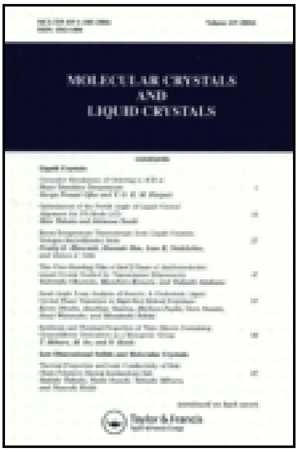

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Unusual Smectic-A Layering in a Homologous Series of Isothiocyanato Compounds

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The smectic-A (SmA) phases exhibited by several homologs belonging to the newly synthesized 4-isothiocyanatophenyl-4′-*n*-alkyloxybenzoate series (n.O.NCS) show unusual features. Although the X-ray studies show that the layer thickness/molecular length ratio (d/l) of the lower homologs is less than 1 indicating a monolayer packing, dielectric studies reveal the existence of strong antiparallel correlations near the isotropic-SmA phase transition, a feature that has hitherto not been observed for any polar monolayer SmA phase. Miscibility studies prove that the SmA phase of these materials is miscible with both the monolayer (SmA_1) and the partial bilayer (SmA_d) phases.

1. INTRODUCTION

It is well known[1-3] that biaromatic materials with a terminally CN or NO_2 end group generally exhibit only the partial bilayer SmA_d phase while similar triaromatic compounds exhibit the monolayer SmA_1 phase for the lower homologs and SmA_d or bilayer SmA_2 phases for the higher homologs. It is therefore of interest to see the nature of the SmA phase of the n.O.NCS series of compounds in which the molecules possess a terminal dipole moment whose magnitude (2.9 Debye) is smaller than that of CN (4.05 D) or NO_2 (4.18 D) groups.[3] In this paper we present the results of our X-ray measurements of the layer spacing for $n = 9$ to $n = 16$ homologs of the n.O.NCS series. We also present, for one representative compound, the temperature variation of smectic layer spacing and the dielectric permittivity in its isotropic phase. These results and the miscibility diagrams indicate an unusual layering of the SmA phase of the n.O.NCS compounds.

2. SYNTHESIS

The corresponding 4-alkylbenzoic acid chlorides were esterified with 4-hydroxyphenyl isothiocyanate which was obtained from 4-amino phenol and carbon disulfide in the presence of dicyclohexyl carbodiimide according to the procedure of Jochims.[4] Purification by column chromatography on silicagel/dichloromethane and subsequent recrystallisation from ether gave the isothiocyanato compounds in yields of 70–90%. Table I shows the transition temperatures of the n.O.NCS compounds along with the corresponding enthalpies obtained from DSC peak areas. Microscopy and thermal analysis failed to reveal any SmA-SmA transition.

3. EXPERIMENTAL

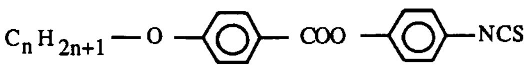
The X-ray studies were carried out using the photographic technique. The sample, filled in a capillary, was aligned by a magnetic field on cooling from the isotropic to the SmA phase. The accuracy in the measurement of d is ±0.015 nm while the temperature was maintained constant to ±0.1 K during each exposure. The dielectric studies have been performed using a set up described elsewhere.[5] The miscibility diagrams have been obtained by optical polarization microscopy of individual mixtures.

