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Polymorphic smectic A phases in perfluoroalkylated mesogenic dimers

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New homologous symmetric dimers are presented in which two-ring monomers are connected by a flexible spacer and perfluorinated chains are introduced in terminal positions. The mesophase behaviour depends on the length and structure of the spacer and on the length of the terminal chains. The most interesting finding is the occurrence of dimorphic SmA phases in the longer chain homologues with odd-numbered spacer. The transition between the dimorphic SmA phases is accompanied by a relatively high enthalpy. Considering the results of XRD measurements and computer simulations, structural models are proposed, based on different conformations of the molecules.

1. Introduction

In terminally polar compounds the dipole–dipole interaction can give rise to the formation of different types of SmA phases; in some systems two or three polymorphic SmA phases occur [1, 2]. Recently, in compounds with pronounced steric asymmetry, different polymorphic SmA and SmC phases have also been reported [3]. On the other hand, non-symmetric dimeric compounds are able to form SmA phases of different types, depending on the length of the flexible spacer and on the length of the terminal chains [4, 5]; here the molecules have a considerably large dipole moment which results in the formation of intercalated and interdigitated structures. However, only in two cases were two SmA phases observed for the same substance [6, 7].

In this paper we present homologous symmetric dimers in which the two-ring monomers are connected by a flexible spacer and perfluoroalkyl chains are introduced in the terminal positions. It is known that due to chemical incompatibility, microsegregation of the perfluorinated chains and the hydrocarbon segments can occur, giving rise to some special features of the mesophase structure [8–11]. In addition, steric interactions were shown to play an important role in phase formation. In this work we have explored the effects of sterically and chemically different molecular units on the phase

behaviour and mesophase structure of the compounds under investigation. We will show that some of the compounds under investigation form polymorphic SmA phases. The spacings of the smectic layers in these compounds, being smaller than the molecular length and essentially larger than half of this, are incommensurable with the molecular length L . The results indicate the presence of relatively complex intercalated structures.

2. Experimental

The thermal behaviour of the homologous compounds was studied using polarizing optical microscopy (POM) (Leitz Orthoplan) or differential scanning calorimetry (DSC7, Perkin Elmer). The phase assignment was made by observation of the optical textures and from X-ray diffraction (XRD) patterns. Non-oriented powder samples were studied using the Guinier method, whereas measurements on oriented samples were performed using a diffractometer ($\lambda = 0.154$ nm) with 2D detector (HI-STAR, Siemens AG). Well developed monodomains of the mesophase were obtained by simple alignment on a glass plate; the incident beam was nearly parallel to the glass plate, and because of this geometry only the upper half of the reciprocal space could be observed, the lower part being shadowed by the glass plate.

For the proposed structural models, the intensities of the $00l$ Bragg reflections were calculated numerically and then compared with the experimental values. The

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intensities of Bragg reflections can be written in the form:

$$I(q_z) = \left| \int \rho(z) \exp(iq_z z) dz \right|^2 = F^2(q_z) S(q_z)$$

where

$$F(q_z) = \int \rho_c(z) \exp(iq_z z) dz$$

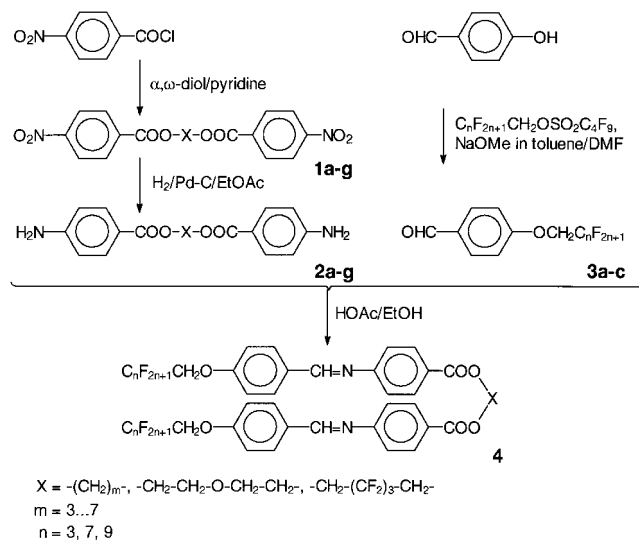
is the molecular form factor, q_z is the z -component of the scattering vector \mathbf{q} and $S(q_z)$ is the structure factor, which is determined by the symmetry of the lattice. Owing to thermal layer fluctuations, the intensities of Bragg reflections should be multiplied by the Debye–Waller factor, $f_{\text{DW}} = \exp(-\sigma^2 q^2)$, where $\sigma = \langle u(\mathbf{r})^2 \rangle$ is the mean squared deviation of the layer undulations from equilibrium positions.

