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SOME UNUSUAL PROPERTIES OF 4-n-DECYLPHENYL-3'-METHYL-4'-(4''-NITROBENZOYLOXY)BENZOATE

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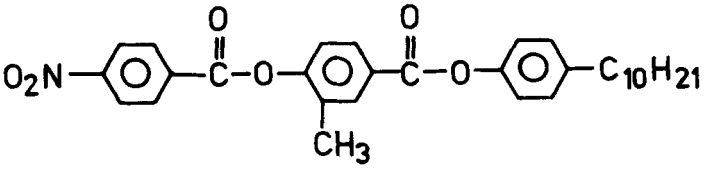
Abstract. 4-n-Decylphenyl-3'-methyl-4'-(4''-nitrobenzoyloxy)benzoate (10 PMNBB) which exhibits the smectic A and nematic mesophases shows a large expansion (∿20%) of the bilayer spacing as it is cooled in the mesomorphic range. This is accompanied by a reversal in the sign of the dielectric anisotropy which becomes negative at lower temperatures.

Mesogenic compounds with the strongly polar cyano and nitro end groups are now known to exhibit a variety of interesting properties such as reentrant mesomorphism,[1-4] coexistence of incommensurate density waves[5] and polymorphism of the A phase.[6-9] From energy considerations, neighbouring molecules in such compounds should have antiparallel correlations,[10,11] which lead to the formation of bilayers.[12] Changes in the structure of the bilayers are responsible for these interesting phenomena.

10 PMNBB, whose structural formula is given below, was synthesized by condensing p-nitrobenzoyl



chloride with 4-n-decylpheny1-3'-methy1-4'-hydroxybenzoate (in pyridine) which itself was prepared by the acid catalysed esterification of 3-methyl-4-hydroxybenzoic acid with 4-n-decylphenol following the procedure of Lowrance.[13] The compound was purified by column chromatography on silica gel, eluted with benzene/hexane, followed by recrystallisation from absolute alcohol. The transition temperatures were determined using a polarising microscope equipped with a Mettler FP5 hot stage. The transition enthalpies were determined using a Perkin-Elmer DSC-2 apparatus. The transition data are as follows:

$$\text{crystal} \xrightarrow[21.6\ \text{kJ/mole}]{77^{\circ}\text{C}} S_A \xleftrightarrow[62\ \text{J/mole}]{108.5^{\circ}\text{C}} \text{N} \xleftrightarrow[1.13\ \text{kJ/mole}]{150^{\circ}\text{C}} \text{Iso}$$

The layer spacings were determined in magnetically aligned samples contained in a Lindemann capillary tube using Cu-Kα radiation and a bent quartz crystal monochromator. The layer spacing increases continuously as the temperature is decreased, the rate of increase rising at lower temperatures (Fig. 1). In the N phase the layer spacing corresponding to short-range ordered (cybotactic) groups was also calculated using the Bragg formula. There is no discontinuity in the spacing at the AN transition point (T_{AN}). The calculated length of the molecule using Dreiding models is $\ell \simeq 33$ Å. The bilayer expands from $d \simeq 1.5\ell$ at the highest temperature to $d \simeq 1.75\ell$ before crystallisation takes place. This is one of the largest variations in the layer spacing measured for any compound. Schematic drawings of the proposed structure of the bilayers at two extreme temperatures are shown in Figure 2.

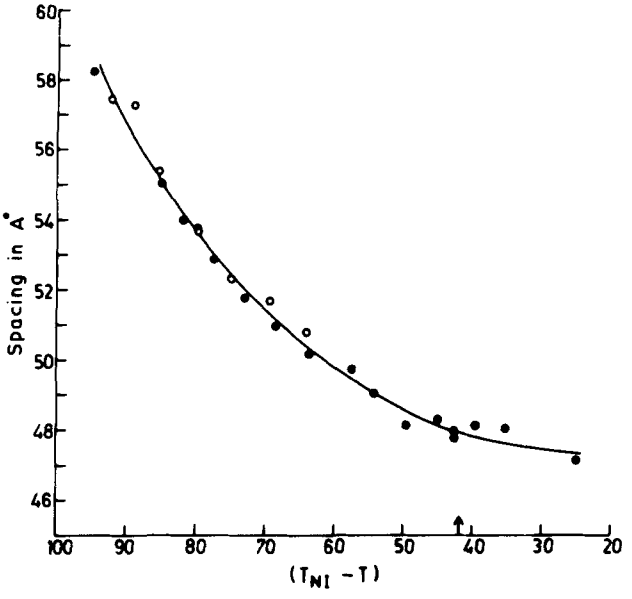


FIGURE 1. Temperature variation of bilayer spacing of 10 PMNBB. o and ● represent two independent measurements on different samples. The vertical arrow stands for T_{AN}.

The second order reflection which is hardly visible at higher temperatures becomes quite noticeable at lower temperatures. Another interesting feature is that the outer ring is unusually weak.