4. RESULTS AND DISCUSSIONS

The values of the d/l ratio for the $n = 9$ to 16 homologs have been plotted (Figure 1) as a function of the chain length for two temperatures in the SmA phase, viz., 92°C, which is close to the SmA—isotropic temperature and 70°C which is close to the crystallization temperature. It is seen that d/l is less than 1 for $n < 12$ and greater than 1 for higher homologs. Although this trend is somewhat similar to that seen for triaromatic HK-NO_2 (4-(4′-alkyloxybenzoyloxy)-4′-nitrobenzene) series,[6] there is an additional special feature for the present n.O.NCS series: The

TABLE I

Melting and clearing temperatures (°C) and transition enthalpies (kj/mol) of the n.O.NCS homologs along with their molecular lengths l (nm)



n.O.NCS		SmA		iso	ΔH_m	ΔH_{AI}	l (nm)
9.O.NCS	70.4	.	93.9	.	33.6	2.95	2.906
10.O.NCS	76.4	.	96.0	.	43.3	3.14	3.033
11.O.NCS	81.9	.	95.4	.	47.3	3.55	3.160
12.O.NCS	88.5	.	96.4	.	46.2	3.42	3.287
14.O.NCS	81.0	.	95.1	.	43.5	3.92	3.541
16.O.NCS	79.4	.	92.8	.	59.8	4.82	3.795

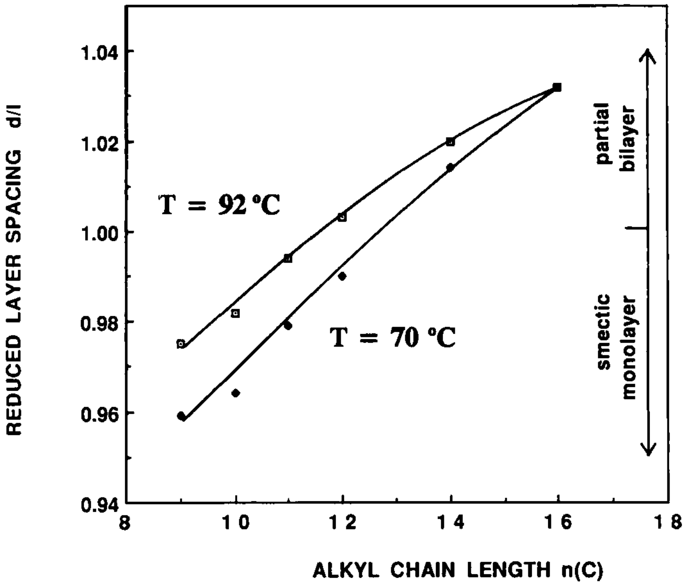


FIGURE 1 Layer spacing to molecular length (*d*/*l*) ratio for the n.O.NCS series of compounds. n(C) is the number of the carbon atoms in the alkyl chain.

d/*l* ratio is less than 1 even for very long alkyl chains indicating that the monolayer nature of the phase is retained even up to $n = 12$. The temperature variation of the smectic layer spacing d for 10.O.NCS is shown in Figure 2. A pronounced increase of d is seen with increasing temperature. This behavior is different from that seen so far for the SmA_1 phase of other polar materials with a temperature independent layer spacing. This result in turn indicates that there should be something unusual about the nature of the layering in the SmA phase of the n.O.NCS compounds.

It may be relevant to recall the results of recent X-ray reflectivity studies on a similar NCS-substituted material, viz., 4-isothiocyanatophenyl-4-(trans-4-heptylcyclohexyl)-benzoate.[7] It was shown[7] that for this material, unlike for a terminally cyanosubstituted material,[8] there is no bilayer-like order at the free surface of the bulk monolayer A-phase. It is therefore suggested that the dipolar order in the A-phase of the NCS-substituted material should be similar to that of a "classical" or non-polar smectic-A, i.e., there should be a up-down disorder of the dipoles on a molecular scale. To see if this is the case, we have measured the dielectric permittivity (ε_{is}) in the isotropic phase of 10.O.NCS for which a strong dependence of the layer spacing with temperature was observed in the SmA phase. These results are shown in Figure 3. (This figure shows data only in the isotropic phase, a good homeotropic alignment required for $\varepsilon_{\parallel}$ measurements was not possible to achieve in the SmA phase). As the temperature is increased, ε_{is} initially shows an increase over a temperature range of about 4 K leading to a maximum of ε_{is} after which the usual decreasing trend (associated with μ^2/kT behavior) is seen. The anomalous decrease seen in the isotropic phase on approaching the isotropic-SmA phase transition is indicative of the build-up of pronounced local antiparallel correlations.