Structural modelling was carried out using the Cerius35 Molecular Modelling software. Initial conformers created according to some assumptions about the structure were minimized by the Cerius35 software. Then a powder X-ray pattern was simulated. Since only SmA phases were observed, only $00l$ reflections were considered. The criteria of the model's validity were the correspondence of the Bragg reflection angles and the ratios of the intensities with our experimental data. These comparisons were mostly qualitative because not all effects and not all possible conformers were considered. However, in the case of our compounds, the relatively small changes of the molecular conformation did not lead to strong changes in the simulated X-ray powder pattern. Therefore, among our model we had to distinguish between principally different conformers; we did not need to know the very exact conformation. Mainly this allowed us to use the minimization methods for obtaining approximate bond lengths and bond angles and also some tendencies for conformer formation (for example the formation of a 'U-shaped' conformer).

3. Materials

The compounds were prepared by condensation of two parts of the appropriate 4-(1H,1H-perfluoroalkoxy)-benzaldehyde **3** with one part of the respective α,ω -alkylene bis(4-aminobenzoate) **2** in ethanolic solution containing acetic acid. The α,ω -alkylene bis(4-aminobenzoates) **2** were synthesized by esterification of 4-nitrobenzoyl chloride with the appropriate α,ω -alkylenediols in pyridine to give **1** and subsequent catalytic reduction. The 4-(1H,1H-perfluoroalkoxy)benzaldehydes **3** were produced by alkylation of 4-hydroxybenzaldehyde with the corresponding 1H,1H-perfluoroalkyl perfluorobutane-sulphonate. The final substances were recrystallized at

least four times from a DMF/ethanol mixture. The synthetic route is shown in the following reaction scheme, and typical preparations described in the following paragraphs.



3.1. α,ω -Alkylene bis(4-nitrobenzoates) **1a–g**

1,7-Heptylene bis(4-nitrobenzoate) (1e): 4-nitrobenzoyl chloride (7.42 g, 40 mmol) was added to a solution of 1,7-heptandiol (2.64 g, 20 mmol) in pyridine (50 ml) at room temperature. The temperature increased and the mixture was held under refluxing conditions for an additional 2 h. After cooling, the mixture was stirred into crushed ice (1000 g) and acidified with dilute HCl. The precipitate was separated, washed with H_2O and recrystallized from 2-propanol to afford 7.83 g (91%) of **1e** as pale yellow crystals. $^1\text{H NMR}$ (CDCl_3): $\delta = 1.46\text{--}1.83$ (m, 10H, $(\text{CH}_2)_5$), $\delta = 4.36$ (t, $J = 6.6$ Hz, 4H, $-\text{COOCH}_2-$), $\delta = 8.18$ (d, $J = 9.0$ Hz, 4H, aromatic H), $\delta = 8.27$ (d, $J = 9.0$ Hz, 4H, aromatic H). The other homologues and the derivatives **1f** and **1g** were prepared using a similar procedure; melting points are given in table 1.

Table 1. Melting points ($^\circ\text{C}$) of the intermediate compounds **1** and **2**. Many of the compounds show a wide variety of crystal modifications; the highest recorded temperature is given.

X	No. Compounds 1	No. Compounds 2
$(\text{CH}_2)_3$	1a	2a
$(\text{CH}_2)_4$	1b	2b
$(\text{CH}_2)_5$	1c	2c
$(\text{CH}_2)_6$	1d	2d
$(\text{CH}_2)_7$	1e	2e
$(\text{CH}_2)_2\text{O}(\text{CH}_2)_2$	1f	2f
$\text{CH}_2(\text{CF}_2)_3\text{CH}_2$	1g	2g

^a Commercial product (Aldrich).

