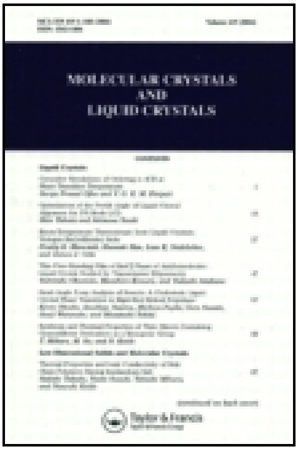

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Density, Dielectric and X-ray Studies of Smectic A-Smectic A Transitions

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Version of record first published: 17 Oct 2011.

To cite this article: B. R. Ratna , C. Nagabhushana , V. N. Raja , R. Shashidhar , S. Chandrasekhar & G. Heppke (1986): Density, Dielectric and X-ray Studies of Smectic A-Smectic A Transitions, Molecular Crystals and Liquid Crystals, 138:1, 245-257

To link to this article: http://dx.doi.org/10.1080/00268948608071763

Mol. Cryst. Liq. Cryst., 1986, Vol. 138, pp. 245–257
0026-8941/86/1384–0245/$20.00/0

Printed in the United States of America

Density, Dielectric and X-ray Studies of Smectic A–Smectic A Transitions

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(*Received October 30, 1985; in final form February 15, 1986*)

We report here the results of detailed density, dielectric and x-ray studies on three systems exhibiting different types of Smectic A–Smectic A transitions. It is found that although the layer spacing shows marked changes at the transitions, the corresponding density changes are extremely small. In every case studied, the dielectric anisotropy shows a pronounced decrease on going over to the lower temperature smectic A phase. This decrease can be correlated with the structural changes.

Keywords: A–A transitions, density, dielectric and x-ray studies

1. INTRODUCTION

It is now well established that when the constituent molecule of a triaromatic mesogen has a strongly polar end group, several types of Smectic A phases are observed. The different A phases identified so far are the monolayer (A_1), the partially bilayer (A_d) and the bilayer (A_2) phases in addition to the antiphase $\tilde{A}$.[1] Transitions between all these forms of A have been reported,[2] with the sole exception of the A_d–$\tilde{A}$ transition which has not yet been observed. Recently we reported[3,4] the observation of yet another kind of A–A transition, viz., a transition from an A_d phase with a temperature dependent layer spacing to another A_d phase with a temperature independent layer spacing. In this paper we present results of our density, dielectric and x-ray studies on three systems exhibiting A_d–A_1, A_1–A_2 and A_d–A_2 transitions.

2. EXPERIMENTAL

(a) Materials

The systems studied are listed below along with the sequences and temperatures of transitions (in °C) obtained in the cooling mode:

(i) 43 mole % mixture of 4-octyloxyphenyl-4′-nitrobenzoyloxy benzoate ($DB8ONO_2$) in 4-decyloxyphenyl-4′-nitrobenzoyloxy benzoate ($DB10ONO_2$)

$$I \xrightarrow{224} N \xrightarrow{193.7} A_d \xrightarrow{123.7} A_1 \xrightarrow{119.8} \tilde{C} \xrightarrow{100} A_2 \xrightarrow{98} C_2$$

(Melting temperature ≈95.7°C)

(ii) 10.5 mole % mixture of terephthal-bis-4-*n*-butylaniline (TBBA) in 4-*n*-pentylphenyl-4′-cyanobenzoyloxybenzoate (DB5CN)

$$I \xrightarrow{253.5} N \xrightarrow{128.3} A_1 \xrightarrow{126.9} A_2$$

(Melting temperature ≈119°C)

(iii) 4-*n*-heptylphenyl-4′-cyanobenzoyloxy benzoate (DB7CN)

$$I \xrightarrow{234.8} N \xrightarrow{169.4} A_d \xrightarrow{162} A_2$$

(Melting temperature ≈121°C)

The chemical formulae of the substances are given in Figure 1.

