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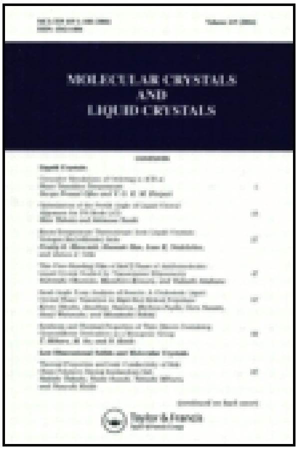

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X-Ray Diffraction Studies of 10O.14 and 10O.8

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X-Ray Diffraction Studies of 10O.14 and 10O.8

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The compounds N(*p*-*n*-decyloxybenzylidene)*p*-*n*-tetradecylaniline, 10O.14, and N(*p*-*n*-decyloxybenzylidene)*p*-*n*-octylaniline, 10O.8 of the well known nO.m homologous series exhibit FG and ACFG phase sequence variants. The molecular tilt in the tilted smectic C, F and G phases is measured by X-ray diffraction studies. The measured tilt angles are small and show temperature independence in the F phase.

Keywords: X-ray diffraction, N(p-n-decyloxybenzylidene)p-n-tetradecylaniline, N(p-n-decyloxybenzylidene)p-n-octylaniline, smectic F and G phase transitions, interlayer spacings, tilt angles

INTRODUCTION

Liquid crystals exhibiting hexatic F phase are of considerable interest because of their structural properties and the associated uncommon phase sequence variants.[1] Some of the unusual phase sequences reported in the nO.m homologous series are AFG (9O.4),[1,2] NACBFG (5O.6),[1,3] ABF (8O.10)[4] and FG (10O.14),[5] and the TBAA series show ACIFG (TBAA10),[6] and CIFG (TBAA12)[7] phase sequences. The compound 10O.14 is unusual in that it exhibits a direct melting of the smectic F phase into the isotropic phase. This phase transition has been reported in *p*-*n*-alkanoloxy *p*-*n*-octyloxybiphenyl esters.[8] The special feature of this transition (smectic F-isotropic liquid) is that the long-range bond orientational order, positional order, and orientational order vanish simultaneously. Generally, mesophases exhibiting a 2D long-range bond orientational order, such as the smectic hexatic B, I, and F phases, undergo transition to other smectic phases and not to the isotropic phase.

We have reported phase sequences in 10O.m ($5 < m < 17$) series.[5,9] Lower homologues (m even and <12) exhibit an ACFG phase variant, while members with an odd number of carbon atoms ($m < 11$) show an orthogonal smectic B phase between the A and G phases replacing the tilted C and F phases. In higher homologues (m even >10), an AFG (10O.12, 10O.16)[5] phase sequence is noted, with the exception of 10O.14 as mentioned before. As part of a systematic study of

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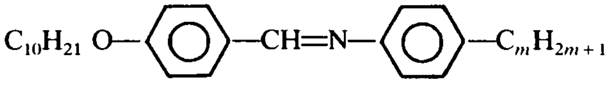
synthesis, characterization and phase transitions in nO.m. compounds, we present in this paper our X-ray diffraction results in N(*p*-*n*-decyloxybenzylidene) *p*-*n*-tetradecylaniline, 10O.14 and N(*p*-*n*-decyloxybenzylidene) *p*-*n*-octylaniline, 10O.8 of 10O.ms.

EXPERIMENTAL

The synthesis and characterization of the compounds are described earlier.[5,9] The molecular formulae and transition temperatures (°C) from differential Scanning Calorimetry (DSC), Thermal Microscopy (TM), and from the literature[5,9] are given below.



m = 8	I 92.7	A 87.6	C 85.8	F 85.2	G 44.9 K
ΔH	8060	—	5343	—	42538*
	89.8	84.8	82.2	81.8	43.0#
	89.1	—	82.3	—	42.3
ΔH	8385	—	5251	—	42635
m = 14	I		88.5	F 87.1	G 66.3 K
ΔH			8474	5394	61514
			83.5	82.2	68.5#
			81.5	—	64.9
ΔH			15400		52350

TM data; *J/mole.

The X-ray diffraction studies were carried out on a Phillips X-ray diffractometer. A typical sample-to-detector distance varied between 25–30 cms. Diffraction patterns were acquired using a linear position-sensitive detector (home built with 160 μm spatial resolution) and they were further analyzed using a nuclear data multichannel analyzer (MCA) interfaced to an IBM-compatible PC. The temperature of the sample was controlled to within ±0.1°C using a home built heating stage. In order to improve the precision of the measured *d* spacing, the diffraction peak profile was fitted to a Gaussian lineshape (χ^2_{Type} = 1–2) to measure *d* spacing with ±0.2 Å resolution.

