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## Liquid Crystals

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## Smectic A phases with strings of interdigitated molecules in swallow tailed compounds†

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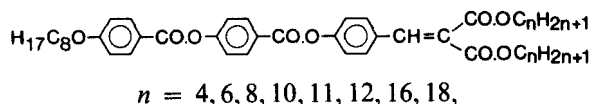
(Received 1 February 1988; accepted 20 April 1988)

X-ray diffraction studies are reported of smectic A phases exhibited by swallow-tailed compounds. The special molecular shape consisting of regions having differing space filling requirements results in antiparallel packing of the molecules; this influences the conformations of the alkyl chains. The layer spacings show unusually good agreement with the molecular lengths and this is the case for molecules with long and short aliphatic chains. We have observed also an additional incommensurable structural element which we believe to be unique for non-polar, low molar mass compounds. The X-ray diffraction patterns provide evidence for the existence of strings of interdigitated molecules.

### 1. Introduction

The rich diversity in the molecular architecture of mesogens has led to a great variation in the liquid-crystalline properties as well as to many modifications of the well-known smectic structures, for example the  $S_A$  phase. The structure of liquid-crystalline phases of laterally branched compounds has been discussed in preceding papers [1, 2]. The existence of liquid-crystalline phases in compounds with branched terminal chains has also been demonstrated [3-5]. These substances possess an exceptionally asymmetric molecular shape and consequently, the packing of the molecules should result in special steric effects.

Here we present X-ray studies of the homologous series, the di- $n$ -alkyl 4-(4-(4- $n$ -octyloxy-benzoyl oxy)-benzoyloxy)-benzylidenemalonates [4];



all eight members exhibit  $S_A$  phases. Figure 1 shows the dependence of the transition temperatures on the length of the alkyl chains for these swallow-tailed compounds [4]. The mnemonic used for this series is  $S_n$  where  $n$  denotes the number of carbon atoms in the alkyl chains.

### 2. Experimental

The thickness ( $d$  value) of the smectic layers as a function of temperature has been determined by using small angle equipment to within an experimental error in the Bragg angle of  $\pm 0.01^\circ$ . Oriented samples could be obtained for all the homologues by applying a magnetic field of about 1.2 T. In selected cases, the  $d$  values have also been

† Liquid-crystalline swallow-tailed compounds, part III; Parts I, II and III, see [4], [15] and [19], respectively.

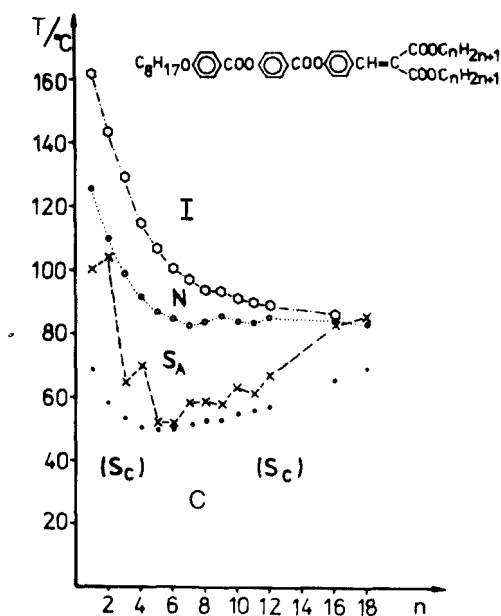


Figure 1. The dependence of the transition temperatures on the length of the alkyl chains for the  $S_n$  compounds [4].

measured using a Guinier method. The lengths,  $L$ , of the molecules have been estimated using CPK models.

### 3. Results

Figure 2 shows that the  $d$  values exhibit a clear temperature dependence which becomes more pronounced as the length of the swallow tail is increased. The values can be approximated by a linear regression;  $d = a + mT$  where  $T$  is the temperature in °C and the increase,  $m$ , of the different homologues is shown in figure 3.

In figure 2, the temperature ranges of the  $S_A$  phases are indicated by marks. The octadecyl homologue ( $S_{18}$ ) exhibits a monotropic  $S_A$  phase. The estimated molecular lengths with their associated errors are also shown in figure 2. It is apparent that, with the exception of  $S_{16}$  and  $S_{18}$ , the  $d$  values measured in the lower temperature regions of the  $S_A$  phases agree very well with the molecular lengths  $L$ . The diffraction patterns of the oriented samples (see, for example figure 4) exhibit Bragg spots on the meridian which lies in the field direction, and perpendicular to these are outer crescent-like diffuse scattering maxima. This is a characteristic pattern of the  $S_A$  phase. However, in addition several orders of diffuse scattering maxima are visible, and these are schematically indicated by crosses in figure 5. The density wave 'd' of these maxima is incommensurable with the layer periodicity. Also, they are observed at the same averaged Bragg angles for all the homologues. The number and intensities of these maxima are greater for the shorter chain homologues, for which up to seven orders may be observed, suggesting that the fraction of the additional structural elements within the phase changes with alkyl chain length.