(b) Apparatus

The density measurements were made using an Anton Paar high precision digital instrument consisting of a high temperature microcell (DMA 602 MH, sample volume ≈0.3 cm^3) and a processing unit (DMA 60). The measuring cell consisted of a hollow U-shaped glass

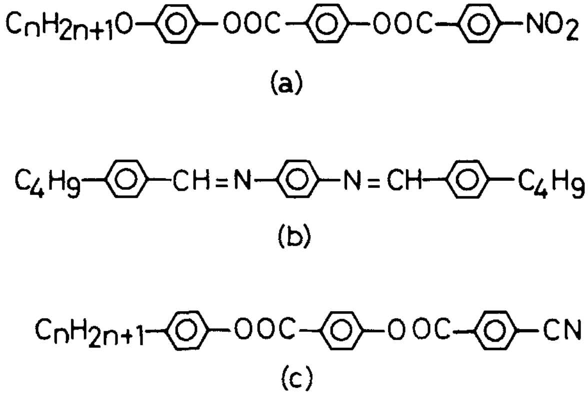

FIGURE 1 Chemical formulae of (a) DBnONO$_2$, (b) TBBA and (c) DBnCN. n denotes the number of carbon atoms in the end chain.

tube filled with the sample under investigation. The tube was electromagnetically excited to vibrate at its natural period whose square is proportional to the density of the sample. Because of difficulties in maintaining the temperature of the cell to better than ±50 mK above 100°C, the density data presented here are reckoned to have a relative precision of 5×10^{-5} g cm^{-3}.

The static dielectric constants ($\epsilon_\parallel$ and $\epsilon_\perp$) as well as the low frequency dispersion of $\epsilon_\parallel$ were studied using a Hewlett Packard Impedance Analyser (4192A). The sample, typically 50–100 μm thick, was aligned in the nematic phase by a 1.5 Tesla magnetic field and cooled to the smectic phase in the presence of this field. The sample was in an environment of dry nitrogen during the measurements. The temperature of the sample was determined to ±25 mK.

X-ray studies were performed on magnetically oriented samples contained in 0.5 mm diameter Lindeman glass capillaries using monochromatic copper K_α radiation and a flat photographic film. The constancy of temperature during any exposure (typically about 20 minutes) was ±0.1°C. The relative accuracy in the determination of the temperature variation of the layer spacing is ±0.1 Å or better.

3. RESULTS AND DISCUSSION

(a) X-ray studies

Figures 2–4 show the variation of the layer spacing (d) with temperature for the DB8ONO$_2$/DB10ONO$_2$ mixture (or DB NO$_2$ mixture for short), the TBBA/DB5CN mixture and DB7CN respectively.

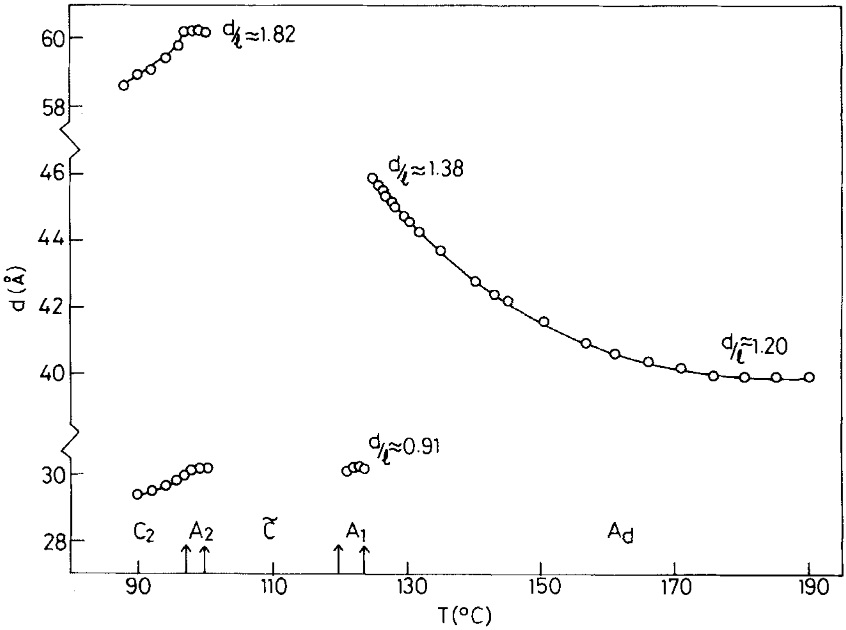

FIGURE 2 Variation of the layer spacing (d) with temperature in the A_d, A_1, A_2 and C_2 phases of 43 mole % mixture of $DB8ONO_2$ in $DB10ONO_2$.

