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## Liquid Crystals

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S. Diele<sup>a</sup>; D. Lose<sup>a</sup>; H. Kruth<sup>a</sup>; G. Pelzl<sup>a</sup>; F. Guittard<sup>b</sup>; A. Cambon<sup>b</sup>

<sup>a</sup> Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Halle/S., Germany <sup>b</sup> Laboratoire de Chemie Organique du Fluor, Universite De Nice-Sophia Antipolis, Nice Cedex, France

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# Liquid crystalline phases of perfluorinated compounds with segregated sublayers

by S. DIELE\*, D. LOSE, H. KRUTH, G. PELZL

Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg,  
Mühlpforte 1, 06108 Halle/S., Germany

F. GUITTARD and A. CAMBON

Laboratoire de Chimie Organique du Fluor, Université De Nice-Sophia Antipolis,  
F-06108 Nice Cedex 2, France

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The liquid crystalline polymorphism ( $S_A$ ,  $S_B$ , CrE) and the structures of the phases of *N-n*-perfluoralkylethyl-(4-phenylbenzylidene)imines are described. It is shown that the smectic layer consists of two sublayers in to which the incompatible moieties of the compounds segregate. It is proved that the perfluoralkyl chains remain disordered until crystallization occurs, whereas with decreasing temperature, the aromatic parts are ordered in types of  $S_B$  and CrE structure.

## 1. Introduction

Variation of rod-like molecular architecture gives rise to the structural peculiarities of the known liquid crystalline phase types.

Addition of polar groups in terminal positions has led to subgroups of the conventional  $S_A$  and  $S_C$  phases [1-3]. Lateral or terminal branches enhance steric interactions and can result in incommensurable periodicities [4] or transitions within the  $S_A$  and  $S_C$  phases [5]. Another way of modifying the properties of smectic layers involves the partial substitution of hydrogen atoms by fluorine atoms. Recently, numerous compounds containing perfluoralkyl groups have been synthesized [6-10]. As the most simple examples, semi-fluorinated alkanes [9,11-15] can be considered in which the fluorinated and hydrogenated parts are assumed to be organized in different sublayers [12,15]. In the case of polyphilic compounds, two or more chemically different moieties are linked and tend to segregate into different structural sub-units [16-23] if additional interactions do not prevent this. In the present paper the structures of the liquid crystalline phases of new compounds which consist of a biphenyl unit linked via a short spacer to a fluorinated alkyl chain are discussed. Since steric interaction is strongly related to the incompatibility of molecular moieties of different chemical structure, separation of these two parts takes

place. This has been proved by X-ray measurements and a model of the layer structure is postulated.

## 2. Experimental

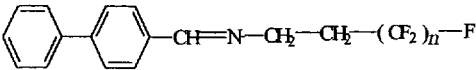
The synthesis and characterization of the new compounds have been described in a previous paper [24]. The phase transitions were detected by DSC measurements (DSC 7, PERKIN ELMER) and polarizing optical microscopy (LEITZ orthoplan). The phases were identified by texture observations, as well as by X-ray studies. The X-ray studies of non-oriented samples were performed using a Guinier-goniometer (HUBER Diffraktionstechnik GmbH) and  $\text{CuK}_\alpha$  radiation. The patterns, especially the diffuse scattering, have been evaluated by a peak fit program. Oriented samples of different quality prepared in glass capillaries were obtained by slow cooling of the sample from the isotropic state. A magnetic field was not applied. The patterns were recorded with a 2D detector (HI-STAR Area Detector, Siemens AG).

## 3. Results

The phase behaviour and transition temperatures of the homologous *N-n*-perfluoralkylethyl-(4-phenylbenzylidene)imines are listed in table 1. It is seen that all members of the series exhibit a  $S_A$  phase. The short chain homologues form, additionally, a CrE (**B4**, **B6**) and an  $S_B$  phase (**B6**). The  $S_A$  phase appears under the polarizing microscope with the well known fan-shaped texture. The  $S_B$  phase adopts a paramorphic fan-shaped

\* Author for correspondence.

