion type. However, as the alkyl and alkoxy chain lengths are asymmetrically increased, the packing considerations become important and influence the order of the nematic–smectic A phase transition. The thermal ranges of the nematic and smectic A phases in the 5O.*m* series as a function of *m*, the alkyl chain length, are shown in figure 1. The compound 5O.12 exhibits a sharp decrease of the nematic thermal range (a three-fold reduction in its nematic phase extent) and yet its N–S_A transition is very weakly first order (as determined from density data [3]) tending to second order as for 5O.10. This behaviour is not expected from any molecular field theory. These theories predict an increasingly first order nature of the N–S_A transition, with the overall increase in molecular length.

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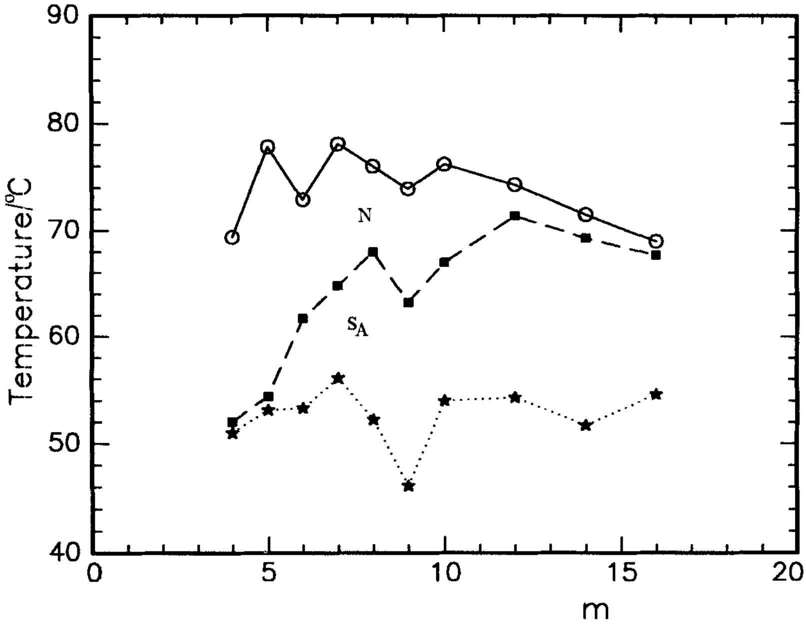
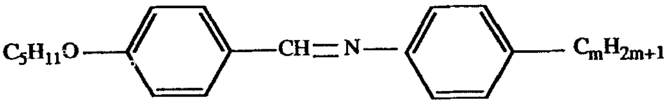


Figure 1. Nematic and smectic A thermal ranges of the 5O.*m* compounds. Open circle, closed square, and filled stars correspond to the nematic–isotropic, nematic–smectic A, smectic A–smectic B (or higher order smectics or crystal) phase transitions, respectively.

Nevertheless, the *M* value (0·992) for 5O.12 [3] is large compared to the values 0·955 [5, 11, 12] and 0·963 [13] reported for the TCP of the mixtures 4O.6 + 6O.4 and 4O.8 + 6O.8 of the *n*O.*m* series, respectively. Also from figure 1, clearly, a sudden and dramatic decrease of the nematic thermal range with the increase of the smectic A range occurs at $M = 6$ and 12 (a three-fold (two-fold) reduction in the nematic phase extent occurs in going from 5O.10–5O.12 (5O.5–5O.6), respectively; also see [4]). The N–S_A transition of 5O.6 ($M = 0{\cdot}967$) shows a weak first order nature while the compounds 5O.5 ($M = 0{\cdot}933$) and 5·07 ($M = 0{\cdot}954$) exhibit a second order nature consistent with the reported value of *M* for the *n*O.*m* series. However, our density data on 5O.12 [3] showed a smaller density jump of 0·06 per cent that deviates significantly from an expected value of about 0·5 per cent for $M = 0{\cdot}992$, in the *n*O.*m* homologous series. These observations motivated us to synthesize the higher homologues of 4O.*m* and 5O.*m* compounds with $m = 14$ and 16 and to study the mesomorphic behaviour and the nature of the N–S_A transition. Here we report the synthesis, characterization and our preliminary X-ray results of *d*-spacing in S_A and S_B phases of 5O.12, 5O.14 and 5O.16.