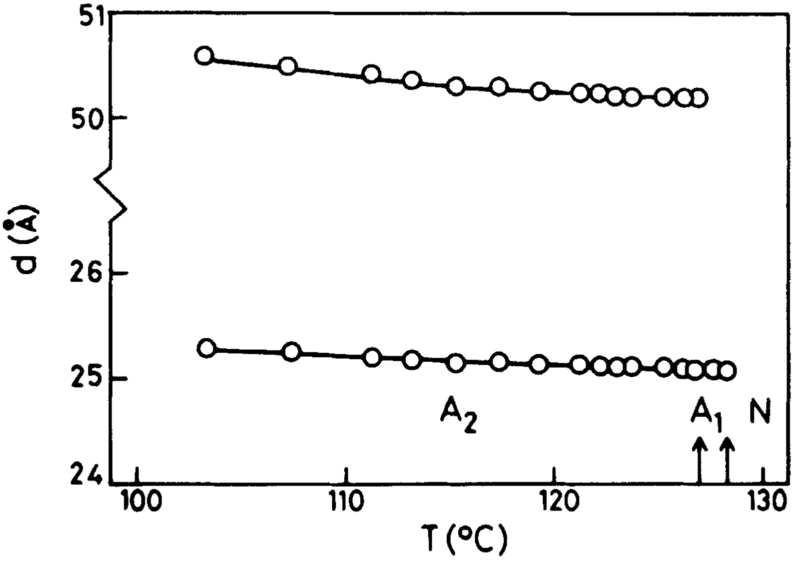

FIGURE 3 Temperature variation of the layer spacing in the A_1 and A_2 phases of 10.5 mole % mixture of TBBA in DB5CN.

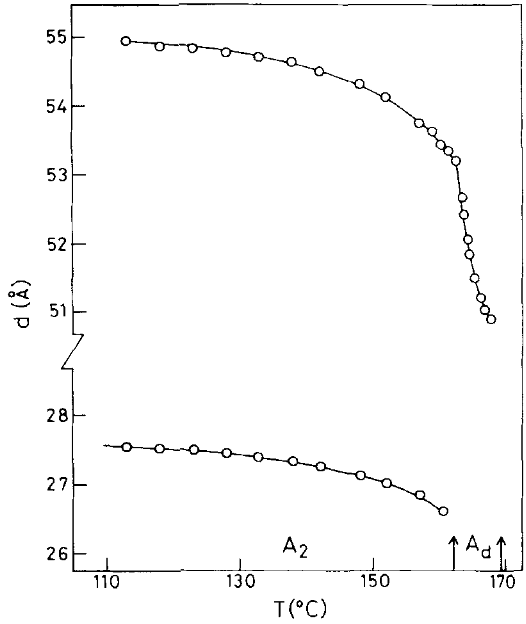

FIGURE 4 Temperature variation of the layer spacing in the A_d and A_2 phases of DB7CN.

In the case of the $DBNO_2$ mixture (Figure 2) d increases in the A_d phase continuously with decreasing temperature, a trend which is similar to that observed in pure $DB9ONO_2$.[2,5] At the A_d–A_1 transition d/*l* drops abruptly from 1.38 to 0.91 (*l* is the length of the fully extended molecule as measured with the aid of a Dreiding model). For the A_1–A_2 transition in the TBBA/DB5CN system, the appearance of the diffraction spots with a bilayer periodicity ($d/l \approx 1.84$) signals the onset of the A_2 phase, the monolayer periodicity ($d/l \approx 0.92$) varying smoothly through the A_1–A_2 transition (Figure 3). Both the periodicities show only a small linear increase with decreasing temperature in the A_2 phase. For DB7CN (Figure 4) the layer spacing in the A_d phase shows a strong increase with decreasing temperature as a precursor to the A_d–A_2 transition. Similar observations have been made by the Bordeaux group for the A_d–A_2 transition in other systems.[6-8]