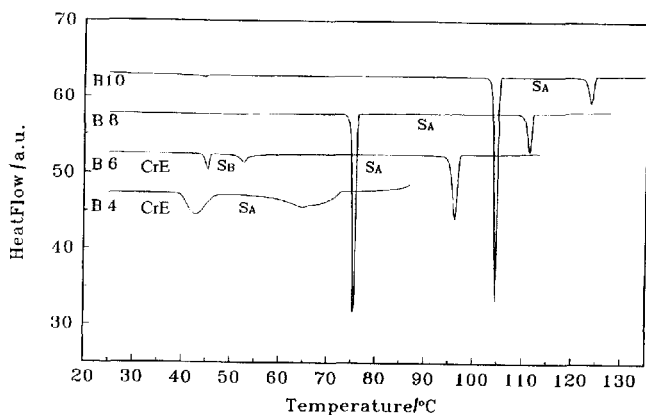
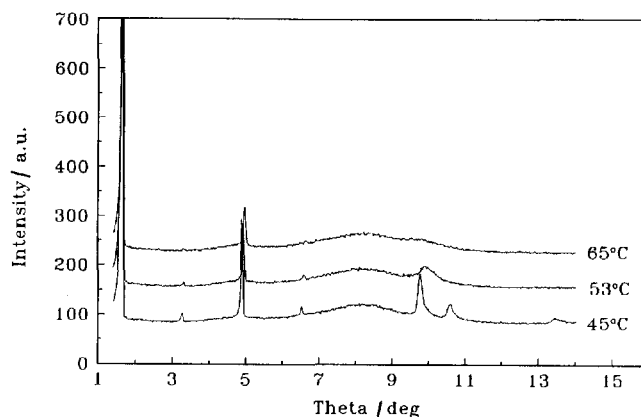
Table 1. Structural formulae, phase transition temperatures ( $^{\circ}\text{C}$ ) and code names.

		
Code	$n$	Transition scheme
<b>B4</b>	4	Cr 25 CrE 48 S <sub>A</sub> 68 I
<b>B6</b>	6	Cr 53 (CrE 50) S <sub>B</sub> 56 S <sub>A</sub> 100 I
<b>B8</b>	8	Cr 87 S <sub>A</sub> 115 I
<b>B10</b>	10	Cr 109 S <sub>A</sub> 128 I

texture, whereas the characteristic paramorphic fan-shaped texture with additional concentric arcs indicates the CrE phase [25]. The thermal behaviour is different for the compounds **B4/B6** and **B8/B10**, respectively; the DSC curves (figure 1) of the higher homologues display a distinct melting peak, whereas the lower homologues do not tend to crystallise.

The X-ray patterns of all the substances exhibit a strong reflection in the small angle region and its higher orders (figure 2), indicating the smectic layer structure. Dependent upon the phase under investigation, a broad diffuse scattering (S<sub>A</sub> phase), one strong narrow reflection (S<sub>B</sub> phase) or several reflections (CrE phase) can be observed in the wide angle range. The appearance of an additional diffuse scattering at a Bragg angle of about  $\theta \approx 8^{\circ}$  in the patterns of all the liquid crystalline phases is a peculiarity of the perfluorinated substances under investigation and will be discussed below.

The scattering diagram of the CrE phase (**B4**, **B6**) has been evaluated on the basis of an orthorhombic unit cell which is supported by the patterns of oriented samples. By slow cooling from the S<sub>A</sub> phase, a very well oriented monodomain of the CrE phase of compound **B4** has been obtained. The pattern shows the spot-like reflections of the layer periodicity and distinct maxima

Figure 1. DSC curves of the homologues **B4**, **B6**, **B8**, **B10**; heating rate  $10\text{ K min}^{-1}$ .Figure 2. X-ray diffraction patterns of compound **B6** in the CrE, S<sub>B</sub> and S<sub>A</sub> phases. The diagrams are shifted by 50 a.u. with respect to each other.

at the outer reflections (figure 3). The  $q_z$  component of the scattering vector ( $z$  is identical with the direction of the layer normal) is half of the scattering vector  $q(=q_z)$  of the layer reflection. The pattern points to an extinction of the reflections  $[(h0l): h+l=2n]$  leading to a doubling of the  $c$  parameter. The observed reflections, their indexing and the lattice parameters of the orthorhombic cell of the CrE phases are listed in table 2. In the case of **B6**, a monodomain of sufficient quality could not be obtained. Therefore conclusions concerning the extinction of the reflections cannot be given. The values listed for compound **B6** are calculated under the assumptions of the same packing found in **B4**.