The diffuse scattering planes perpendicular to the meridian may be explained by identical and parallel, but uncorrelated, rows in physical space [6]. Similar results have been obtained for other compounds for example, TBBA in the  $S_G$  phase [7]. However,

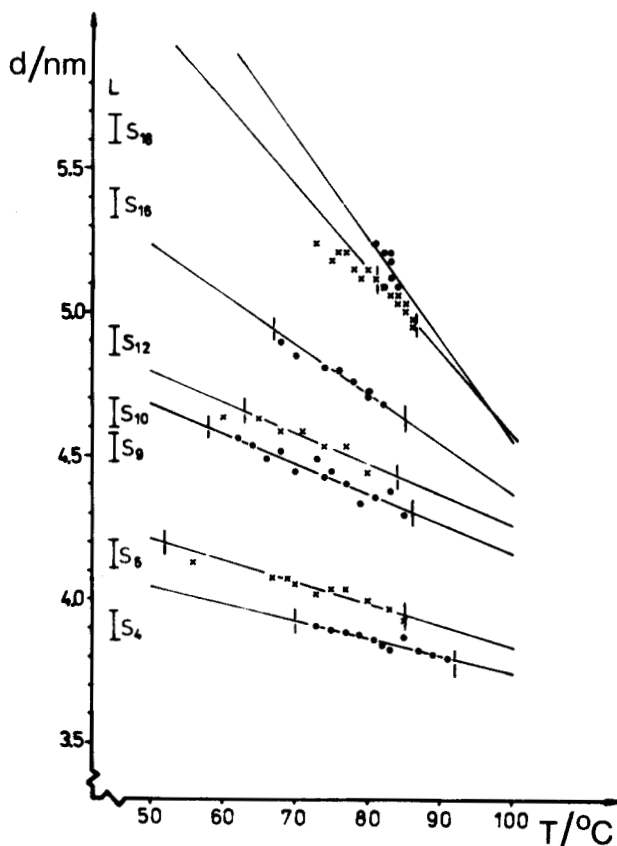


Figure 2. The  $d$  values of the  $S_n$  compounds as a function of temperature. The bars besides the ordinate indicate the all-trans molecular lengths.

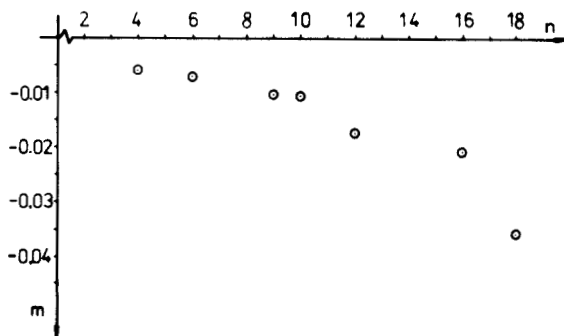


Figure 3. The temperature dependence of the  $d$  values as a function of alkyl chain lengths for the  $S_n$  series.

in such examples the density wave has always been commensurate with the molecular lengths.

#### 4. Discussion

Figure 6 shows the  $d$  values at  $70^\circ\text{C}$ , which generally corresponds to the onset of the  $S_A$  phase region, as a function of the number,  $n$ , of the carbon atoms in the

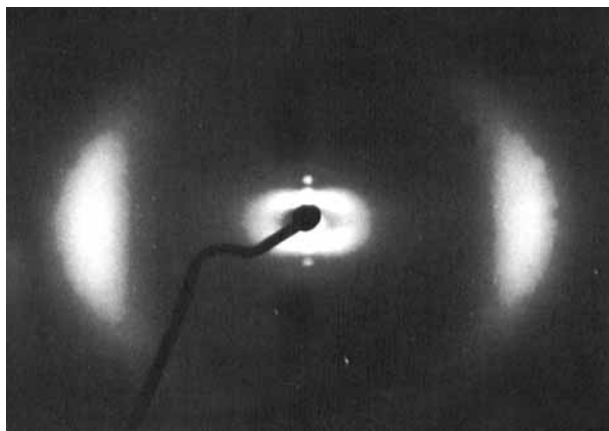


Figure 4. An X-ray diffraction pattern of an oriented sample of  $S_{10}$  at  $78^\circ\text{C}$  in the  $S_A$  phase.

