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Dielectric Studies of Monolayer Smectic A Phases of Strongly Polar Liquid Crystals

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We have investigated the monolayer smectic (A_1)-nematic transition in the fourth, sixth and eighth homologs of 4-(4′-alkoxybenzoyloxy)-4′-cyanoazobenzenes. Although the A_1-N transition is second order in all the three compounds dielectric studies reveal that the changes in dipolar ordering accompanying the transition are substantially different in the three cases.

Keywords: dielectric studies, polar A phases, monolayer phases

1. INTRODUCTION

The discovery of reentrant nematic behavior[1–3] in compounds whose molecules possess a strongly polar end group led to considerable activity in the synthesis of terminally cyano- or nitro-substituted tri-aromatic compounds.[4] Amongst the first such compounds to be synthesised were 4-octyloxybenzoyloxy-4′-cyanostilbene (T_8) by the Bordeaux Group[3] and 4-nonyloxybenzoyloxy-4′-cyanoazobenzene (9OBCAB) by Heppke et al.[5] In both these cases the interesting result was found that in addition to the nematic, smectic A and reentrant nematic phases, there was a second smectic A at the lowest

temperature. Although initially referred to as the reentrant smectic A, it has since been shown to be a monolayer A (A_1) phase with a layer spacing (d) > the molecular length (ℓ) in contrast to the higher temperature partially bilayer (A_d) phase wherein $\ell < d < 2\ell$. Thus it was clear that compounds whose molecules possess a strongly polar end group can exhibit both A_1 and A_d phases. Although there have been a large number of dielectric studies on the A_d phase of many compounds[6] there appears to have been no systematic study of the A_1 phase of strongly polar systems so far. In this paper we present the results of our dielectric studies on three homologs belonging to the nOBCAB series, viz., 4, 6 and 8 OBCAB, all of which exhibit the A_1 phase.

2. EXPERIMENTAL

The transition temperatures of the compounds are given in Table I. X-ray diffraction studies were carried out to probe the layer spacing (d) in the smectic A phase. These experiments were conducted on magnetically oriented samples using monochromatic Cu K_α radiation and a flat photographic film. The constancy of temperature during any exposure was ± 0.1°C. The relative accuracy in the determination of d is reckoned to be ± 0.1Å.

The dielectric constants were measured using a Hewlett-Packard Impedance Analyser (HP 4192 A) in the frequency range 1 kHz–13 MHz. The sample, typically abut 50 μm thick, was oriented in the nematic phase by a 15 kG magnetic field and cooled into the A_1 phase in the presence of this field. The temperature of the sample was measured to an accurary of ± 25 mK.

3. RESULTS AND DISCUSSIONS

DSC runs showed that the smectic A-nematic transition is second order for all the three compounds.[7] Figure 1 gives the variation of

TABLE I

Transition temperatures of the compounds

Compound	Transition temperature (in °C)		
	K-A (or N)	A-N	N-I
4OBCAB	110.2	108.5	297.0
6OBCAB	107.4	127.0	275.2
8OBCAB	92.8	99.0	257.5

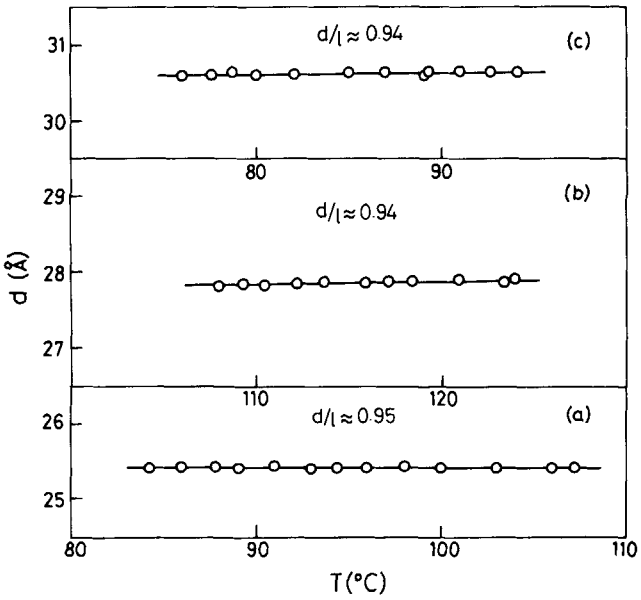

FIGURE 1 Temperature variation of the layer spacing (d) in the A phase of (a) 4OBCAB (b) 6OBCAB and (c) 8OBCAB.