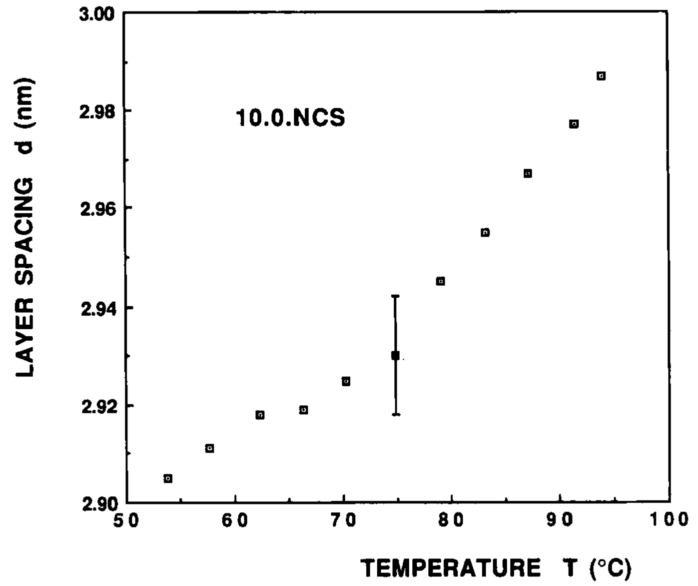


FIGURE 2 Temperature variation of the layer spacing (d) for 10.O.NCS (The accuracy in the measurement of d is indicated by the error bar).

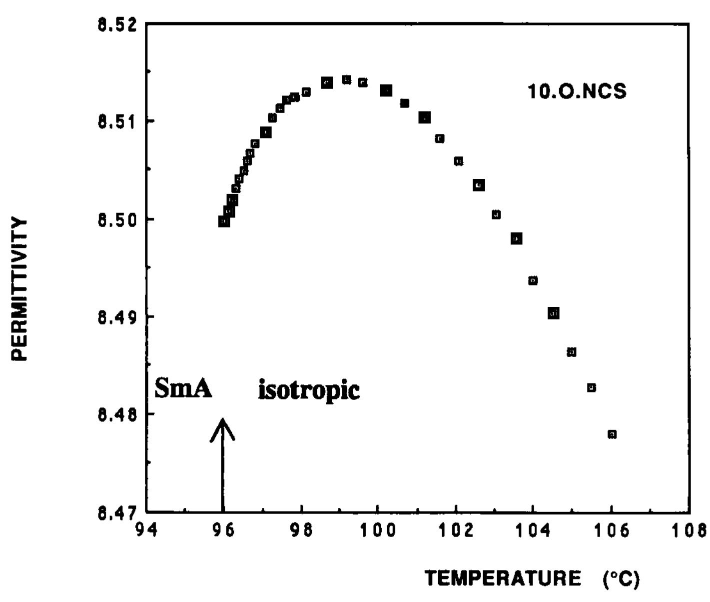


FIGURE 3 Temperature variation of the static dielectric permittivity in the isotropic phase of 10.O.NCS.

This result is similar to that observed earlier in the isotropic phase of terminally CN-substituted materials exhibiting the SmA_d—isotropic transition.[9-11] As far as we are aware such a pronounced local antiparallel correlation has not been observed for any monolayer SmA phase so far.

Thus we have shown that although the magnitude of the *d*/*l* value is less than 1 and therefore the SmA phase should in principle be classified as monolayer $\mathrm{SmA_1}$ phase, both the temperature variation of *d* and ε_{is} indicate a type of layering which is in fact reminiscent of $\mathrm{SmA_d}$. Is the SmA phase of n.O.NCS therefore $\mathrm{SmA_1}$ or $\mathrm{SmA_d}$?