1,5-(3-Oxapentylene) bis(4-nitrobenzoate) (**1f**): ^1H NMR (CDCl_3): $\delta = 3.88$ (t, $J = 4.9$ Hz, 4H, $\text{O}-\text{CH}_2-$), $\delta = 4.53$ (t, $J = 4.9$ Hz, 4H, $-\text{COO}-\text{CH}_2-$), $\delta = 8.13-8.24$ (m, 8H, aromatic H).

1,5-(1H,1H,5H,5H-Perfluoropentylene) bis(4-nitrobenzoate) (**1g**): ^1H NMR (CDCl_3): $\delta = 5.02$ (t, $J = 14.9$, 4H, $-\text{COOCH}_2\text{CF}_2-$), $\delta = 8.17-8.27$ (m, 8H, aromatic H).

3.2. α,ω -Alkyne bis(4-aminobenzoates) **2a-g**

1,7-Heptylene bis(4-aminobenzoates) (**2e**): **1e** (7.83 g, 1.82 mmol) was dissolved in ethyl acetate (200 ml) and hydrogenated at atmospheric pressure in the presence of 5% palladium on charcoal (0.5 g). After 1 h, four equivalents of hydrogen (1.7 l) were absorbed. The catalyst was removed by filtration, the ethyl acetate was evaporated and the crude product was recrystallized from ethanol to yield 6.65 g (98%) of **2e**. ^1H NMR (CDCl_3): $\delta = 1.42-1.76$ (m, 10H, $(\text{CH}_2)_5$), $\delta = 4.01$ (s, 4H, NH_2), $\delta = 4.24$ (t, $J = 6.5$ Hz, 4H, $-\text{COOCH}_2-$), $\delta = 6.62$ (d, $J = 8.6$ Hz, 4H, aromatic H), $\delta = 7.83$ (d, $J = 8.6$ Hz, 4H, aromatic H).

1,5-(3-Oxapentylene) bis(4-aminobenzoate) (**2f**): ^1H NMR ($[\text{D}_6]\text{DMSO}$): $\delta = 3.74$ (t, $J = 4.7$, 4H, $-\text{OCH}_2-$), $\delta = 4.23$ (t, $J = 4.7$, 4H, $-\text{COOCH}_2-$), $\delta = 5.95$ (s, 4H, $-\text{NH}_2$), $\delta = 6.54$ (d, $J = 8.6$ Hz, 4H, aromatic H), $\delta = 7.62$ (d, $J = 8.6$ Hz, 4H, aromatic H).

1,5-(1H,1H,5H,5H-Perfluoropentylene) bis(4-aminobenzoate) (**2g**): ^1H NMR ($[\text{D}_6]\text{DMSO}$): $\delta = 4.89$ (t, $J = 14.7$, 4H, $-\text{OCH}_2\text{CF}_2-$), $\delta = 6.15$ (s, 4H, $-\text{NH}_2$), $\delta = 6.58$ (d, $J = 8.6$ Hz, 4H, aromatic H), $\delta = 7.65$ (d, $J = 8.6$ Hz, 4H, aromatic H).

The melting temperatures of the amino compounds **2b-g** are given in table 1.

3.3 4-(1H,1H-Perfluoroalkoxy)benzaldehydes **3a-c**

4-(1H,1H-Perfluoro-octyloxy)benzaldehyde (**3b**): A solution of sodium methoxide (0.54 g, 10 mmol), 1H,1H-perfluoro-octyl perfluorobutanesulphonate (6.82 g, 10 mmol) and 4-hydroxybenzaldehyde (1.22 g, 10 mmol) in toluene/DMF (3:1, 50 ml) was stirred and heated under reflux for 2 days. The mixture was poured into H_2O (200 ml). The organic phase was separated and, after drying over anhydrous Na_2SO_4 , the solvents were removed under vacuum. The crude aldehyde was recrystallized from cyclohexane to give 3.85 g (76%) of **3b** as white crystals, m.p. 44–45°C. ^1H NMR (CDCl_3): $\delta = 4.54$ (t, $J = 12.7$ Hz, 2H, $-\text{CF}_2\text{CH}_2\text{O}-$), $\delta = 7.06$ (d, $J = 8.6$ Hz, 2H, aromatic H), $\delta = 7.87$ (d, $J = 8.6$ Hz, 2H, aromatic H), $\delta = 9.92$ (s, 1H, $-\text{CH}=\text{O}$).