2. Experimental

Liquid crystals were synthesized following the method described elsewhere [14]. The thermal microscope (TM) and DSC measurements were carried out using a Zeiss polarizing microscope attached to an Instec temperature controlled hot stage and Metler DSC 30 with TC 10A processor, respectively. The molecular formula of the mesogens is



The X-ray diffraction studies were carried out on a Phillips X-ray diffractometer. Typical sample-to-detector distances varied between 25–30 cm. Diffraction patterns were acquired using a linear position sensitive detector (homebuilt) with 95 μm spatial resolution and a Nuclear Data multichannel analyser (MCA) interfaced to an IBM compatible PC. The temperature of the sample was controlled to within ±0·1°C using a homebuilt heating stage. To improve the precision of the measured *d*-spacing, the diffraction peak was fitted to a gaussian profile ($\chi^2 = 1$–2) to measure the *d*-spacing with $\sigma = 0{\cdot}2$ Å.

3. Results and discussion

The liquid crystalline phases exhibited by these compounds were identified according to their microscopic textures. The enthalpies (kJ mol^{-1}) of the transitions were determined by DSC. The results are given in the table. The variation of the layer thickness (*d*-spacing) with temperature in the smectic phases of all three compounds is shown in figure 2 (*a*)–(*c*). The variation of the *d*-spacings [15, 16] in the smectic A and smectic B phases with the alkyl chain number for the 5O.*m*s is presented in figures 3 and 4, respectively.

The structural data on the lower homologues of the *n*O.*m*s suggest that there might be interdigitation, and therefore, a different type of molecular packing in these compounds. Generally, when the S_{Ad} or interdigitated smectic A phase is formed, the first order nature of the N–S_A transition is significantly reduced. For example, the liquid crystal S_2 (a mixture of cyanobiphenyls), which exhibits a nematic thermal range of only 0·7°C, shows a small discontinuity in the nematic order parameter [17]. The motivation for these X-ray studies was to examine the possibility of an induced interdigitated smectic phase when the alkyl chain length (*m*) is increased.

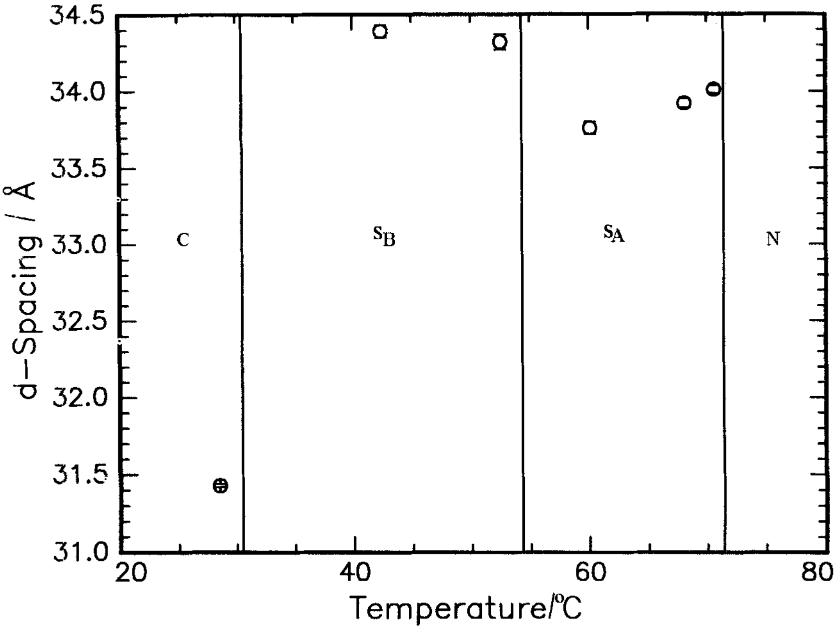
The salient features of our X-ray data are:

(i) The decrease of the smectic A *d*-spacing with the decrease in temperature in 5O.12 and 5O.14 (see figures 2 (*a*) and (*b*)) is unexpected. Because the molecular ordering increases with a decrease in temperature, the *d*-spacing should remain constant or show a slight increase when the lower temperature phase is an orthogonal phase such as a smectic B [15, 16].

