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$S_A - S_A$ TRANSITION IN 4-n-DECYLPHENYL-3'-METHYL-4'-(4"-CYANOBENZOYLOXY)BENZOATE

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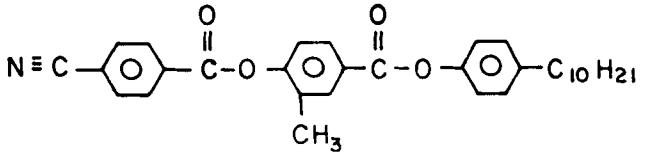
4-n-Decylphenyl-3'-methyl-4'-(4"-cyanobenzoyloxy) benzoate (10 PMCBB) exhibits two smectic A phases with a jump of $\sim$0.4 Å in the bilayer spacing at the $S_A - S_A$ transition point. There are some interesting differences in the thermal evolution of the layer spacing of this compound compared to that of its nitro-analogue, viz., 10 PMNBB.

Recently we[1] reported some unusual properties of 4-n-decylphenyl-3'-methyl-4'-(4"-nitrobenzoyloxy)benzoate (10 PMNBB). It showed a large expansion of the bilayer spacing as it was cooled in the S_A phase accompanied by a reversal of the sign of the dielectric anisotropy. In this letter, we report our Xray and thermal studies of 10 PMCBB, in which the nitro-group of 10 PMNBB is replaced by the cyano-group.

10 PMCBB, whose structural formula is given below



was prepared by the condensation of 4-cyanobenzoyl chloride with 4-decylphenyl-3'-methyl-4'-hydroxybenzoate in dry pyridine. The latter compound itself was obtained by the

acid catalysed condensation of 3-methyl-4-hydroxybenzoic acid with 4-n-decylphenol following the procedure of Lowrance.[2] The compound was purified by column chromatography on silica gel, eluted with hexane/benzene and finally recrystallised from absolute ethanol. The transition temperatures which could be determined visually using a polarizing microscope equipped with a Mettler FP5 hot stage are as follows:

$$\text{Crystal} \xrightarrow{58^{\circ}C} S_A \xleftrightarrow{139^{\circ}.5C} N \xleftrightarrow{169^{\circ}.5C} \text{Iso}$$

Calorimetric investigations on a Perkin-Elmer DSC-2 apparatus showed that the above three transitions (with increasing temperature) have enthalpies of transition of 14.1 kJ/mole, 60 Joule/mole and 1.38 kJ/mole respectively. Further the thermograms also showed a very weak transition at $124.5^{\circ}C$, which looked like a change in slope or at any rate indicated a transition with an enthalpy change less than $\sim$5 Joule/mole. This suggested that the substance has an $S_A - S_A$ transition of the type studied by the Bordeaux group in a few systems.[3-6]

We undertook a detailed Xray investigation of the substance to confirm the existence of this transition. The diffraction patterns of monodomain samples were recorded photographically by using monochromatic copper Kα radiation.[1] The spacing increases substantially with decrease of temperature as shown in fig.1. The molecular length of 10 PMCBB calculated with Dreiding models is $\ell \approx 33$ Å. The measured layer spacing thus corresponds to that of a bilayer, which is brought about by strong antiparallel correlations between neighbouring molecules because of the presence of the strongly