the layer spacing (d) with temperature in the A phase of the three systems. It is seen that in every case d/ℓ (where ℓ is the length of the molecule in its most extended configuration) is less than 1. Thus the A phase of these compounds can be classified as the monolayer (A_1) phase. Also, d/ℓ is seen to be independent of temperature throughout the A phase, a feature which has already been observed in several systems exhibiting the A_1 phase.[8-10]

The variation of the static dielectric constants ($\epsilon_\parallel$ and $\epsilon_\perp$) with temperature for the n = 4, 6 and 8 compounds are shown in Figures 2–4 respectively. A feature of the result on 4OBCAB (Figure 2) is the sharp drop in $\epsilon_\parallel$ observed at the N-A_1 transition, the value dropping to nearly 14 from a value of about 20 in the nematic phase. On the other hand the value of $\epsilon_\perp$ is practically unchanged through the N-A_1 transition. In the case of 6OBCAB (Figure 3) the change in $\epsilon_\parallel$ at the transition is very small (~0.6) and somewhat less sharp. Finally for 8OBCAB, the change in $\epsilon_\parallel$ is hardly perceptible (Figure 4). These results show that for 4OBCAB the antiparallel correlations in the nematic and A_1 phases are substantially different whereas for 8OBCAB these correlations are similar in the two phases. This is also supported by the x-ray studies of Hopf[11] which showed that the nematic phase

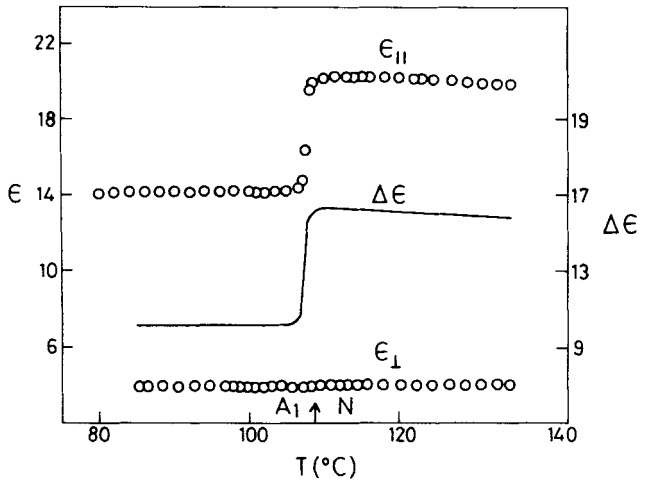

FIGURE 2 Temperature variation of the static dielectric constants ($\epsilon_{\parallel}$ and $\epsilon_{\perp}$) and the dielectric anisotropy ($\Delta\epsilon$) in the neighborhood of the smectic A_1-nematic (A_1-N) transition for 4OBCAB.

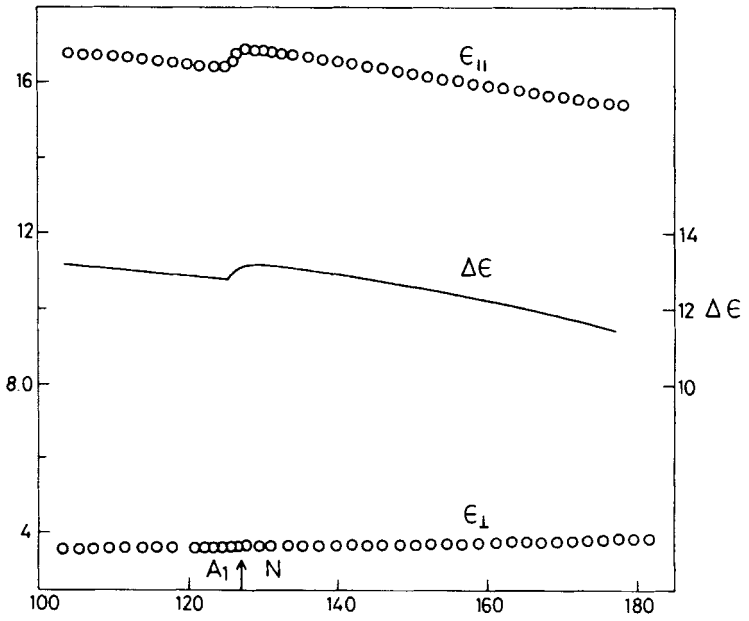

FIGURE 3 Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$ and $\Delta\epsilon$ near the A_1-N transition for 6OBCAB.

