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Studies on the Smectic Phase of Some Schiff's Bases With a Terminal Trifluoromethyl Group†

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(*Received November 14, 1984*)

Some terminally substituted trifluoromethylbenzylideneanilines have been synthesized with a view to investigate an unidentified smectic phase which exhibits an unusual texture as observed under the polarizing microscope. This phase was first reported by Griffin et al.[2] for the compound N-(4-*n*-decyloxybenzylidene)-4′-trifluoromethylaniline. In a comparable compound but with reversed imine linkage the nature of this smectic phase remains unchanged. Also if the terminal *n*-decyloxy group is replaced by an *n*-decyl group the nature of the smectic phase remains the same except that it is observed at a considerably lower temperature. We observe that this smectic phase has uniaxial symmetry when studied with a polarizing microscope as well as with NMR techniques; the latter showing an order parameter $S \simeq 0.8$ for this phase. X-ray diffraction patterns show this phase to be crystal smectic B.

INTRODUCTION

The observation of a direct isotropic-to-smectic liquid crystalline phase transition is not uncommon,[1] but, for certain well ordered smectic phases, this may lead to the occurrence of unusual textures exhibited by the materials when observed under the polarizing microscope.[2–5] For example, Walton and Goodby[5] have reported on some unusual textures of a smectic phase that forms directly below the isotropic melt, which, in fact, assisted them in discussing the tilted character of the molecular organization within the layers.

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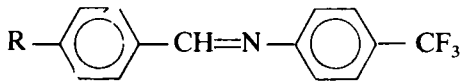
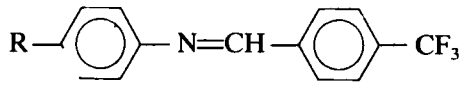
Recently, Griffin *et al.*[2] reported the occurrence of an unidentified enantiotropic smectic phase in the compound N-(4-*n*-decyloxybenzylidene)-4′-trifluoromethylaniline (I, R = $C_{10}H_{21}O$—)



(I)



(II)

directly below the isotropic melt: K(68)S?(77.7)I. Here, the transition temperatures are in parenthesis and in degrees Celcius; the letters K and I denote respectively the crystalline solid and the isotropic melt, and "S?" an unclassified smectic phase. A classification of this smectic phase was left an open question in part due to the unusual textures exhibited by the material under the polarizing microscope.[2]

In this work we decided to further investigate (i) the materials (I) in an attempt to assist in the classification of the smectic phase of the decyloxy homolog, and (ii) the materials (II) to study the influence of the reversal of the imine linkage on the stability and nature of the polymorphism. We note first that although Cox *et al.*[6] have recently reported that the octyloxy homolog (R = $C_8H_{17}O$—) of (I) exhibits a smectic B, S_B, phase, one cannot infer that the "S?" phase of the decyloxy homolog is also S_B. Although several examples of a direct isotropic to S_B phase transition are known,[3,4,6-9] some are crucially dependent on the molecular chain length.[7] That is, shorter chain length homologs may exhibit a smectic A, S_A, phase, longer chain length homologs a smectic C, S_C, and only for a few intermediate chain lengths may the $S_B \leftrightarrow I$ phase transition be observed to occur.[7] We note also that the hexyloxy homolog (R = $C_6H_{13}O$—) of (I) does not show any mesomorphism at all.[10]

MATERIALS PREPARATION

All of the starting materials needed for the preparation of the Schiff's bases (I) and (II) are commercially available.

N-(4-*n*-decyloxybenzylidene)-4′-trifluoromethylaniline (I, R = $C_{10}H_{21}O$—) was prepared by refluxing a mixture of 4-trifluoromethylaniline (1 mol) and 4-decyloxybenzaldehyde (1 mol) in absolute ethanol with a few drops of glacial acetic acid. After 3–4 hours of

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reflux the reaction mixture was cooled and the isolated product was recrystallized several times from absolute ethanol until the clearing point remained constant.