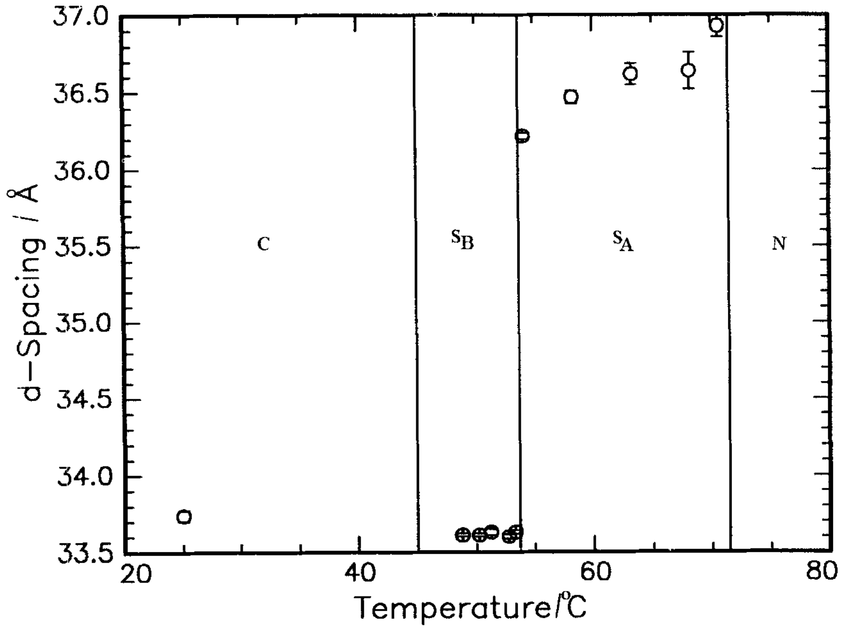
(ii) The *d*-spacing in the smectic A phase of 5O.16 is about 2·5 Å smaller than the expected *d* value (see figure 2 (*c*) and 3), and it remains constant (within ±0·3 Å) throughout the S_A phase.

(iii) The *d*-spacing in the smectic B phase of 5O.12 is consistent with its lower homologues (cf. figure 4). But, in 5O.14, we find an unexpected decrease in the *d*-spacing.

		I–N	N–S_A	S_A–S_B	S_B–C
$m = 12$	T/°C (DSC)	74·3	71·4	54·3	30·5
	ΔH/kJ mol^{-1}	1·380	0·396	2·229	38·859
	T/°C (TM)	74·1	70·9	54·7	28·3
$m = 14$	T/°C (DSC)	71·5	69·3	51·7	43·0
	ΔH/kJ mol^{-1}	1·833	0·722	2·476	45·471
	T/°C (TM)	71·2	68·9	51·6	40·8
$m = 16$	T/°C (DSC)	69·0	67·7		54·6
	ΔH/kJ mol^{-1}	1·870	0·643		57·570
	T/°C (TM	68·8	67·4		55·1


34.5
34.0
33.5
33.0
32.5
32.0
31.5
31.0
d-Spacing / Å
20
40
60
80
Temperature/°C
C
S_B
S_A
N

(*a*)


37.0
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d-Spacing / Å
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(*b*)

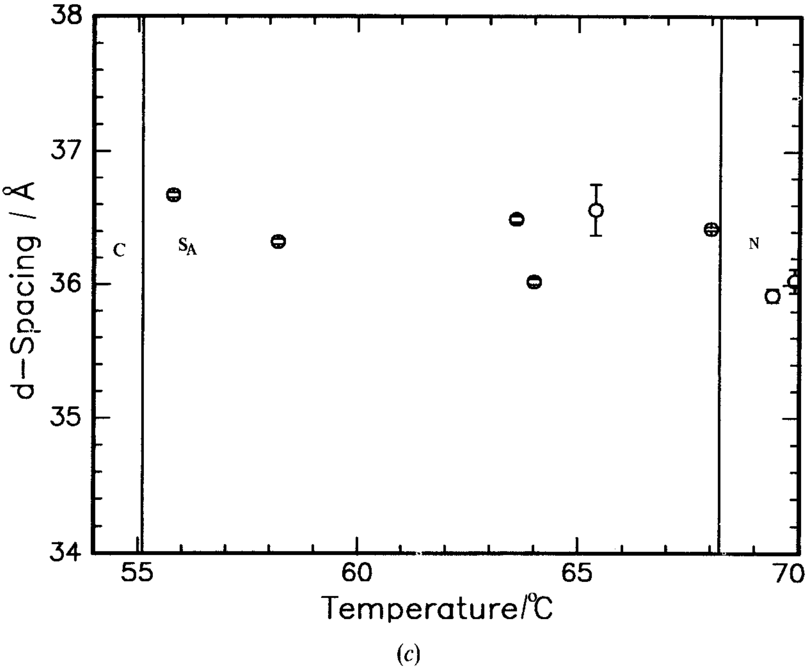

Figure 2. Temperature variation of the *d*-spacing in (*a*) 5O.12, (*b*) 5O.14, and (*c*) 5O.16. Vertical lines separate different phases.