RESULTS AND DISCUSSION

X-Ray Studies of 10O.8

We present in Figure 1 the variation of *d* spacing in the smectic A, C, F and G phases of 10O.8. The *d* spacing decreases in the smectic C phase, from which the molecular tilt angle (ϕ = arccos (d/d_a) where *d* and d_a are the *d* spacings in the

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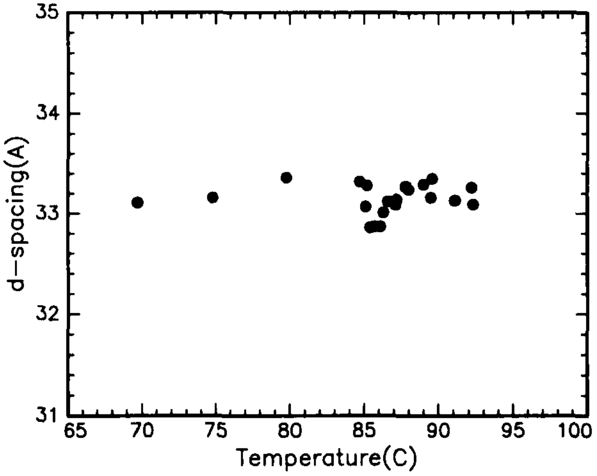


FIGURE 1 Temperature variation of *d*-spacing in 10O.8.

tilted smectic phases and smectic A phase)) is determined. The maximum tilt angles observed in the smectic C, F, and G phases are 10° ± 1°, 10° ± 1°, and 7° ± 2°, respectively. There is an abrupt change in the tilt angle at the FG phase transition.

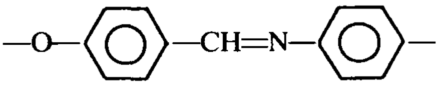
In the smectic G phase, the tilt angle increases with the decrease in temperature. However, the magnitude of the tilt angle variation is small. The detailed temperature variation of the tilt angle in the smectic F phase could not determined due to its narrow thermal range (0.6°C) and the limited temperature resolution (0.1°C) of the heating stage.

X-Ray Studies of 10O.14

As this material exhibits no smectic A phase, the length of the molecule is assumed to be 43.14 Å for the calculation of the molecular tilt in the F and G phases. This value is arrived at from the experimental data on 5O.m[3,10,11] and nO.8[10,12] compounds. We have adopted the following procedure to calculate the assumed *d* spacing of 43.14 Å. From the available experimental data, the smectic A layer spacing *d* is plotted as a function of alkyl (*m*, Figure 2, 5O.m) as well as alkoxy (*n*, Figure 3, nO.8) chain lengths, respectively. Then we write the overall molecular length, $d(m, n)$, in the smectic A phase as

$$d(m, n) = d_{\text{core}} + md_m + nd_n \tag{1}$$

where d_m or n is the slope obtained from the d vs m or n plots, and d_{core} is the length of:



segment. We find $d_m = 1.27 \pm 0.07$ Å, $d_n = 0.94 \pm 0.08$ Å and $d_{\text{core}} = 13.78 \pm$

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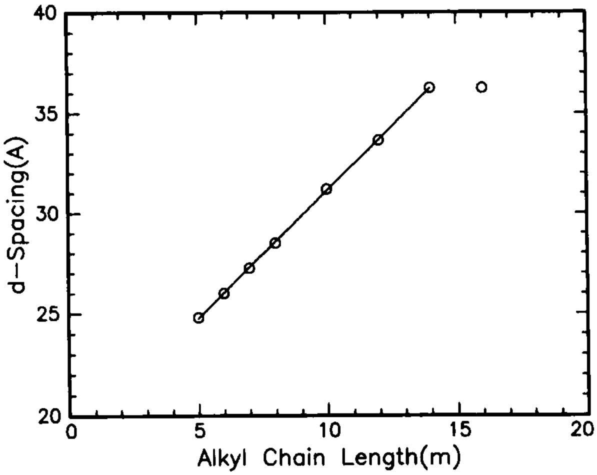

FIGURE 2 Alkyl chain length dependence of *d*-spacing in the smectic A phase of 5O.ms.