The  $d$  values (thickness of the smectic layer) are nearly independent of the temperature, e.g.  $d$  increases by  $0.06\text{ nm}$  with decreasing temperature in case of compound **B6**.

Figure 4 presents the layer periods ( $d^A$ ) in the S<sub>A</sub> phase of the four homologues in comparison with the lengths of the molecules. It follows from figure 4 that  $d^A > L$ . The difference  $\Delta = d^A - L$  is a function of the length of the perfluorinated chain. These results point to a bilayer S<sub>A</sub> phase of the S<sub>Ad</sub> type constituted by dimers. The X-ray data suggest a model with antiparallel aligned molecules which are shifted with respect to each other so that the aromatic parts overlap. A model with overlapping perfluoroalkyl chains can be excluded, since in this case the difference  $\Delta$  should be independent of the length of the perfluorinated chain. This type of molecular arrangement leads to a smectic layer which is built up from sublayers consisting of perfluorinated chains and aromatic parts. This conclusion can be supported by a consideration of the packing density in both sublayers. The cross sections of two aromatic parts ( $2\delta_a$ ) correspond to that of one perfluorinated chain ( $\delta_F$ ). The difference between the two values in the present case

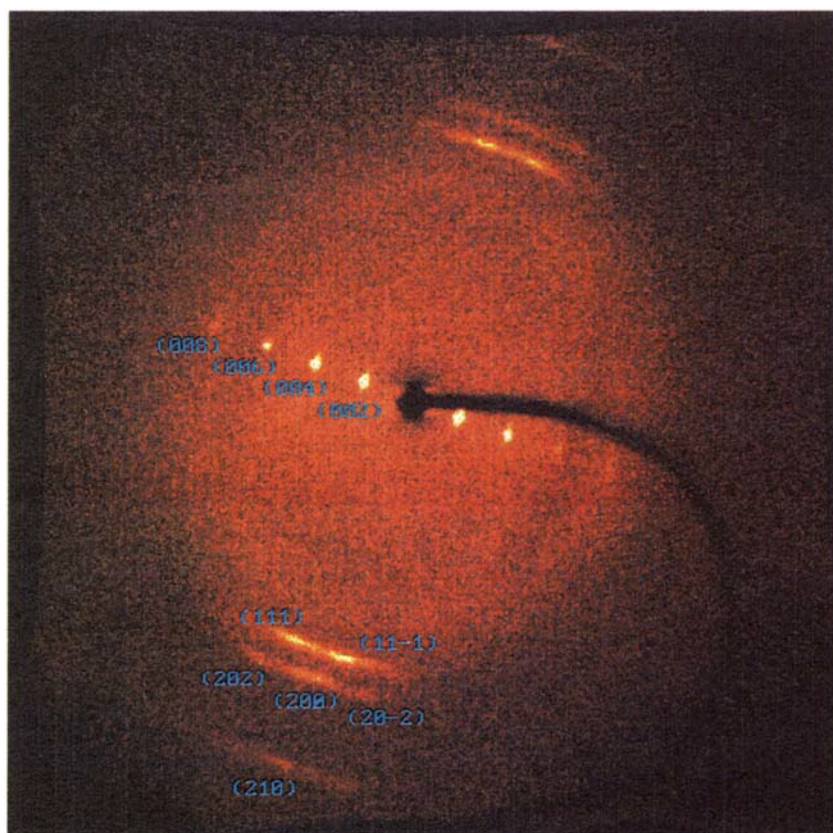


Figure 3. X-ray pattern of a monodomain (compound **B4**) of the CrE phase ( $T=40^{\circ}\text{C}$ ) together with the Miller indices.