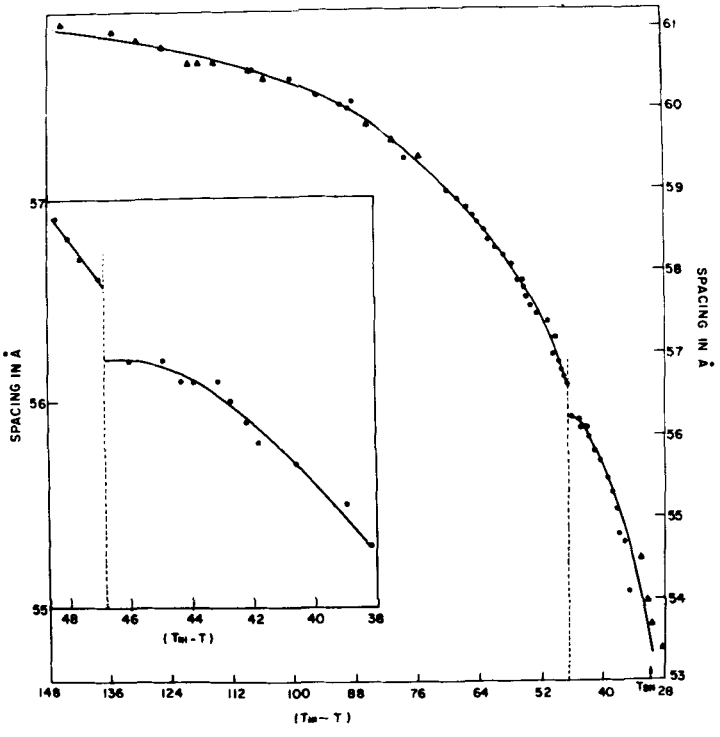


FIG.1: Temperature variation of bilayer spacing of 10 PMCBB. Different symbols represent independent measurements. An $S_A - S_A$ transition occurs with a jump in the spacing at the temperature corresponding to the dashed line. The region around this transition point is shown on a magnified scale in the inset.

polar cyano end group at one end of the molecule.[7-9] The bilayer spacing $d \simeq 1.6\ell$ close to the $S_A - N$ transition temperature and increases to $d \simeq 1.85\ell$ at the lowest temperature before crystallisation takes place.

From Fig.1, it is clear that the rate of increase of layer spacing decreases as the temperature is lowered. Further, there is a clear jump of $\sim$0.4 Å in the layer spacing at $\sim 15^{\circ}$ below $T_{S_{AN}}$. The rate of increase of d slows down

somewhat as the sample is cooled to this temperature, before the jump occurs (see inset of fig. 1). The jump was confirmed by three independent experiments. The lower temperature S_A phase gives rise to a relatively strong second order reflection, whose intensity increases with decrease of temperature.

Our microscopic observations on a homeotropically aligned sample taken between a slide and a coverslip showed a general shrinkage of the boundary as the sample was cooled. Presumably the number of layers between the slide and coverslip remain unaltered and as the layers expand on cooling, the boundary shrinks to conserve density. There was some enhancement in the shrinkage at the temperature corresponding to the $S_A - S_A$ transition. On heating the sample, the boundary again expanded.

It is interesting to compare the thermal evolution of the layer spacing of 10 PMCBB with that of 10 PMNBB, the latter compound having a nitro end group instead of the cyano end group of the former. The layer spacing variation of 10 PMNBB[1] is reproduced in figure 2. It is clear that the cyano compound not only has an $S_A - S_A$ transition which is not observed in the nitro compound, but the curvature of the layer spacing variation itself changes sign between the two cases.

The $S_A - S_A$ transition in 10 PMCBB corresponds to a jump in the layer spacing from about 1.7ℓ to $\sim 1.72\ell$. We tentatively classify this as an $S_{A_{d1}} - S_{A_{d2}}$ transition.

Investigations on other homologues of both 10 PMCBB and 10 PMNBB are in progress and will be reported elsewhere.

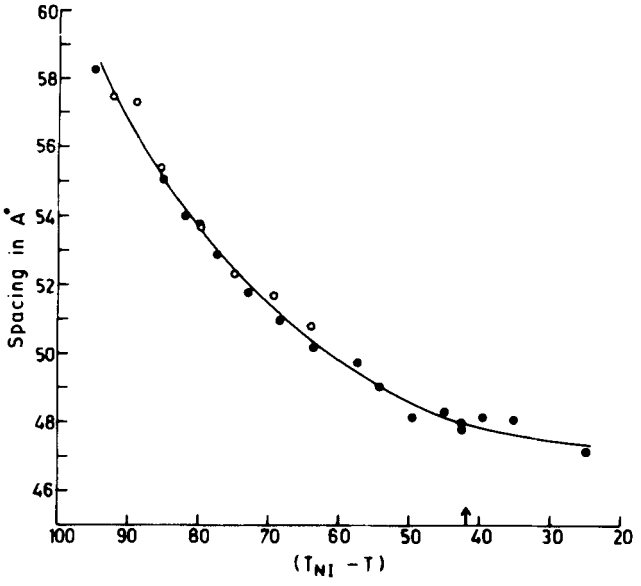


FIG.2: Temperature variation of bilayer spacing of 10 PMNBB (from Ref. 1).

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