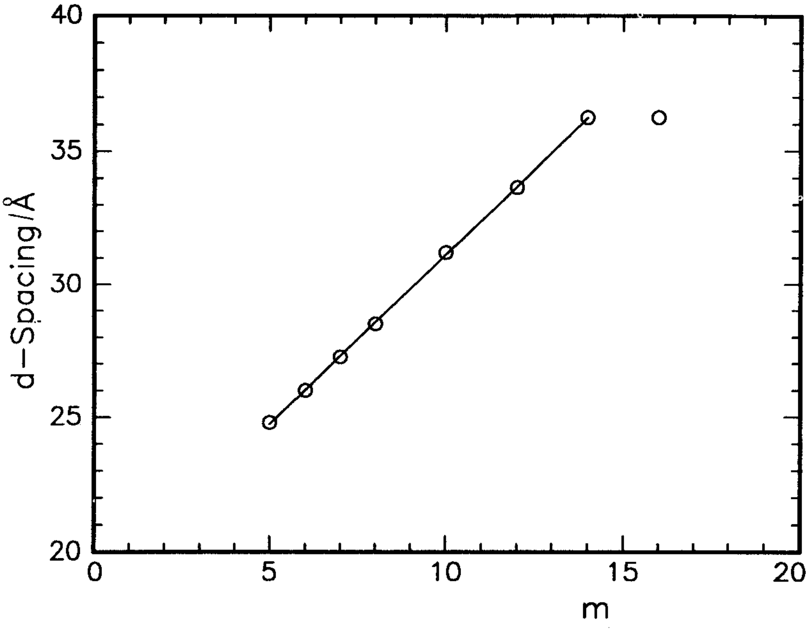

Figure 3. Alkyl chain length dependence of the *d*-spacing in the smectic A phase of the 5O.*m*s.

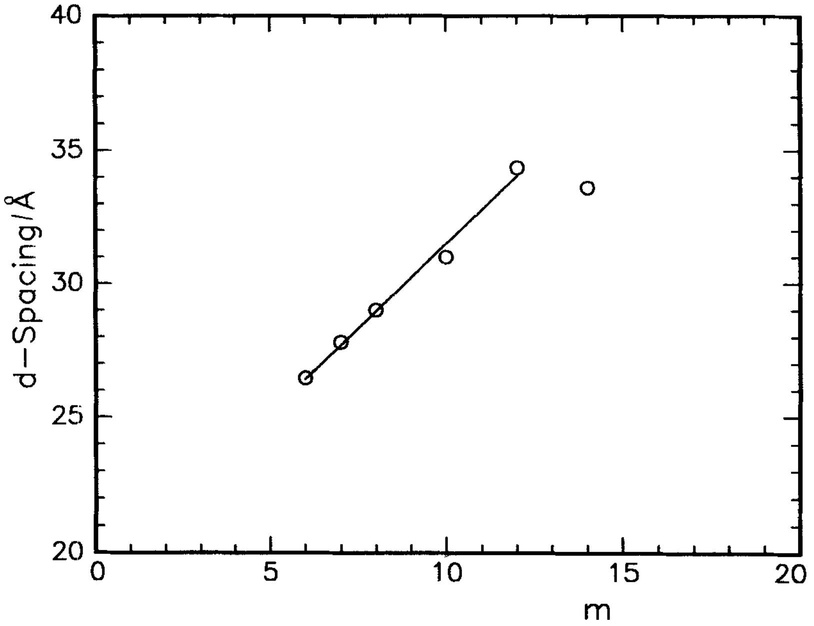

Figure 4. Alkyl chain length dependence of the *d*-spacing in the smectic B phase of the 5O.*m*s.

It can be inferred from our X-ray results that these three compounds show different types of molecular packing arrangements in the orthogonal smectic A and B phases deviating from the lower homologues. The results can be rationalized in terms of interdigitation of the molecules in the smectic layers. Using simple geometric considerations (see figure 5), we can write $d_{obs}=n(2-p)l/2$ where n is 1(2) for monolayer(bilayer), $0\leq p\leq 1$ is the extent of interdigitation, and l is the molecular length. Both l and p can be temperature dependent. Thus, for a monolayer smectic phase, d decreases linearly with p and is cut into half at $p=1$. Using the extrapolated value of d as l for 5O.16 in the smectic A phase (figure 3), we find $p=0{\cdot}13$ with the corresponding values for 5O.14 and 5O.12 of 0·04 and 0·02, respectively.