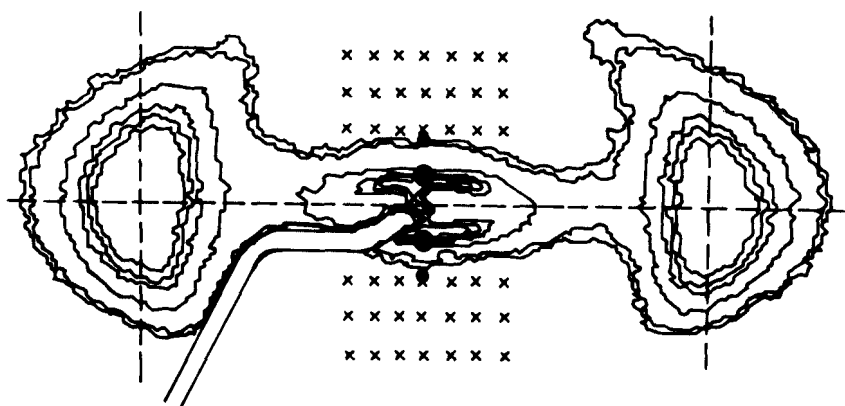


Figure 5. Microdensitometer plot of a diffraction pattern; the inserted crosses indicate the diffuse strips.

swallow tails. Also, the averaged spacings, 'd', are plotted. The good agreement of the  $d$  values at  $70^\circ\text{C}$  with the molecular lengths is surprising.

If we consider compounds that are symmetrically substituted by alkyl chains, then, usually, an increasing difference between the molecular and the layer spacing is found with increasing chain length. Such differences have led to quite different interpretations of the layer structure in the  $S_A$  phase [8–11]. The simplest model explains the difference by non-all-trans conformations of the alkyl chains. Similar differences would be expected in the phases under discussion. However, although homologues with long aliphatic chains have been investigated, such differences have not been observed. The intersection of the linear regression ( $d/\text{nm} = 3.37 + 0.129n$ ) with the ordinate at 3.37 nm agrees very well with the non-swallow-tailed part of the molecule shown in figure 7. The increase in  $d$  of 0.129 nm per methylene group agrees well with the values reported for rigid paraffinic chains of 0.127 nm [12]. Therefore, the smectic layers must be composed of molecules arranged in an antiparallel manner within a monolayer and this is shown in figure 8. This antiparallel packing of the molecules is also supported by dielectric measurements [13–15]. The existence of

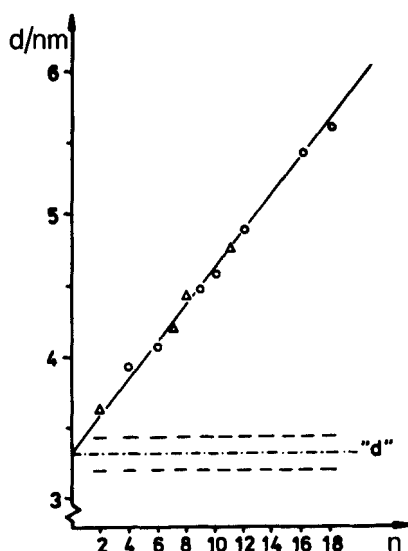


Figure 6. The  $d$  values at  $70^{\circ}\text{C}$  as a function of the chain length. The circles and triangles correspond to different measurements; ' $d$ ' represents the period of the strings together with its smallest and greatest deviations.