(b) Density

Since the maximum working temperature of the density cell was about 150°C, we could not measure the density of DB7CN near the A_d–A_2

transition. Figure 5 shows the variation of density with temperature for the TBBA/DB5CN mixture in the neighbourhood of the A_2–A_1 transition. The density varies smoothly through the transition with no pretransition effects. The behaviour is very similar to that observed for a known second order A–N transition,[9] indicating that this A_2–A_1 transition is also probably second order. Chan et al.[10] carried out x-ray scattering studies on TBBA/DB6CN mixtures and showed that the order of the A_1–A_2 transition changes from first to second with increasing concentration. Precise calorimetric measurements are underway to determine whether the A_1–A_2 transition in the TBBA/DB5CN mixture for the concentration studied by us is truly second order. Figure 6 gives a plot of density versus temperature near the A_1–A_d transition in the DB NO_2 mixture. The density appears to show a pretransition effect at this transition. However, the increase in density at the transition is extremely small (less than 0.02%) which is remarkable in view of the abrupt decrease by about 30% in the layer spacing on going over from the A_d to the A_1 phase (see Figure 2). High resolution studies of the in-plane structure factors

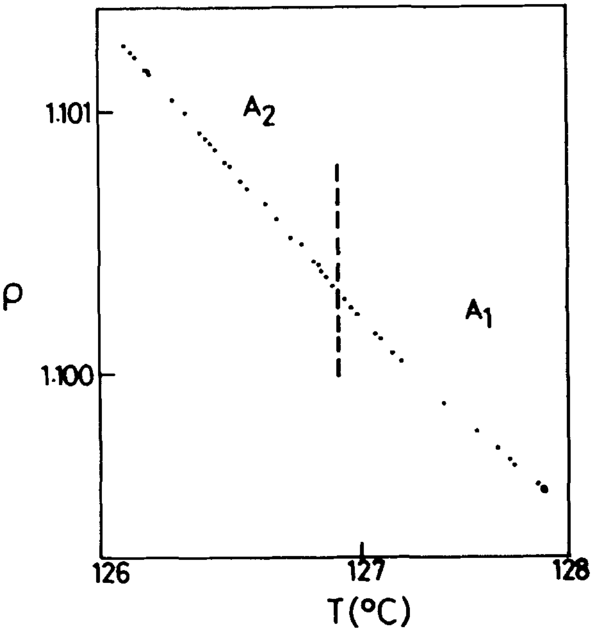

FIGURE 5 Temperature variation of the density (ρ) in the vicinity of the A_1–A_2 transition in the TBBA/DB5CN mixture.

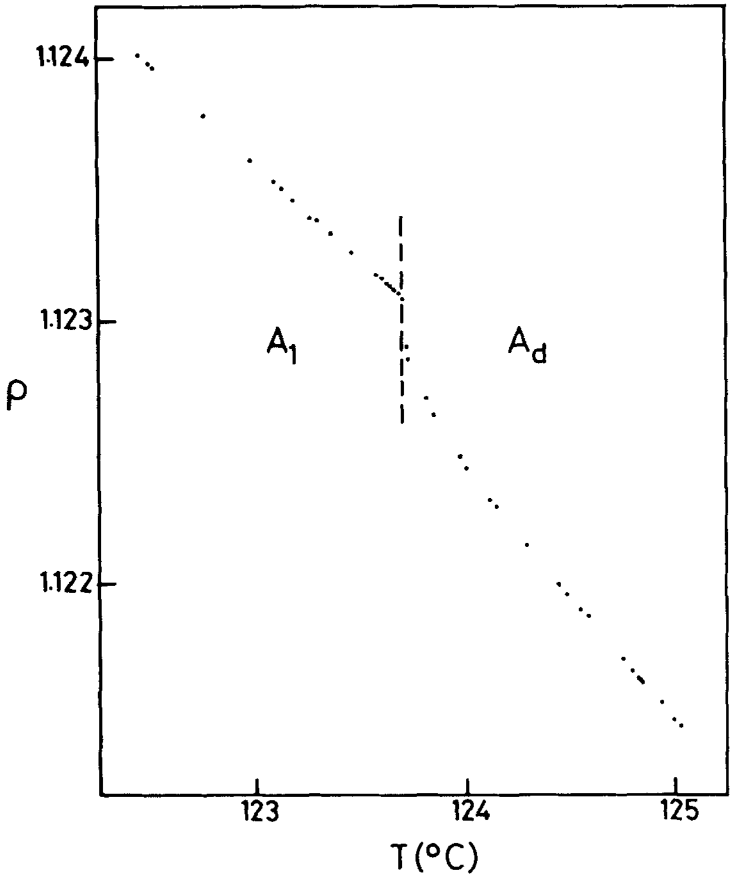

FIGURE 6 Temperature variation of the density (ρ) in the vicinity of the A_d–A_1 transition in the DBNO$_2$ mixture.