Thus, the tendency of interdigitation starts from the 5O.12 compound and is complete in 5O.16. Although an observable decrease of the *d*-spacing in the smectic A phase of 5O.12 is noted, this tendency is not reflected in its smectic B phase. However, in 5O.14, the decrease of the *d*-spacing in the smectic A phase is sufficient to induce an interdigitated B phase ($p=0{\cdot}17$). Thus, 5O.16 is a unique compound to exhibit temperature independent interdigitation in the A phase, which is strong enough to quench the formation of the B phase altogether. Our X-ray results suggest the phase sequence variants for these compounds as: 5O.12, (N–S_A–S_B); 5O.14, (N–S_A–S_{Bd}); and 5O.16, (N–S_{Ad}) [18].

Notably, liquid crystals forming the S_{Ad} phase have a single alkyl chain, unlike the *n*O.*m* compounds. For example, systematic studies of interlayer spacing in 4-phenylbenzylidine-4′-alkyl anilines (*m*-X), ($3\leq m\leq 15$) were reported by Benattar *et al.* [19]. Variation of d as a function of m in this series differs from the *n*O.*m*s in that the higher homologues show an increase in the *d*-spacing over the estimated molecular length. These results can also be explained in terms of the interdigitation model. Packing for the lower homologues ($m\leq 7$) corresponds to complete interdigitation ($p=1$) (see figure 5 (*c*)). As the alkyl chain length is increased, we may postulate a mixing incompatibility

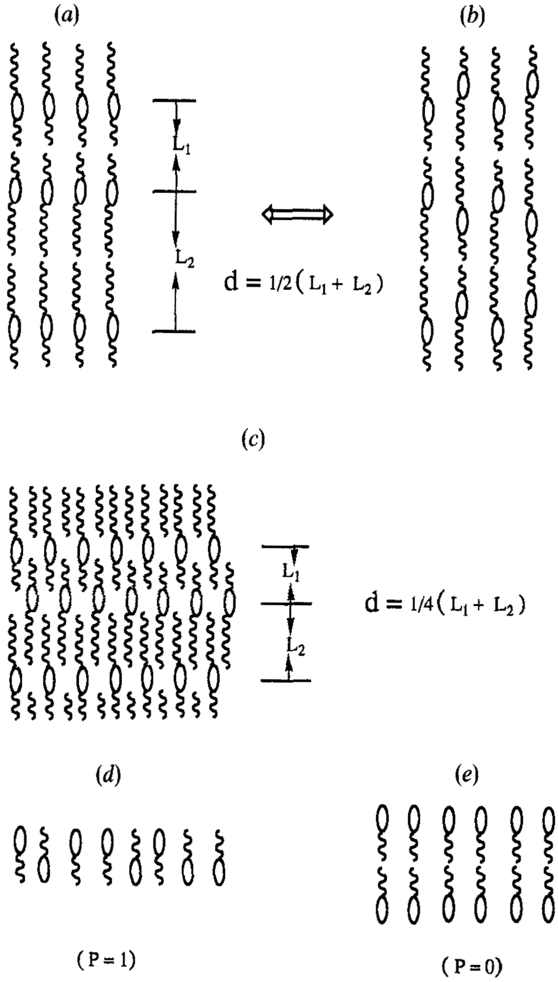

Figure 5. Molecular packing and observed *d*-spacings for the monolayer/bilayer smectics. (*a*) Idealized packing for the *n*O*ms* where short (long) chains face each other. (*b*) Statistical orientational distribution for the short and long chains. Observed *d*-spacing which reflects the average $((L_1 + L_2)/2)$ distance between the higher electron density cores in successive layers. (*c*) Similar to (*a*), except the chains of the molecules from the adjacent layers mix (i.e. interdigitation). (*d*) and (*e*) show packing similar to (*c*) and (*b*) respectively, for a bilayer type of smectic A(B) phase.

of the alkyl chains with the core leading to a reduction in p and hence an increased *d*-spacing compared to the molecular length. Thus for $m = 15$, we estimate $p = 0{\cdot}93$ and, in the limit of large m, we expect to see a bilayer type of arrangement for this homologous series (cf. figure 5(*e*)).

4. Conclusion

The molecular picture emerging from these studies is that, through interdigitation, the free energy of core interaction and efficient chain packing can be simultaneously minimized leading to the formation of S_{Ad} and S_{Bb} phases in these highly asymmetric (unbalanced) 5O.*m* homologues. Future studies of higher homologues of 4O.*m* and 3O.*m* are planned to confirm these effects and will provide a possibility of obtaining a S_{Ad}–N phase transition, where the molecular length is not commensurate with the phase symmetry of the smectic order parameter (i.e. the interlayer spacing).

The compounds 5O.14 and 5O.16 are the first to exhibit a partially interdigitated smectic A phase to interdigitated smectic B phase and nematic to interdigitated smectic A phase transitions in the *n*O.*m* series, respectively.

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