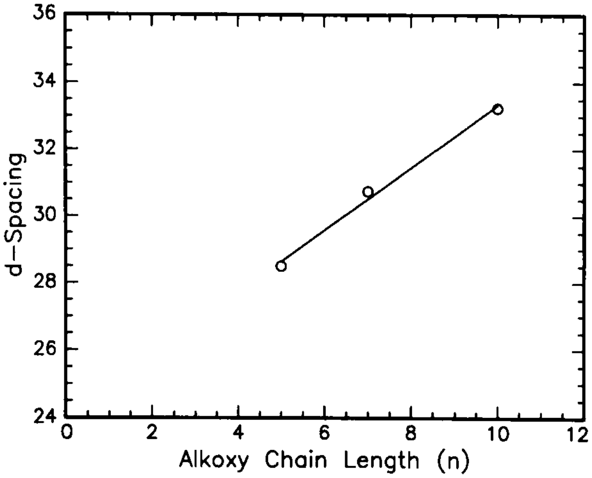

FIGURE 3 Alkoxy chain length dependence of *d*-spacing in the smectic A phase of nO.8s.

0.6 Å. These results indicate that there is a significant difference in the incremental length due to the variation of alkyl and alkoxy chains. From this it is certain that the alkoxy chain is more tilted with respect to the core than the alkyl chain, and simple addition of 1.27 Å for the evaluation of chain lengths of molecules is not justified. Thus for example, in the case 10O.8, if we assume $d_{10O.8} = d_{5O.8} + 5 \times 1.27$, then the calculated value is 34.85 ± 0.40 Å, but the experimental value, 33.3 ± 0.03 Å, is well below this estimate.

Using Equation 1, we evaluate the chain length of 10O.14 for an all-stretched molecule. The value is 40.96 ± 2.18 Å. The large uncertainty is expected because of the cumulative errors. This value of *d* is well below the value obtained experimentally for the tilted F and G phases. Therefore, we considered the *d* value as high as 43.14 Å for the evaluation of molecular tilt. Our ongoing studies examine

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10O.m compounds which exhibit A and F phases to assess the molecular length in this homologue.

Figures 4 and 5 show the variation of the layer spacing and the tilt angle with temperature, respectively. In view of the uncertainty in the molecular length, the tilt angles reported in Figure 5 represent the maximum limit of the molecular tilt. The tilt angle (13°) is independent of temperature in the F phase within experimental uncertainty. It attains saturation ($\phi = 18°$) in the smectic G phase.

In 10O.8, with ACFG phase sequence, the tilt angle never exceeds 12°. An interesting difference between the two compounds studied is that the tilt angle actually decreases at the FG phase transition for 10O.8, while in 10O.14 it exhibits a constant tilt angle in the smectic F phase and increases continuously upon entering the smectic G phase. In this respect, the decrease in tilt angle at the FG transition in 10O.8 is more reminiscent of FB phase transition rather than the FG transition.

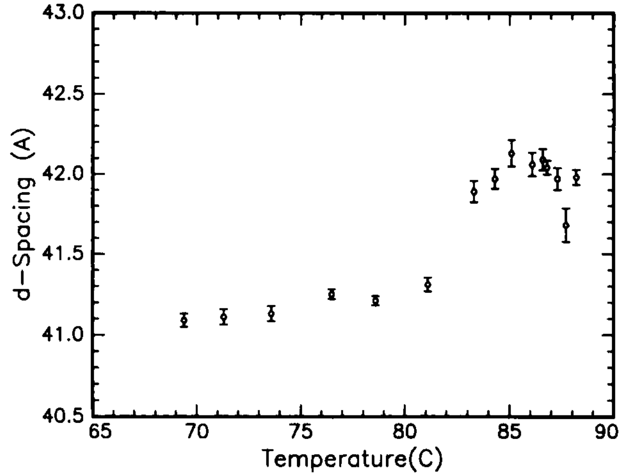

FIGURE 4 Temperature dependence of *d*-spacing in 10O.14.

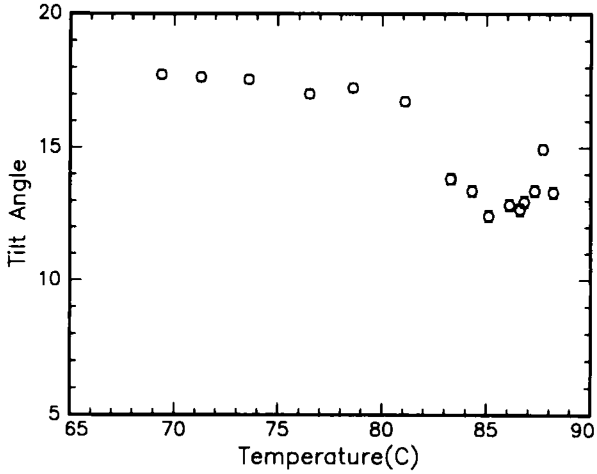

FIGURE 5 Temperature dependence of tilt angle in 10O.14.

