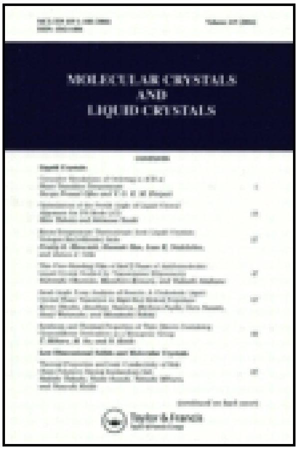

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The Density Of 4 n-Octyl-4-Cyano-Biphenyl (8CB)

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THE DENSITY OF 4 n-OCTYL-4'-CYANO-BIPHENYL (8CB)

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ABSTRACT The density of 8CB has been measured between 28 and 50°C and the volume change at the S_A-N and N-I transitions determined. The S_A-N appears to be first order. The implications of the results are discussed with respect to the molecular packing in the unusual structure of the cyanobiphenyls in which the layer spacing is about 1.4 times the molecular length.

The density of relatively few liquid crystalline substances has been measured and yet this is a very fundamental property for understanding the phase behaviour and especially the transitions involving mesophases.

The cyanobiphenyls are interesting because they have low temperature mesophases and smectic layer spacings (or, in the case of nematics, layer-like correlations) about 1.4 times the molecular lengths,[1,2] which might be described as a modified bilayer structure.

8CB has the following phase behaviour -

$$\text{Crystal} \xrightarrow{21.1^{\circ}C} S_A \xrightarrow{33.5^{\circ}C} N \xrightarrow{40.5^{\circ}C} I$$

Transition enthalpies were measured using a DSC 2 and found to be as follows -

$$\frac{\Delta H}{\text{kJ mol}^{-1}} : \text{Cr} \rightarrow S_A : 23 \;;\; S_A \rightarrow \text{N},\ 0.2 \;;\; \text{N} \rightarrow \text{I},\ 0.7$$

The S_A-N transition appeared to be as sharp as the others, consistent with a first order change.

We have measured the density as a function of temperature by a method, similar to that described by Torza & Cladis [3] in which approximately 2g of material were contained in a pyrex vessel having two vertical arms of precision 0.5mm bore tubing. These contained mercury and the 8CB-mercury meniscus was inside the main vessel. The height of the mercury columns gave a direct measure of the volume change, the whole cell being contained in a water thermostat and its temperature maintained constant to within ± 0.020K. Two tubes were used simply to facilitate the filling of the cell. In a separate experiment a vessel of volume ∿ 2.8cm^3 with a single 0.5mm capillary and completely filled with 8CB was used to determine directly the volume changes at the transitions $S_A \rightarrow N$ and $N \rightarrow I$ by measuring the volume of sample expelled at the transition. Each of the above experiments was done on two different samples.

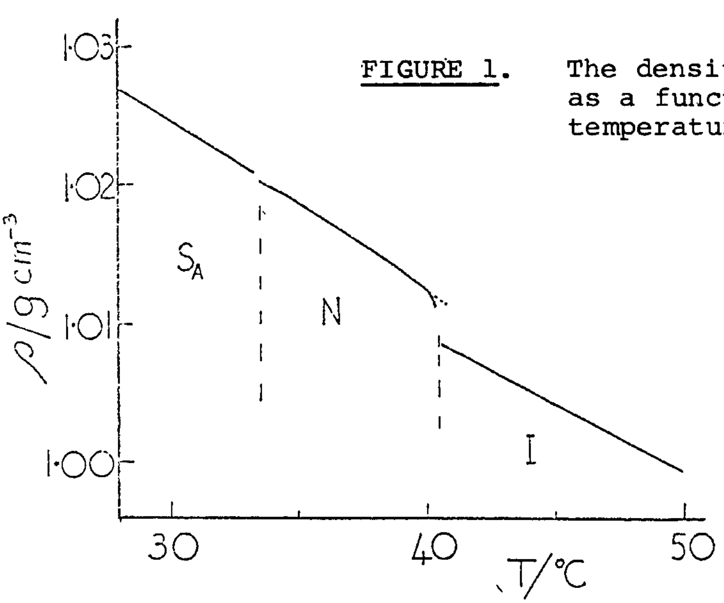

FIGURE 1. The density of 8CB as a function of temperature.

The density is shown as a function of temperature in figure 1. The S_A-N transition appeared to occur sharply within 0.1 K and the N - I was complete within ∿ 0.5 K. The volume changes at the transitions were as follows -

$\Delta V/\mathrm{cm}^3\,\mathrm{mol}^{-1}$: S_A - N, 0.14 ± 0.04; N - I, 0.95 ± 0.15

The observations are consistent with first order transitions in both cases with some pretransition volume expansion before the N - I transition. In this substance T_{S_AN}/T_{NI} = 0.98 for which a first order S_A - N transis predicted by McMillan's [4] theory although there are theoretical grounds for believing that such transitions should always be at least weakly first order [5].