(of the kind carried out by Kortan et al.)[11] would be of interest in these systems to see if there are any significant differences in the in-plane ordering in the different A phases.

(c) Dielectric studies

Figures 7–9 give the temperature variation of the principal dielectric constants ($\epsilon_{\parallel}$, $\epsilon_{\perp}$) and the dielectric anisotropy ($\Delta\epsilon$) for DBNO$_2$, TBBA/DB5CN and DB7CN respectively. A common feature of all the three diagrams is the reduction in $\Delta\epsilon$ on going over to the lower temperature A phase, this being the most dramatic for DB7CN. We shall now discuss the trends of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ for the three cases.

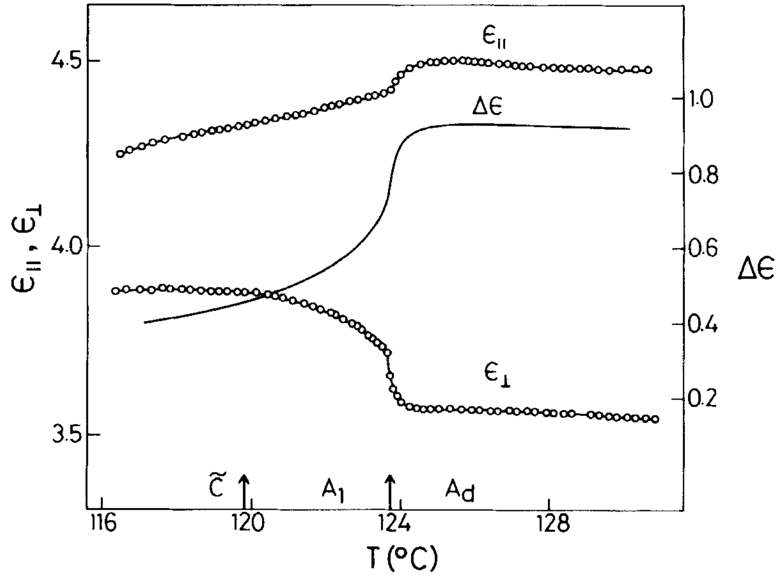

FIGURE 7 Temperature variation of the principle dielectric constants ($\epsilon_{\parallel}$, $\epsilon_{\perp}$) and the dielectric anisotropy ($\Delta\epsilon$) near the A_d–A_1 transition in the DB NO_2 mixture.

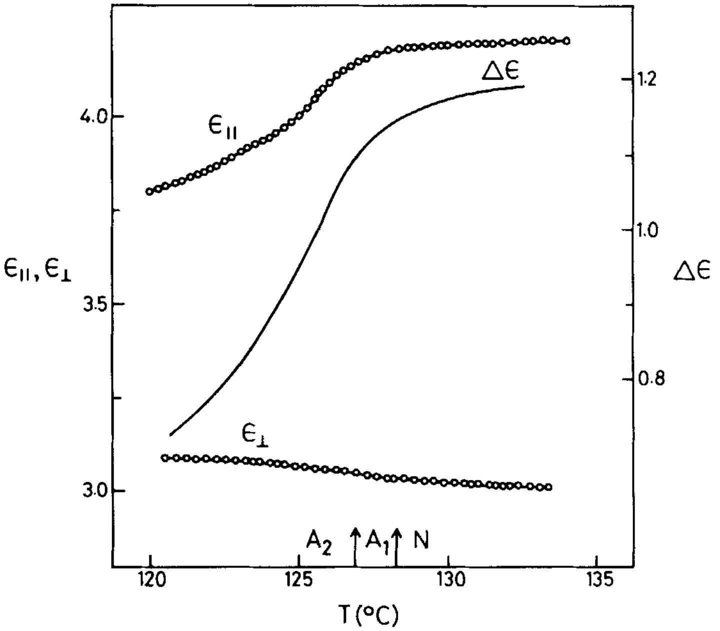

FIGURE 8 Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$ and $\Delta\epsilon$ in the N, A_1 and A_2 phases of the TBBA/DB5CN mixture.