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Interestingly, the higher homologues in the nO.m series exhibit relatively small tilt angles which makes them well suited for study of the critical behavior of the bond orientational order. For example, the TBAA and OSI systems studied by the MIT group[13,14] show molecular tilt angles as high as 37°. Thus, the ordering field[15] term used to analyze the fluid to hexatic transition can be significant. This ordering term arises from the coupling between the molecular tilt and the bond orientational order. In the limit of the zero ordering field (or low molecular tilt), the Landau-Ginzburg-Wilson Hamiltonian for the hexatic-fluid transition reduces to the X-Y model and permits careful test of the theoretical phase diagram reported by Aharony *et al.*[14] However, in this paper we focus mainly on the FG transition.

In order to further examine the nature of the tilted 2D smectic F to the 3D smectic G phase transition, we investigated the variation of the Bragg peak intensity associated with the molecular length. The data for 10O.8 and 10O.14 are shown in Figures 6 and 7, respectively. The peak intensity appears to follow a power law behavior in both compounds at the G to F transition. We have not performed the power law analysis of the intensity due to insufficient temperature resolution on our X-ray setup.

Qualitatively, the intensity of the Bragg peaks reflects the strength of the interlayer (smectic) positional ordering. Therefore, near the FG transition we expected and observed such an enhanced ordering. This is because the F phase does not have a long-range positional order in the direction normal to the layer while the smectic G phase does. In this respect, the studies reported by Birgenau *et al.*,[13] who analyzed in-plane molecular packing (to extract hexatic order parameters), are relevant. They suggest that this transition is weakly first order in the TBAA series due to coupling with the cubic term in the crystalline smectic G order parameter.

In our present study, we find that FG transition is first order in 10O.14, but it appears to be weakly first order in 10.O8 based on the DSC data. Even though the DSC thermograms for 10O.14 do show a strong first order FG transition, we

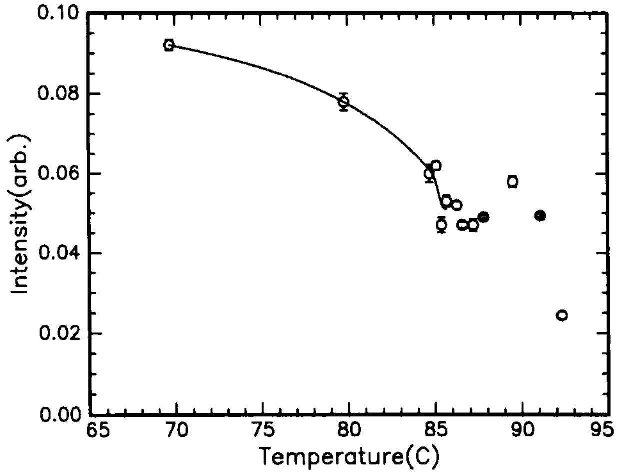

FIGURE 6 Bragg peak intensity as a function of temperature in 10O.8.

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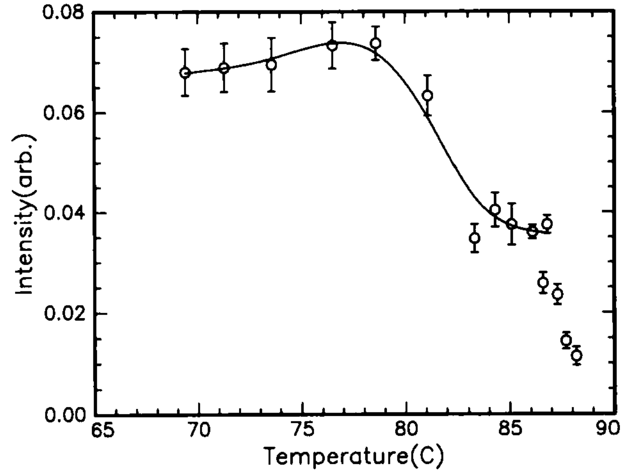

FIGURE 7 Bragg peak intensity as a function of temperature in 10O.14.

have not observed the corresponding peak in 10O.8. Also, the power law behavior of the diffraction peak intensity in 10O.8 is more strongly developed than in 10O.14 implying a weaker first order FG transition in this material. Therefore, it appears that the 10O.8 sample may lie far away from the triple point associated with the fluid(SmC)-hexatic(SmF)-crystalline(SmG) phases.[13,14]

At present we do not know: 1) what governs the order of the FG transition? and 2) what is the appropriate order parameter for this transition? Development of the long-range positional ordering suggests enhanced smectic A order may be used as a primary order parameter, though other symmetry-related order parameters are possible. A coupling of the positional (smectic A type) order parameter with the bond orientational order parameter can produce a tricritical point. However, this mechanism does not explain our results since the extent of the smectic F phase is larger in 10O.14 than the 10O.8, i.e., the susceptibility associated with the bond orientational order parameter is expected to induce a stronger first order FG transition in 10O.8. More systematic studies of this transition are needed before we can begin to address these preliminary findings.

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