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Intercalated smectic-A structures in a new class of laterally branched substances

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Intercalated smectic-A structures in a new class of laterally branched substances

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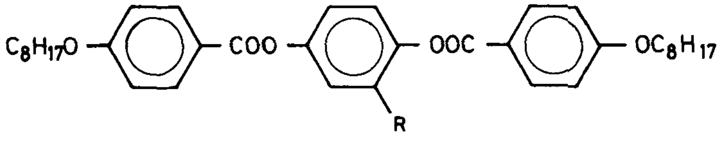
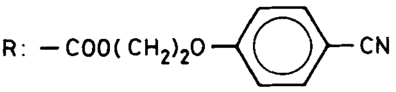
X-ray, DSC and optical studies of a new class of substances with aromatic rings in the lateral branches are reported. The thermal behaviour of the substances is discussed. The X-ray measurements lead to a structural model of the S_A phases consisting of layer structures with intercalating molecules.

In several papers [1, 2] the properties of laterally branched 1,4-bis-(4-subst.-benzoyloxy)-2-n-alkylbenzenes were reported, all of which exhibit nematic phases. The liquid-crystalline properties of these compounds which were most unexpected because of the long lateral branches in the molecules may be explained by the assumption that the parts of the lateral alkyl chains exceeding five carbon atoms are nearly parallel to the basic molecule [3]. This interpretation is in accord with the essential elements of molecular statistical theories of liquid crystals [4]. It should be emphasized that all of these compounds are nematic. X-ray investigations have proved the existence of cybotactic groups in the nematic phases [9].

Now we have included in our investigations substances which have large lateral branches with aromatic rings. In contrast to the compounds with lateral non-aromatic chains [1, 2] and some series with lateral aromatic substituents reported in the literature [5–7] many of our new compounds are smectic. Here we report the results obtained for the two compounds [8]



(1)



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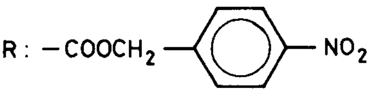

The calorimeteric measurements made using a Perkin Elmer DSC 2 yield the transition schemes

$$\begin{tikzcd}[column sep=large] (1)\ \mathrm{Cr} \arrow[r, "71\cdot8", "16\cdot5"'] & \mathrm{P} \arrow[r, "91\cdot1", "1\cdot18"'] & \mathrm{S_A} \arrow[r, leftrightarrow, "163\cdot9", "9\cdot07"'] \arrow[dll] & \mathrm{I} \\ \mathrm{RT} & & & \end{tikzcd}$$

$$\begin{tikzcd}[column sep=large] (2)\ \mathrm{Cr} \arrow[r, "95\cdot9", "18\cdot25"'] & \mathrm{S_A} \arrow[r, leftrightarrow, "163.9", "5\cdot65"'] \arrow[dl] & \mathrm{I} \\ \mathrm{RT} & & \end{tikzcd}$$

The transition temperatures (above the arrows) are given in degrees centigrade, the enthalpies (below the arrows) in kJ mol^{-1} and RT denotes room temperature. The phase sequence of substance (**1**) is strongly dependent on the thermal history of the sample. Figure 1 shows heating and cooling runs for substance (**1**). Heating a virgin sample the DSC curve shown in (*a*) is obtained. The appearance of a phase labelled P is clearly indicated. On cooling the sample to room temperature (*b*) neither a $S_A \rightarrow P$ nor a $P \rightarrow Cr$ transition peak could be observed. Crystallization takes place after several hours at room temperature or in the present case after 2 hours at − 70°C. Repeating the heating run does not show the $P \rightarrow S_A$ transition (*c*). If the heating and cooling process is limited to a temperature within the existence region of the P phase (*d*) no transition is detectable in the cooling run (*e*). This means that the P phase can be supercooled to room temperature.