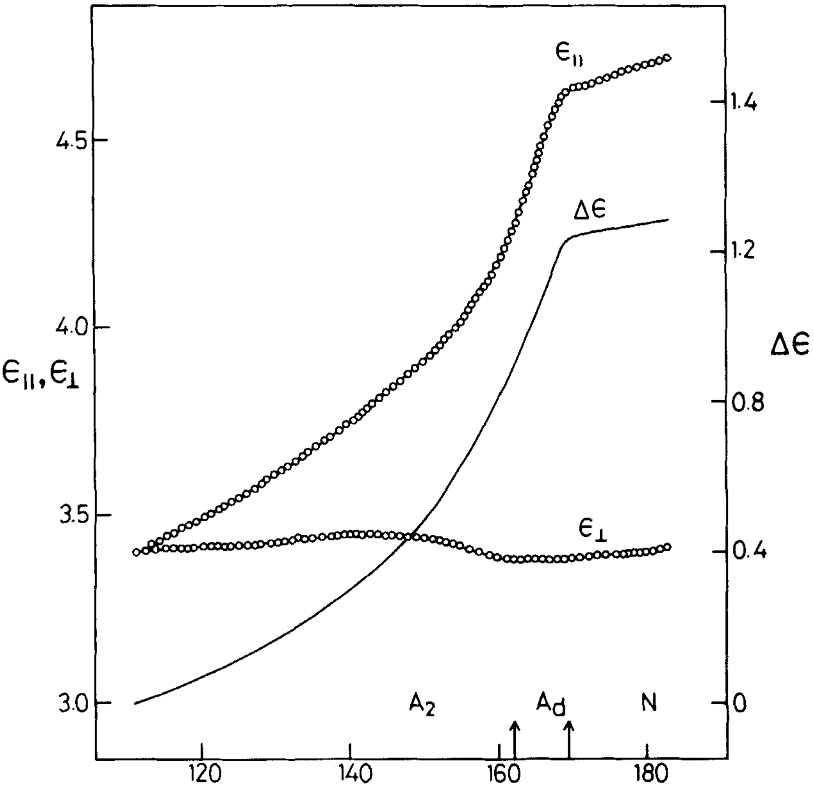

FIGURE 9 Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$ and $\Delta\epsilon$ in the N, A_d and A_2 phases of DB7CN.

The $DBNO_2$ system shows on cooling a small decrease in $\epsilon_{\parallel}$ and a fairly pronounced increase in $\epsilon_{\perp}$ at the A_d–A_1 transition (Figure 7). The increase in $\epsilon_{\perp}$ implies perhaps that the rotation of the molecules about their long axes is more hindered in the A_1 phase than in the A_d phase. The TBBA/DB5CN system also shows essentially similar trends in $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ (Figure 8). In the case of DB7CN (Figure 9) $\epsilon_{\parallel}$ shows a very steep decrease at the N–A_d transition, this decreasing trend continuing right through the A_d–A_2 transition. As a result, the anisotropy goes to nearly zero at the lowest temperature in the A_2 phase. The sharp decrease in $\epsilon_{\parallel}$ even in the A_d phase indicates that the antiparallel correlations increase substantially as a precursor to the formation of the A_2 phase. This may be related to the steep increase of the layer spacing in the A_d phase as the A_2 phase is approached. The anisotropy falling to zero at the lowest temperature