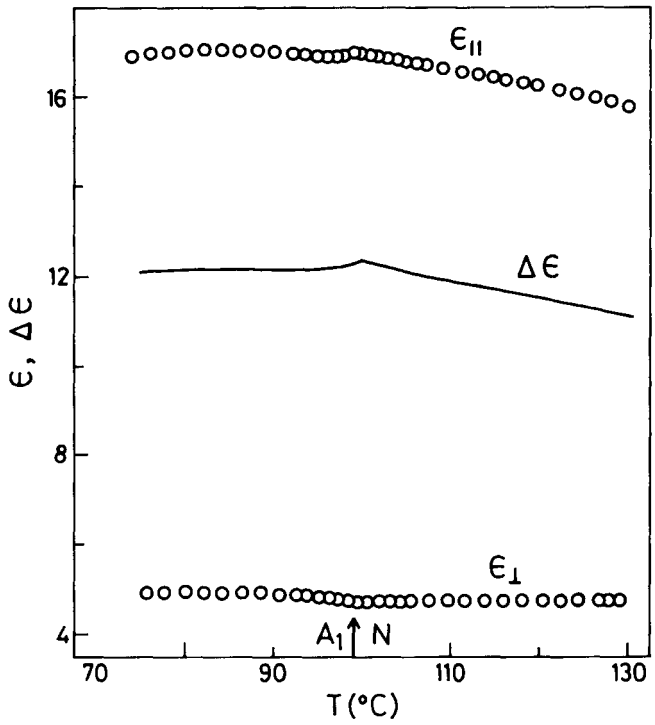

FIGURE 4 Temperature variation of $\epsilon_{\|}$, $\epsilon_{\perp}$ and $\Delta\epsilon$ near the A_1-N transition of 8OBCAB.

of 8OBCAB has stronger cybotactic smectic-like ordering than 4OBCAB. It would be of interest to compare these results with the behavior of $\epsilon_{\|}$ near N-A_2 and N-A_d transitions. However, as far as we are aware, no systematic dielectric study of a homologous series of compounds exhibiting either of these two types of transitions has been carried out so far.

Figure 5 gives the plots of f_R versus 1/T for 4OBCAB, 6OBCAB and 8OBCAB. The activation energies (W) calculated from the slopes of these plots are also given in the same figure. Considering the uncertainty in the determination of W, there is no substantial change in W at the N-A_1 transition.

Thus our results show that although the A_1-N transition is second order for all the three homologs of nOBCAB, the behavior of the dielectric anisotropy in the vicinity of this transition is quite different for the three systems. Similar studies on other homologous series of compounds exhibiting nematic-smectic A_2 and nematic-smectic A_d transitions are being taken up.

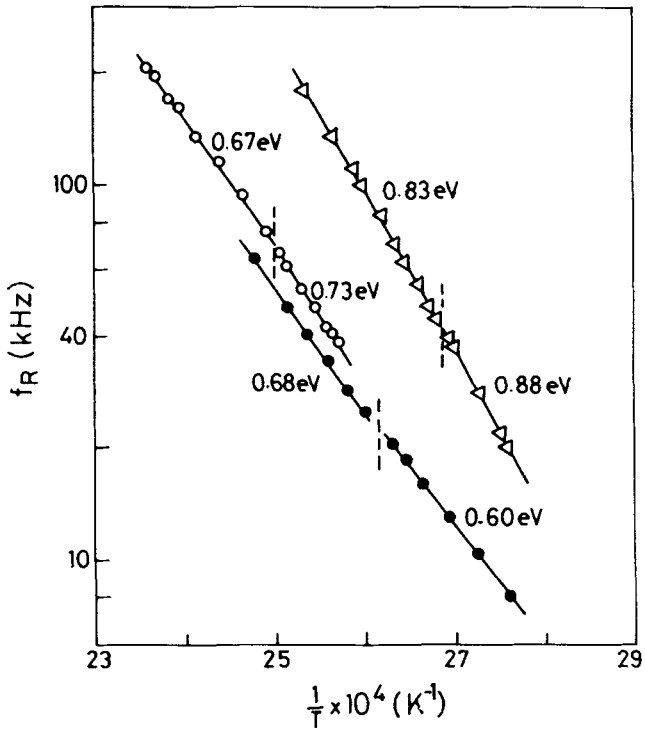

FIGURE 5 Plot of the frequency of relaxation of $\epsilon_{\parallel}(f_R)$ versus 1/T;4OBCAB (●), 6OBCAB (○) and 8OBCAB (▽). The vertical dashed line indicates the A_1-N transition temperature. The activation energies for the A_1 and N phases, determined by a least square fit of the data using a computer (HP 9845B), are also shown.

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