The results of the calorimetric studies are confirmed by X-ray investigations of powder samples studied by the Guinier method. The patterns observed for a virgin

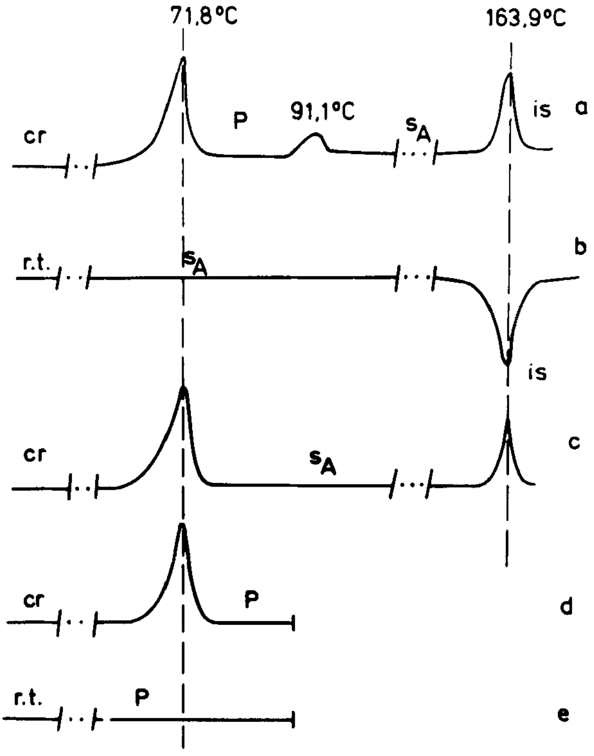

Figure 1. DSC curves of substance (**1**).

sample are shown in figure 2. The Cr → P transition as well as the P → S_A transition can be detected. Repeating studies with the same sample (which now has a different thermal history), do not show the Cr → P, but only a Cr → S_A transition at 72°C. On the other hand cooling a virgin sample, which was heated before to the P phase, to room temperature, only patterns of the P phase were obtained as well as in the subsequent heating run. The pattern of the P phase is characterized by many strong and weak interferences. It looks like a crystalline phase, but the plastic behaviour of the P phase observed by microscopic observation should be emphasized. A virgin sample prepared in a conventional way between two glass plates is subjected to a remarkable alteration of the plastic property at about 72°C. A non-specific microscopic texture appears. Above 92°C a S_A phase is observed characterized by a fan-shaped texture or homeotropic texture dependent upon the experimental conditions. The crystalline character of the microscopic picture is found to be maintained up to 92°C through investigation of a thin film obtained by evaporation of a solution.

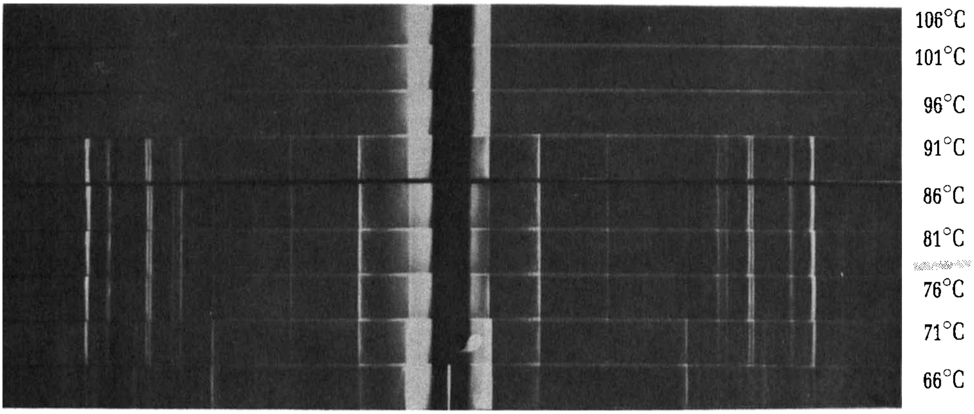

Figure 2. The temperature dependence of the Guinier patterns of substance (**1**).

The classification of the S_A phases of substances (**1**) and (**2**) was made on the basis of X-ray investigations combined with texture observations. Conoscopic observation proves the uniaxial character of the phase. The X-ray patterns obtained from oriented samples of both substances exhibit the typical characteristics of smectic-A phases (figure 3), namely a diffuse, crescent-like outer scattering on the equator of the pattern and inner spots (first and second orders of the layer reflection) on the meridian of the pattern which is the direction of the aligning magnetic field. It can be concluded therefore that the phase exhibits a well defined layer structure. The long axes of the molecules are aligned parallel to the layer normal.