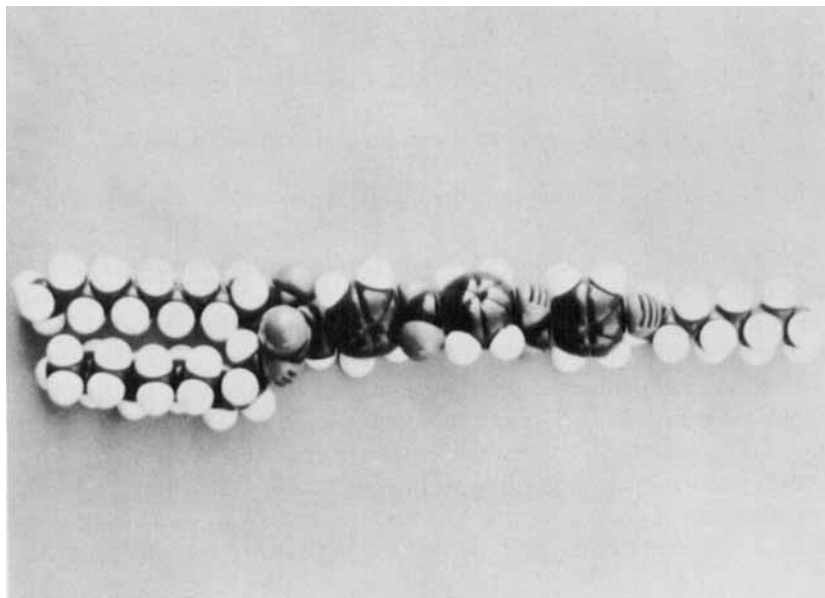


Figure 7. A CPK model of  $S_8$ .

all-trans alkyl chains may be explained by the sterically hindered intrachain mobility resulting from the highly asymmetric molecules. The antiparallel orientation yields a dense packing and reduces the free space in the chain region. The influence of the liquid-crystalline environment on the conformation of alkyl chains has also been observed in other systems; for example, compounds having lateral long chain substituents [16] and compounds with highly asymmetric longitudinal alkyl substituents

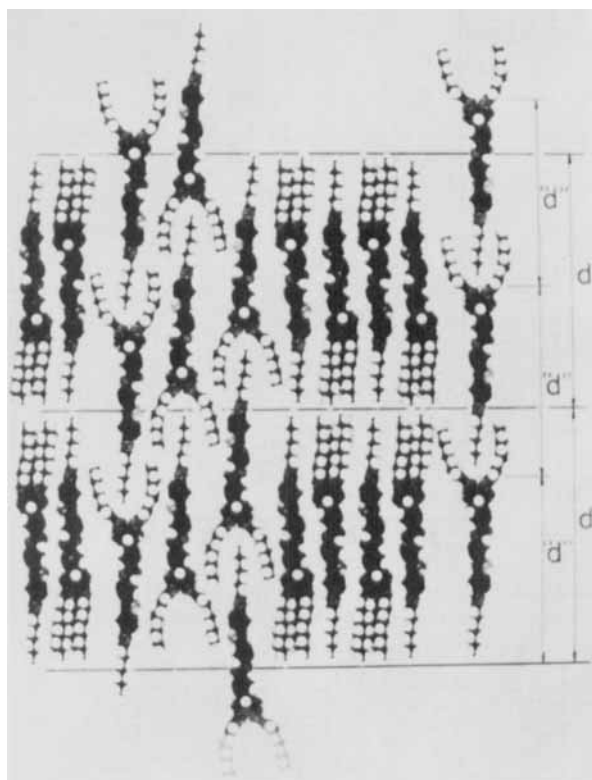


Figure 8. The proposed structure of the smectic A phase.

[18] and has been considered theoretically by Hirokazu and Samulski [17] for smectic phases.

Furthermore, the aliphatic double chains (swallow-tails) must be aligned almost parallel to each other in order to explain the increase of  $d$  with  $n$ . The longer the chains the better this condition is fulfilled. In the higher homologues, however, the differences,  $L - d > 0$ , imply that the chains are adopting non-all-trans conformations and this is reflected in the temperature dependence of  $d$  (figure 2) and its trend in the homologous series (figure 3). The extrapolated spacing, ' $d$ ', which is independent of the length of the swallow tail, corresponds to the intersection of the function  $d = f(n)$  with the ordinate ( $n = 0$ ). According to this, the uncorrelated strings of molecules exhibit a periodicity of approximately 3.37 nm. This density wave is incommensurable with the layer structure and demands the introduction of an additional structure element.

The repeating distance 3.37 nm, may be obtained if some molecules are interdigitated giving strings as sketched in figure 8. These strings pass through the smectic layers in a distorted manner. The decreasing stability of such strings with increasing chain length may be explained by a greater ability for parallel ordering of the longer chains.

Summarizing, these results clearly illustrate the important role of molecular packing in determining the behaviour of highly anisotropic molecules. It results in a layer structure formed by manner molecules aligned antiparallel, and also influences the conformations of the alkyl chains. Furthermore, the special molecular

shape causes structural peculiarities in the form of strings of molecules within the layer structure.

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