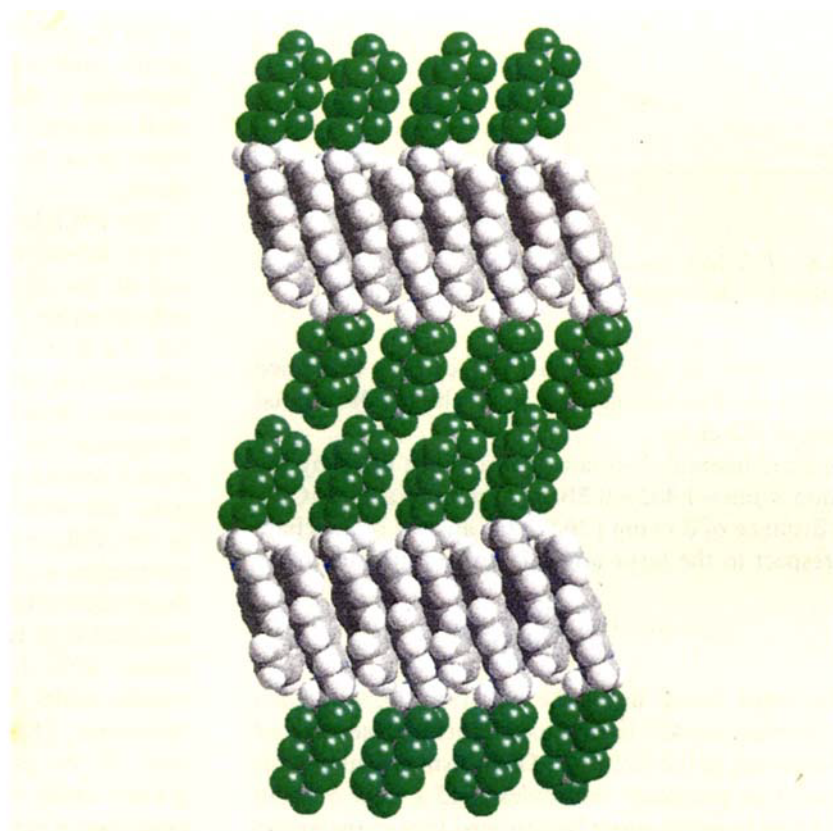
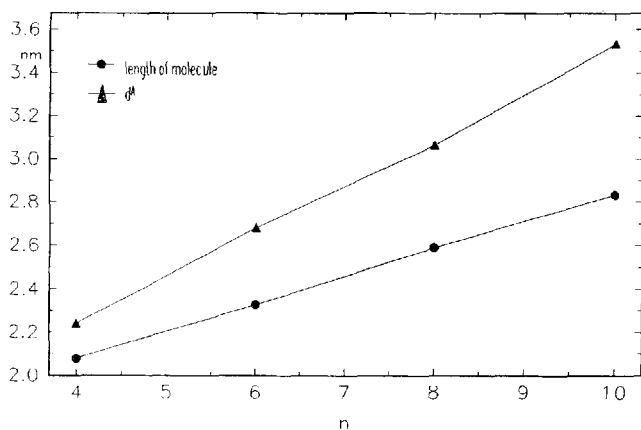


Figure 6. Schematic model of the  $S_A$  structure.

Table 2. Observed and calculated reflections, Miller indices and lattice parameter of the CrE phase.

Compound	<i>h k l</i>	$\theta_{\text{exp}}/^\circ\text{C}$	$\theta_{\text{calc}}/^\circ\text{C}$	<i>a</i> /nm	<i>b</i> /nm	<i>c</i> /nm
<b>B4</b>	002	1.94	—	0.834	0.542	4.55
	004	3.90	3.88			
	006	5.82	5.83			
	008	7.75	7.79			
	110	n.obs.	—			
	111	9.82	—			
	200	10.66	—			
	210	13.50	13.5			
<b>B6</b>	002	1.63	—	0.836	0.546	5.42
	004	3.26	3.26			
	006	4.88	4.90			
	008	6.52	6.53			
	110	n.obs.	—			
	111	9.75	—			
	200	10.63	—			
	210	13.48	13.43			

Figure 4.  $d^A$ -values and lengths  $L$  of the molecules as a function of the number  $n$  of fluorinated carbon atoms.