The layer thicknesses, d, were measured using small angle equipment and recording the intensity between $0{\cdot}2° < \Theta < 2{\cdot}5°$. There is, however, a difficulty in explaining the measured d-values ($d = 34{\cdot}5$ Å for substance (**1**); $d = 34{\cdot}2$ Å for substance (**2**)) of the layer structure on the basis of the molecular geometry. The length of the basic molecule in both cases is $L = 42$ Å and the lengths of the lateral branches are $l = 14$ Å for (**1**) and $l = 12$ Å for (**2**). The layer spacing, d, corresponds roughly therefore to $d \simeq (L/2) + l$. Since any inclination of the molecules can be excluded on the basis of the oriented X-ray patterns, only an intercalation of the alkyl-chains can explain the d-values. The model sketched in figure 4 should be considered as a rough approximation to the molecular packing on a local scale. To avoid ferroelectric properties, the bulk structure would need to consist of the clusters sketched in figure 4 in which both orientations with respect to the *z*-direction exist in statistically equal amounts. The intercalation seems to be a consequence of the bulky lateral branch, which is stiffer than the alkyl chains investigated in [3] and [9]. An intercalation of the

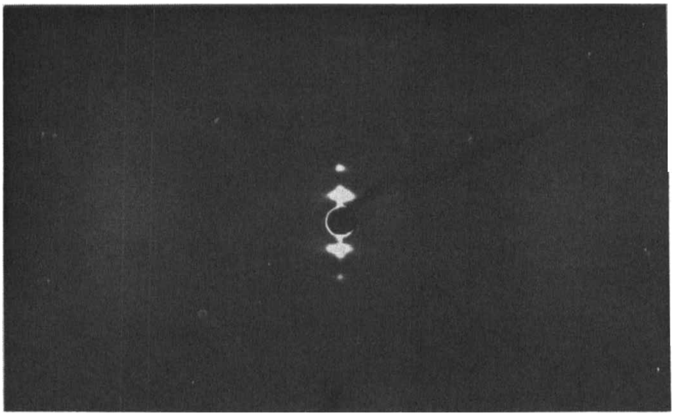

Figure 3. X-ray pattern of an oriented sample of substance (**1**) in the S_A phase (T = 145°C).

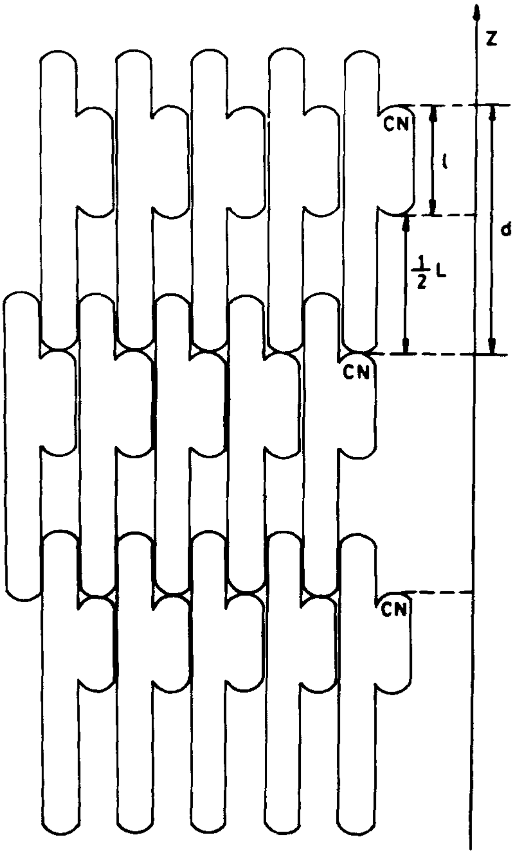

Figure 4. Model of the molecular packing on a local scale.

alkyl chains was reported by us recently in mesomorphic phases of substances with terminal diol groups [10]. Similar structures were reported for derivatives of the pyranosides [11, 12]. Apart from the very different intermolecular interactions in these cases the bulky diol group makes it possible for the chains to be intercalated. Such a structure should always be characterized by a layer spacing, d, which is smaller than the lengths of the molecules or dimers (as far as orthogonal systems are concerned) because only parts of the molecules (usually the aliphatic chains) intercalate into the adjacent layer.

In a recently postulated new family of interdigitated phases [13] the d-values are approximately equal to L. Because of this result the structure of these phases is not related to that of intercalated smectic phases.

Finally the question arises, do the phases under discussion play the same role as the S_{A_d} phases in the case of terminal polar substances? To answer this, further X-ray and miscibility investigations are under way to study especially the relation between intercalated phases and conventional smectics.

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