To resolve this issue, we have carried out miscibility studies of 10.O.NCS with 4-(4′-nonyloxybenzoyloxy)-4′-cyanoazobenzene (HK9-CN) exhibiting both $\mathrm{SmA_d}$ and $\mathrm{SmA_1}$ phases and with terephthal-bis-butyl-aniline (TBBA) which shows a "nonpolar" SmA monolayer phase. These phase diagrams (Figures 4 and 5) show that the SmA phase of n.O.NCS compounds is miscible with the classical nonpolar SmA of TBBA as well as with the monolayer $\mathrm{SmA_1}$ and partial layer $\mathrm{SmA_d}$ of the terminal polar compound. It would thus appear that the n.O.NCS material is, as if it were, in the supercritical region of a $\mathrm{SmA_1}$-$\mathrm{SmA_d}$ critical point. Such a supercritical region has been so far observed for only binary mixtures.[12] The fact that we have seen a similar behavior for a single component system makes it an attractive candidate for carrying out high resolution studies to probe the nature of the region near the $\mathrm{SmA_1}$-$\mathrm{SmA_d}$ critical point. The existence of such a critical point, though predicted by theory,[13] has not been established experimentally. Furthermore, an investigation of the surface order exhibited by the SmA phases of the n.O.NCS homologs would be of considerable interest.

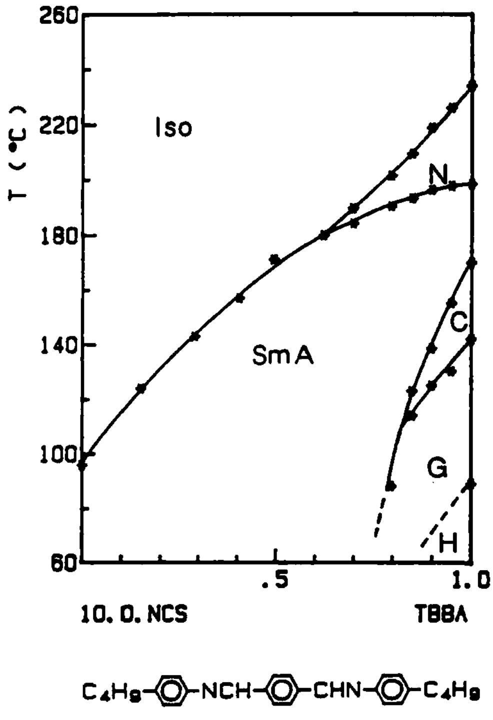


FIGURE 4 Phase diagram of binary mixtures of 10.O.NCS with TBBA. The SmA phase of 10.O.NCS is miscible with the monolayer SmA phase of TBBA.

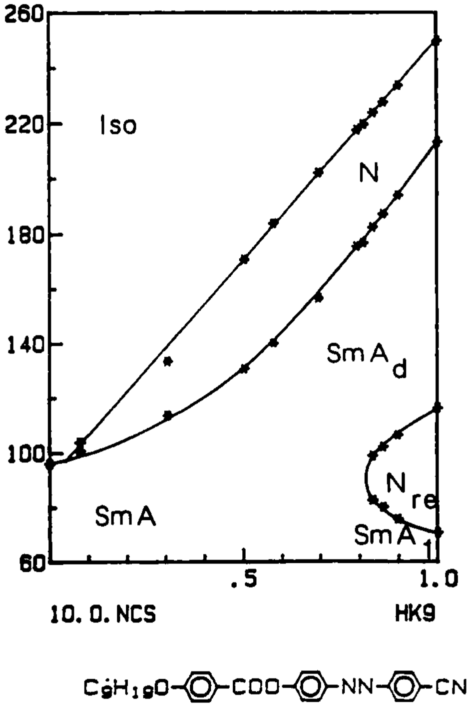


FIGURE 5 Phase diagram of binary mixtures of 10.O.NCS with HK9-CN. The SmA phase of 10.O.NCS is miscible with both the partial bilayer SmA_d phase and with the monolayer SmA_1 phase of HK9-CN.

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