The volume change at the S_A - N transition is very small ($\sim$ 0.05%) while that at the N - I amounts to only 0.35%. These results imply that the changes in local molecular organisation at the transitions must be small. They are consistant with X-ray evidence which shows that the changes occurring at these transitions are essentially changes in long range order - the average local structure is little changed [2].

The magnitude of the molar volumes is of interest with respect to the details of the molecular packing, especially for the cyano compounds because of their modified bilayer structure. Although we do not have any information on the crystal density, the packing in the various liquid phases relative to the densest packing of the crystal may be estimated as follows. The molecule consists of a cyanobiphenyl core of length $\sim$ 12Å and an alkyl tail of effective length $\sim$ 10.5Å (figure 2). From the crystal structures of biphenyl [6] and of n-alkanes [7] the area occupied per molecule normal to the long axis in each case is in the range 19 - 20Å^2 depending on temperature and crystal phase. This implies a minimum volume per molecule for 8CB of $\sim$ 430 - 450Å^3 compared with an average volume per molecule from the density in the S_A phase of 473Å^3. In the isotropic liquid phase this increases only to 484Å^3 at 50°C. The "free volume" in the S_A phase is therefore 5 - 10% which is similar to that found directly for CBOOA [3]. These

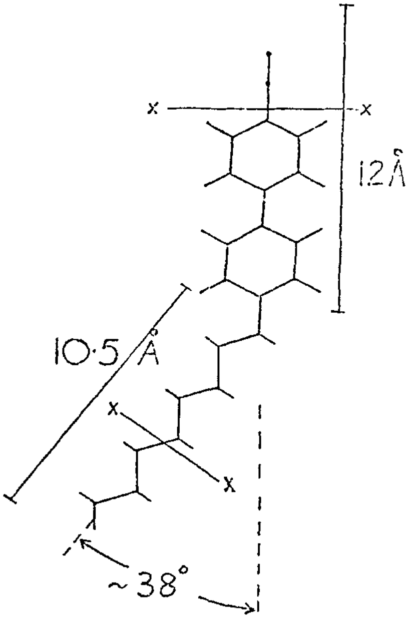

FIGURE 2. Nuclear positions in 8CB. The areas occupied by core and tail portions of the molecule across planes X-X are each 19-20Å^2.

considerations can immediately exclude some of the possible structures proposed for the S_A phase which involve "interpenetration" of tails and/or cores as illustrated in figure 3. Such drawings are in fact quite common but are quite unrealistic as they must imply low average packing and high average molecular volume because of the essentially identical areas of core and tail. The molecules must in fact be relatively efficiently packed and the most likely local packing is probably based on an arrangement like that shown in figure 4. This is suggested also by X-ray diffraction measurements[8] on a range of materials which show that the layer spacings exceed the molecular length by an amount proportional to the length of the tail rather than that of the core of the molecule.

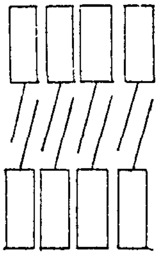

FIGURE 3

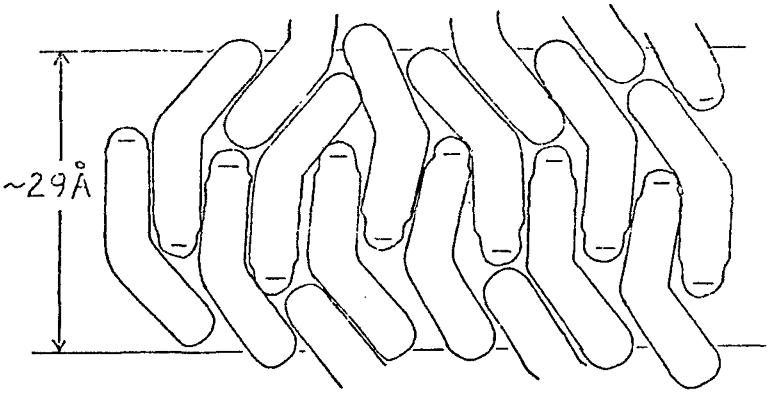

FIGURE 4 Schematic 2-dimensional representation of proposed local structure in an 8CB layer in the S_A phase; approximately to scale, with the width of molecular cores and tails proportional to the square root of their areas. Cyano groups are indicated by negative signs.

The essential feature of the suggested local structure is that the strong dipoles due to the cyano groups tend to be opposed and give efficient packing of the cores while the angle between the tail and core promotes space filling by the tails. A significant amount of disorder, consistent with a smectic order parameter[4] $\langle \cos 2\pi z/d \rangle \sim 0.6$ is an essential feature of the suggested structure. It should be emphasized in conclusion that the molecules are very mobile with translational diffusion constants[9] $\sim 10^{-7}$ cm^2 s^{-1} and they rotate about their long axes with a correlation time of $\sim 10^{-11}$s.[10]

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