( $2\delta_a \approx 0.42 \text{ nm}^2$ ;  $\delta_F \approx 0.31 \text{ nm}^2$ ) [16] can be explained either by a tilt of the chains and/or by a highly disordered packing of the chains.

The experimental  $d$  values (figure 4) are fitted by the equation  $d/\text{nm} = 1.402 + 0.210n$ . Assuming a  $\text{F}_2\text{C}-\text{CF}_2$ -bond distance of  $0.13 \text{ nm}$  [26], a tilt angle  $\alpha$  of the chain with respect to the layer normal can be estimated to be

$$\alpha = \cos^{-1} \left( \frac{1}{2} \frac{0.21}{0.13} \right) = 36^\circ.$$

On the other hand, using the equation  $2\delta_a = \delta_F/\cos \alpha$  [19], a value  $\alpha = 42^\circ$  is obtained. These values exceed those reported in the literature. Dichroism measurements performed on polyphilic molecules yield a value  $\alpha$  about  $30^\circ$  [16]. It must therefore be assumed that in the model

presented here the chains are tilted as well as highly disordered in the sublayer. With respect to this point, the appearance of the additional scattering around  $\theta = 8^\circ$  which is found in all the smectic phases under discussion (even if the second diffuse scattering condenses) seems to be a fundamental result. In order to explain this scattering, both the outer scattering maxima in the  $S_A$  phase (figure 5) have been compared using a profile analysis. It can be seen that the first diffuse scattering is more and more enhanced if the number of perfluorinated C-atoms increases. Therefore this scattering must be caused by the disordered perfluorinated chains.

The FWHM of this scattering is nearly independent of the temperature. In the case of the compounds **B4** and **B6**, the second diffuse scattering condenses to Bragg reflections at the transition into the  $S_B$  or CrE phase, but the first diffuse scattering remains unchanged. In other words, whereas (with decreasing temperature) the aromatic moieties of the molecules are ordered in a hexagonal or orthorhombic cell, the perfluorinated chains remain disordered. That is only possible if both parts are separated from each other and are arranged in two different sublayers as shown in figure 6. Such a separation is proposed by Mahler *et al.* [12] for semi-fluorinated alkanes. But their fluorinated fragments are considered to be ordered in the hexagonal net of the  $S_B$  phase, with the hydrocarbon chains disordered. The results under discussion clearly point to a different behaviour. This can be explained by the fact that in the case of the alkanes, the fluorinated moiety has the greater cross section, whereas in the model discussed here (figure 6), the two aromatic parts of the molecular