N-(4-trifluoromethylbenzylidene)-4′-*n*-decyloxyaniline, (II, R = $C_{10}H_{21}O$—) and N-(4-trifluoromethylbenzylidene)-4′-*n*-decylaniline, (II, R = $C_{10}H_{21}$—) were similarly prepared from 4-trifluoromethylbenzaldehyde (1 mol) and 4-decyloxyaniline or 4-decylaniline (1 mol), respectively. Recrystallization of these Schiff's bases was either accomplished from absolute ethanol or ligroin.

The following transition temperatures were measured from observations under the polarizing microscope:

Material	Homologous Series	R	K—S	S—I
A	I	$C_6H_{13}O$—	—	84.5[a] °C
B	I	$C_8H_{17}O$—	59[b]	82[b]
C	I	$C_{10}H_{21}O$—	67.8	77.8
D	II	$C_{10}H_{21}O$—	95.2[c]	96.6
E	II	$C_{10}H_{21}$—	42.5[c]	42.9

a) Melting point, from Ref. 10; a virtual isotropic to nematic transition at 27°C was determined by extrapolation of transition temperatures of binary mixtures.
b) From Ref. 6.
c) Monotropic transition.

EXPERIMENTAL

All three materials C, D and E exhibited similar textures under the polarizing microscope when in their respective mesomorphic phases. Figure 1 illustrates the flower-like arrangement of the pseudo-isotropic domains (under crossed polars), and visible in the picture is also a long, almost linear, highly birefringent domain. This latter type of habit was observed in all samples to grow rapidly from the isotropic melt and, if curved, exhibited discrete and sharp discontinuity radii lines. In all regards these domains strongly resemble some structures reported by Nehring and Osman (Ref. 4, Figure 7) to occur in some N-(4-*n*-alkylbenzylidene)-4′-*n*-alkylanilines that exhibit a direct I $\leftrightarrow$ S_B phase transition.

Furthermore, for all three materials C, D and E, sufficiently large pseudoisotropic domains could be obtained that revealed under conoscopy that the smectic phase was in all three cases optically uniaxial. This feature greatly reduces the classification of the smectic phase to but a few possibilities among the already known phases.

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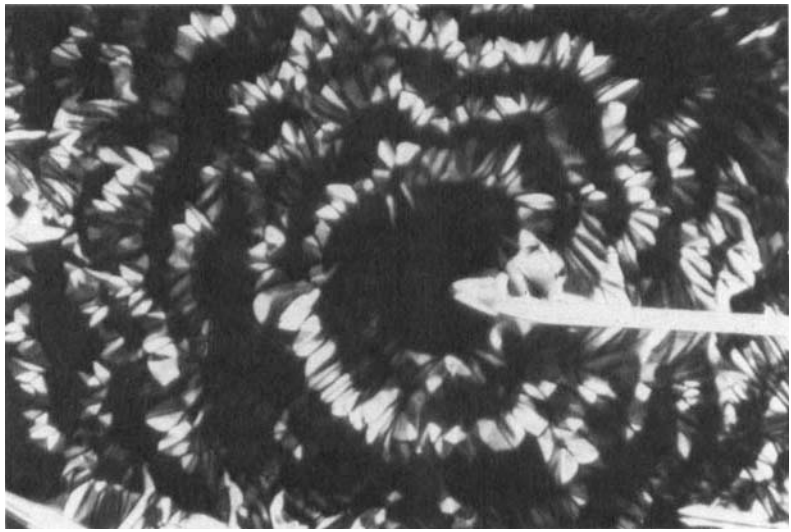

FIGURE 1 Texture of the smectic phase of the material C.

Binary mixtures of the material C, that is, homologous series I with R = $C_{10}H_{21}O$—, with the material 4-*n*-butyloxybenzylidene-4′-*n*-octylaniline (4O.8 for brevity) which exhibits the polymorphism[11] K (38.1) S_B (49.1) S_A (63.3) N (78.8) I, revealed continuity of the smectic phase of material C with the S_B phase of 4O.8. A 1:1 mixture exhibited a direct $S_A \leftrightarrow$ I transition at 94.5–96.7°C, and at 76.9–77.7°C a $S_A \leftrightarrow S_B$ phase transition was observed which was characterized by the usual onset of transition bars.