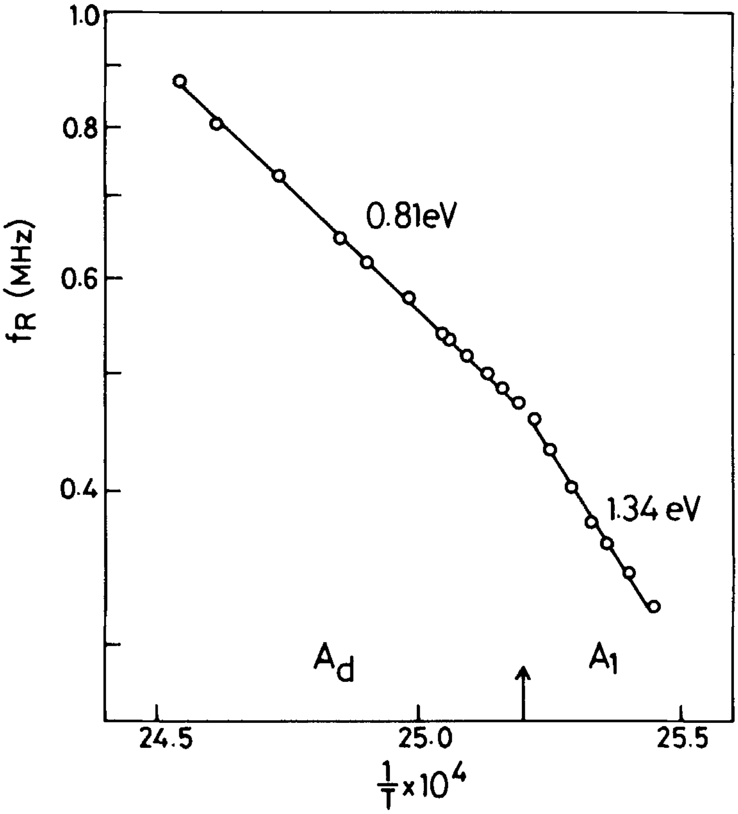

FIGURE 10 Plot of the low frequency relaxation (f_R) of $\epsilon_{\parallel}$ versus 1/T for the DB NO_2 mixture.

in A_2 phase implies that there is almost perfect compensation of the opposing dipoles of neighbouring molecules at these temperatures.

The low frequency dispersion results on the three systems are given as plots of f_R versus $1/_T$ in Figures 10–12 which also show the corresponding activation energies (W). It is seen that $W_{A_d} < W_{A_1}$ for DB NO_2 (Figure 10) and $W_{A_d} < W_{A_2} < W_N$ for DB7CN (Figure 12). In the case of TBBA/DB5CN (Figure 11) $W_{A_2} < W_{A_1} \approx W_N$. It should be pointed out that the data (in the A_2 phase) in close proximity to the A_1–A_2 transition do not fit the Arrhenius plot at all. In fact we have observed a similar deviation from linearity near the N–A_2 transition in DB5CN (unpublished result). The reason for such a behavior is not yet clear to us.

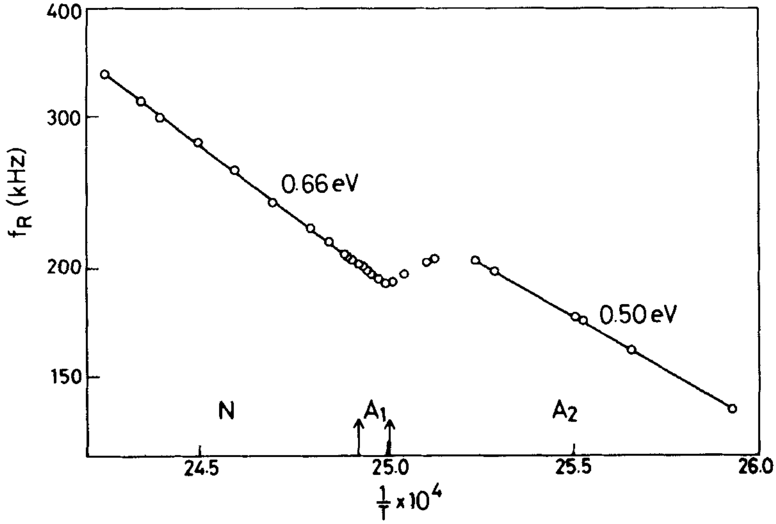

FIGURE 11 Plot of f_R versus 1/T for the TBBA/DB5CN mixture.

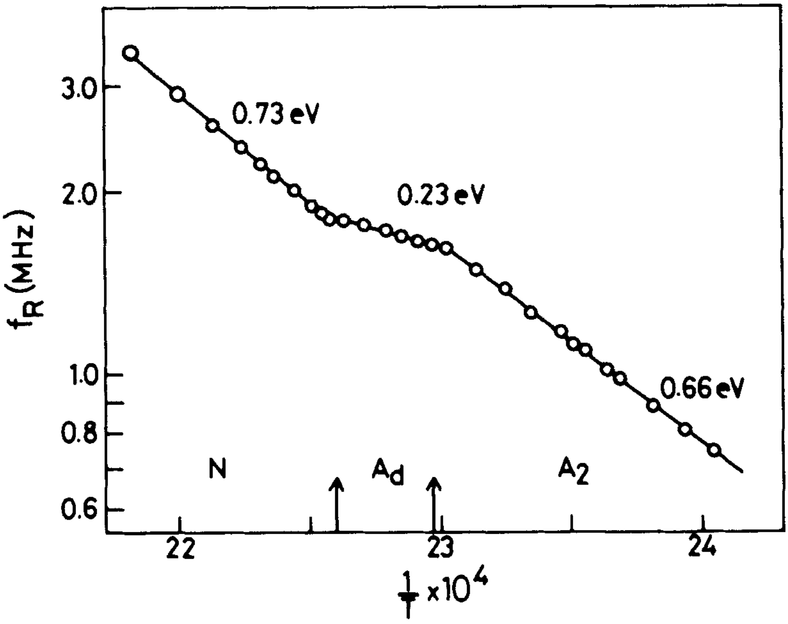

FIGURE 12 Plot of f_R versus 1/T for DB7CN.