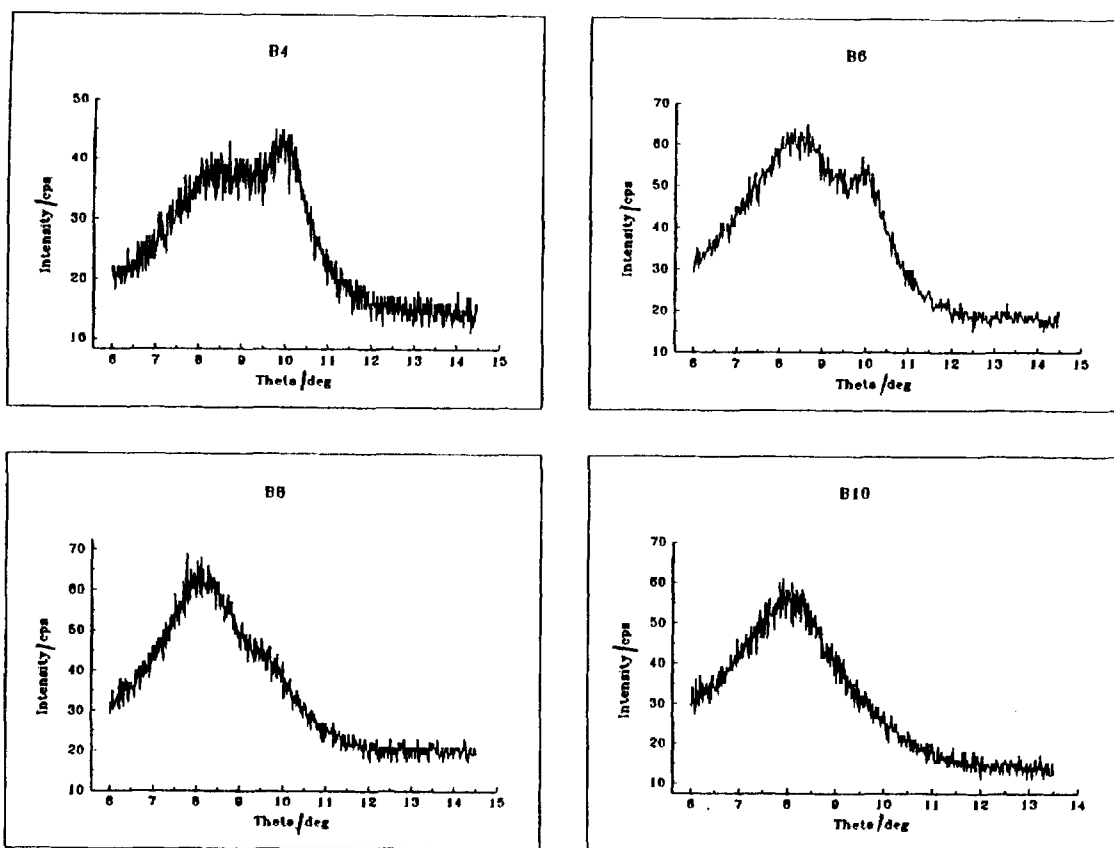


Figure 5. Intensity profile of the wide angle scattering in the  $S_A$  phase of the homologues **B4**, **B6**, **B8**, **B10**.

pair require the larger space. Therefore the steric interactions of the different molecular moieties strongly influence the ordering of these parts. Consequently, different structures of the smectic phases are obtained for compounds with different molecular architectures. The incompatibility of fluorinated and non-fluorinated parts does not necessarily lead to structural peculiarities. Monolayer  $S_A$  phases with antiparallel aligned molecules have been reported for semifluorinated alkanes [13, 14] or polyphelic compounds [16]. A transition of an  $S_{A1}$  into an  $S_{Ad}$  is reported in [27, 28]. By adding cyano groups  $S_{Ad}$  and  $S_{Cd}$  phases are observed [18]. In the case of terminally branched compounds, the packing determines the structure and yields  $S_{A1}$  phases [29]. However, if the perfluorinated part is enlarged in these compounds, undulated structures [7, 29] are observed as a result of a balance between the packing needs and the incompatibility of the different molecular parts.

#### 4. Summary

The results obtained prove the appearance of phases of the type  $S_A$ ,  $S_B$  and  $CrE$ . The layer thickness is found to be greater than the length of the molecule in each case, so that the designation  $S_{Ad}$  (and consequently  $S_{Bd}$

and  $CrE_d$ ) can be used by analogy with terminally polar substances [1, 2]. The layer structure of the phases consists of two sublayers which are built up from the fluorinated and non-fluorinated moieties of the molecules, respectively. The building units of both sublayers behave differently with decreasing temperature: whereas the fluorinated chains remain disordered until crystallization occurs, the aromatic parts of two homologues are arranged in a hexagonal or orthorhombic lattice. This different structural order of different parts of the molecules as a function of temperature is possible because of the local separation of the chemically incompatible moieties. In this respect, the behaviour resembles the microphase separation observed in liquid crystalline phases of diluted polysiloxane side chain polymers [30].

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