The principal dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ were measured using a Weyne-Kerr bridge (Model B642) on a 100 μ thick sample aligned with a magnetic field of ∿12 KGauss. The results are shown in Fig. 3. In the isotropic phase ε_{is} is practically independent of temperature and has quite a low value of 4 for a compound with the nitro end group. Both the ester groups are oriented in the molecule in such a way that the longitudinal components of their dipole moments oppose the NO_2 dipole

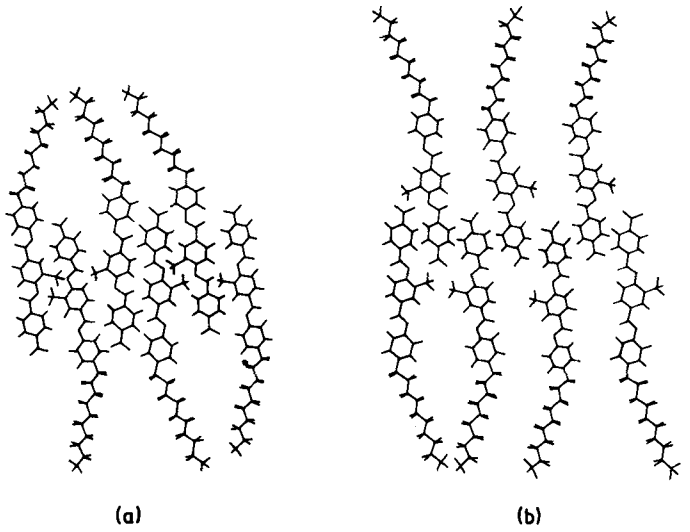


FIGURE 2. Schematic drawings of the structures of the bilayers in (a) higher temperature range, and (b) lower temperature range of the A phase. Actually the three phenyl rings are not likely to be coplanar.

moment. Further, the ester groups make appreciable contributions to the transverse component (μ_t) of the net dipole moment of the molecule. The exact value of μ_t depends on the conformation of the molecule which is not known.

In the nematic phase, $\Delta\varepsilon$ has a positive value of ~ 1, which increases slightly as the temperature is decreased. The mean value $\bar{\varepsilon}[=(\varepsilon_{||} + 2\varepsilon_{\perp})/3]$ is slightly less than ε_{iso} at T_{NI}, as is expected for such compounds.[10] At T_{AN} $\varepsilon_{||}$ decreases while $\varepsilon_{\perp}$ increases so that there is a perceptible decrease in $\Delta\varepsilon$. As the temperature is decreased further in the A phase, $\varepsilon_{||}$ decreases and $\varepsilon_{\perp}$ increases and $\Delta\varepsilon$ reverses sign and becomes negative at $T_{NI}-T \simeq 88.5^{o}$. As shown in Fig.3, $\bar{\varepsilon}$ increases with decrease of temperature over a large range.

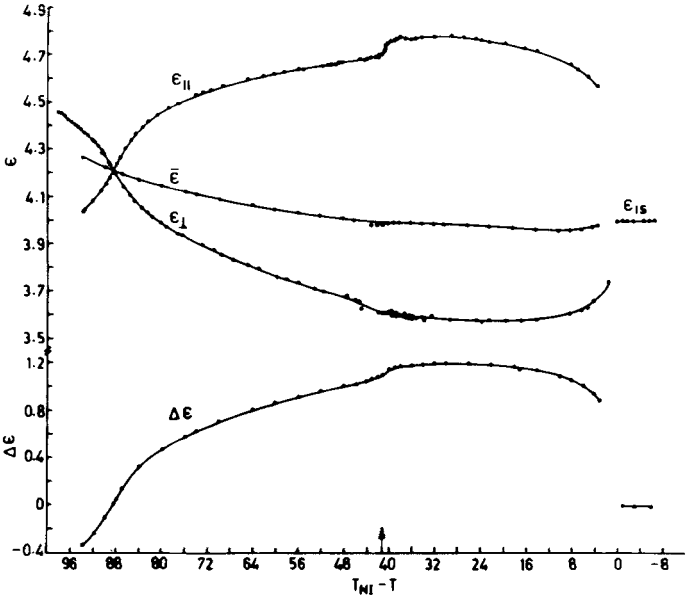


FIGURE 3. Temperature variations of the dielectric constants (upper section) and the dielectric anisotropy (lower section) of 10 PMNBB.

A reversal in the sign of $\Delta\varepsilon$ has been observed earlier in the A phase of two compounds[14,15] which do not have strongly polar end groups, and do not form bilayers. It has been argued in these cases that the smectic layering favours an antiparallel correlation between μ_ℓ and parallel correlation between μ_t of neighbouring molecules. In any case, even according to the theory of Maier and Meier,[16] $\varepsilon_{\parallel}$ depends on $(\mu^2/T)\left[1-(1-3\cos^2\beta)s\right]$ and $\varepsilon_{\perp}$ on $(\mu^2/T)\left[1+\frac{1}{2}(1-3\cos^2\beta)s\right]$. Hence, when β, the angle between the net dipole moment μ and the long axis of the molecule is $>54.7^{\circ}$, the dipolar contribution to $\Delta\varepsilon$ will be negative. This contribution decreases with increase of temperature and the polarizability anisotropy $\Delta\alpha$ which is always positive for such linear molecules tends to make $\Delta\varepsilon$ positive at higher temperatures.

(An analogous reversal in the sign of Kerr constant is observed in the isotropic phase of p-azoxyanisole.[17]) Such an argument can account for the trends in the dielectric constants (including that of $\bar{\varepsilon}$) of 10 PMNBB also. However, in this case, the rapid variation of the bilayer spacing may also significantly contribute to the temperature variation of ε. As the NO_2 groups of neighbouring molecules come closer (see Fig. 2), their contribution to $\varepsilon_{||}$ is more effectively reduced. At the same time, the hindrance to the rotation about the long axis is reduced considerably once the CH_3-side group slips out of the influence of the aromatic cores of the immediate neighbours, as seen in Fig.2b, contributing to an increase of $\varepsilon_{\perp}$. It may be noted here that 4-n-hexylphenyl-4'-cyanobenzoyloxybenzoate, a compound similar to 10 PMNBB except that the NO_2 group is replaced by a CN group, the alkyl chain is 7 carbon atoms long and the side CH_3 group is absent, exhibits an S_{A2} phase and shows only a positive (though weak) $\Delta\varepsilon$.[18]

Further studies on this and other homologues of this series are underway. The results along with additional details of the synthetic procedures will be reported elsewhere.

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