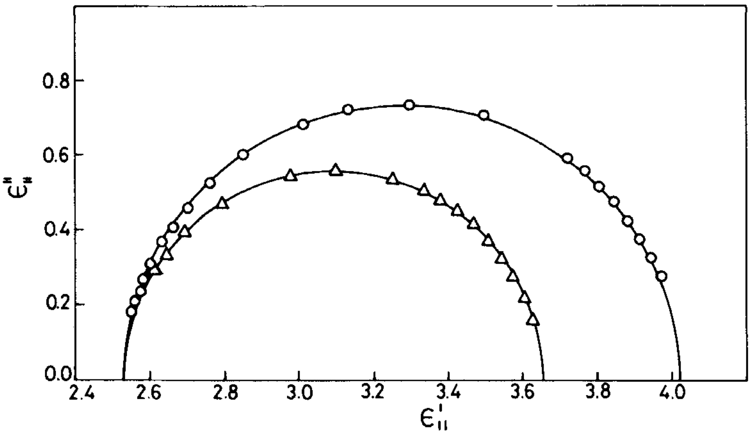

FIGURE 13 Cole–Cole plots in A_2 phase of TBBA/DB5CN mixture; ○: 125.9°C, △: 116.6°C.

It may be recalled that Benguigui and Hardouin[12] have measured the dielectric dispersion of $\epsilon_{\parallel}$ in the A_2 phase of DB6CN and TBBA/DB6CN mixture. They observed two relaxation domains: one with the usual temperature dependence as observed in all smectic A phases and a second one at a lower frequency with a much slower temperature dependence. Benguigui[13] also predicted theoretically the existence of the second relaxation in the A_2 phase. However, Druon et al.[14] observed only a single relaxation in DB6CN, though in the DB6CN/C5 Stilbene mixture they observed two relaxation domains.

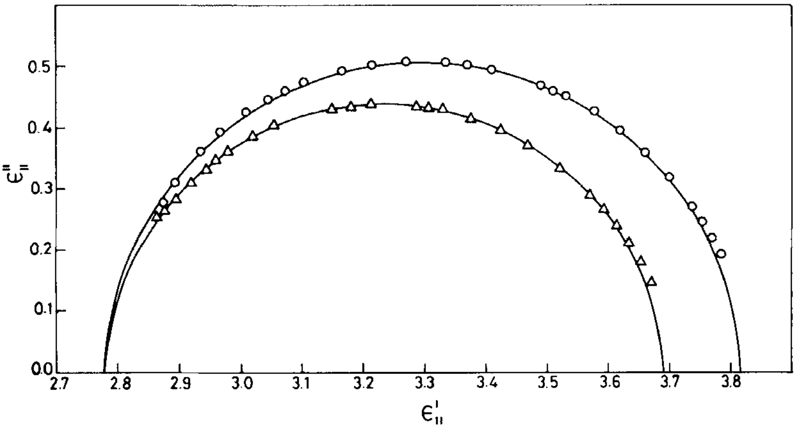

FIGURE 14 Cole–Cole plots in the A_2 phase of DB7CN; ○: 161.3°C, △: 154.2°C.

They argued that the second relaxation domain in the mixture could be either due to the cooperative phenomenon suggested by Benguigui or due to the differences in the interactions of the two different types of molecules with their surroundings. We have not observed any such additional dispersion in the A_2 phase of either DB7CN or TBBA/DB5CN mixture (Figures 13 and 14). Therefore the existence of the double relaxation in the A_2 phase predicted theoretically by Benguigui is still to be proved conclusively.

Acknowledgments

We are extremely thankful to Dr. V. Surendranath for one of the compounds viz., DB5CN. The help of Mr. S. Krishna Prasad in the density experiment is also thankfully acknowledged.

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