We proceeded with the study by using nuclear magnetic resonance (NMR) techniques to characterize the phase. Fluorine NMR resonance did not prove useful due to the poor signal to noise figure of our spectrometer combined with a large line broadening. A binary mixture of (I, R = $C_{10}H_{21}O$—) and ~11 wt% 4O.8 selectively deuterated in the aniline ring was then prepared and deuterium NMR techniques[12] used, instead. The mixture exhibited, as seen under the polarizing microscope, textures similar to those of the pure material and we therefore believe that the inclusion of the deuterium probe did not disturb appreciably the nature of the phase. The results showed distinctly that the absorption spectral splitting followed the $\frac{1}{2}(3\cos^2\theta - 1)$ angular dependence of a uniaxial phase[12] (θ is the angle between the sample director and the external applied magnetic field).

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Furthermore, from the measured spectral splitting of 27.73 kHz we calculate[12] an order parameter of $S \simeq 0.8$.

Our study was concluded by an x-ray analysis of the phases of the material (I, R = $C_{10}H_{21}O$—). X-ray diffraction photographs of the smectic phase were obtained[13] with increasing temperature, starting from the solid phase, and with decreasing temperature, starting from the isotropic phase. The features of these photographs clearly indicate that this smectic phase is a smectic B phase of the type sometimes called "crystal B": (1) there is only one single sharp outer diffraction ring, as in smectic B;[14] (2) the inner diffraction ring shows the grainy texture typical of smectic B (Ref. 15, p. 7); (3) the outer ring sometimes contains sharp diffraction spots, indicating the existence of long-range positional and orientational order in the smectic layers.

DISCUSSION

In view of the results presented above we feel certain that the smectic phase exhibited by the material (I, $C_{10}H_{21}O$—) is the uniaxial smectic B phase exhibited by 4O.8.[16,17] That is, the usually designated crystal S_B phase. This result is further substantiated in that the description of many of the details observed under the polarizing microscope at the $I \rightarrow S_B$ phase transition given by Nehring and Osman[4] describes in full our own observations on (I, $C_{10}H_{21}O$—). Moreover, the high value of the order parameter, $S \simeq 0.8$, is consistent with the value of that parameter measured within the S_B phase of several other materials.[12]

We would like to point out that in the same manner that the binary mixtures of (I, $C_{10}H_{21}O$—) with 4O.8 exhibit a direct $I \rightarrow S_A$ transition for ~1:1 wt. concentration, binary mixtures of (I, $C_{10}H_{21}O$—) with 4-*n*-butyloxybenzylidene-4′-ethylaniline, 4O.2, also exhibit an $I \rightarrow S_A$ phase transition. This feature was first noted by Griffin *et al.*[2] We do not find, however, the $I \rightarrow S_A \rightarrow N$ polymorphism that has been reported in Ref. 2. We believe the nature of this reported polymorphism to reside in poor graphical representation.

The new liquid crystalline materials, (II, $C_{10}H_{21}O$—) and (II, $C_{10}H_{21}$—) are also believed to exhibit a direct isotropic to crystal smectic B phase transition. In these cases, however, the phase transition is monotropic showing that the effect of reversing the central linkage (imine) reduces the stability of the smectic phase. The transition temperatures of (II, $C_{10}H_{21}O$—) are substantially higher than

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those of (I, $C_{10}H_{21}O$—), while those of (II, $C_{10}H_{21}$—) are substantially lower. These results may be explained by arguments similar to those given in Ref. 5. We then relate the changes in polymorphism to the changes in the electronic distribution (charge conjugation) on the molecule brought about by the reversal of the imine linkage group—the only difference between materials (I) and (II). The absence of a tilted phase in our case may be explained by the much reduced dipole moment associated with the imine group as compared to that of the ketone group.[5] Finally, very similar results have been found in the comparison of the polymorphism of 4-*n*-alkoxybenzylidene-4′-cyanoanilines and 4-cyanobenzylidene-4′-*n*-alkoxy and alkyl anilines,[18] which exhibit nematic and smectic A phases.

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