The 4-(1H,1H-perfluorobutoxy)benzaldehyde **3a** was used as the oily raw material for the subsequent reaction. The melting point of 4-(1H,1H-perfluorodecyloxy)benzaldehyde **3c** is 66–68°C.

3.4. Schiff's bases **4**

1,7-Heptylene bis{4-[4-(1H,1H-perfluoro-octyloxy)-benzylideneamino]benzoate} **7/7**: Glacial acetic acid (1 ml) and **3b** (1.06 g, 2.1 mmol) were added to an ethanolic solution of **2e** (371 mg, 1 mmol, in 50 ml). By maintaining reflux conditions, crude **7/7** precipitated in pale yellow flakes. After 1 h, the reaction mixture was cooled and stirred for 24 h. The solids were removed by filtration and recrystallized four times from ethanol/DMF ($\sim 5:1$) to provide 205 mg (15.3%) of **7/7** as white scales. ^1H NMR (CDCl_3): $\delta = 1.48-1.78$ (m, 10H, $(\text{CH}_2)_5$), $\delta = 4.31$ (t, $J = 6.6$ Hz, 4H, $-\text{COOCH}_2-$), $\delta = 4.52$ (t, $J = 12.7$ Hz, 4H, $-\text{CF}_2\text{CH}_2\text{O}-$), $\delta = 7.00$ (d, $J = 8.8$ Hz, 4H, aromatic H), $\delta = 7.17$ (d, $J = 8.6$ Hz, 4H, aromatic H), $\delta = 7.87$ (d, $J = 8.8$ Hz, 4H, aromatic H), $\delta = 8.05$ (d, $J = 8.6$ Hz, 4H, aromatic H), $\delta = 8.35$ (s, 2H, $-\text{CH}=\text{N}-$).

The transition temperatures of all the compounds under investigation are included in tables 2 and 3.

4. Results

Table 2 presents the phase transition temperatures together with the transition enthalpies of the compounds studied; the results for the phase assignment are anticipated. In order to simplify the further discussion, we denote each compound as m/n , where n refers to the length of the perfluorinated chain and m refers to the length of the spacer. It is seen from table 2 that homologues with an odd-numbered spacer and relatively short terminal chains (**3/3**, **5/3**) form one SmA phase only. Corresponding compounds with relatively long terminal chains (**3/7**, **3/9**, **5/7**, **5/9**, **7/7**, **7/9**) form two smectic A phases: the high temperature SmA_H and the low temperature SmA_L phases. It is remarkable that the transition enthalpies SmA_L–SmA_H are relatively high and of the same order of magnitude as the clearing enthalpy (table 2). Compounds with even-numbered spacers exhibit simply a SmC–SmA polymorphism (**4/7**, **4/9**, **6/7**, **6/9**).

Table 3 shows the transition temperatures and enthalpies for the mesogenic dimers with modified alkyl spacers. It is seen that if the central methylene group is exchanged for an oxygen, the phase behaviour is not markedly changed, but the clearing temperatures are somewhat enhanced. Introduction of three CF_2 groups into the spacer decreases the clearing point of **5_f/7** in comparison with the analogous 1,5-pentamethylene linked compound **5/7**. However, the flexibility of the spacer is changed by these variations, and this influences the type of the smectic A phases.

4.1. Texture observations and assignment of phases

The SmA phases of the investigated compounds preferably form a homeotropic or a fan-shaped texture, figure 1(a). In some cases the fan-shaped texture could be obtained only by special treatment of the substrates.

Table 2. Phase behaviour and the transition temperatures (in °C) for compounds **4**. The transition enthalpies (kJ mol⁻¹) are in square brackets. SmA_L and SmA_H refer to low temperature and high temperature smectic A phases, respectively.

<i>m/n</i> ^a	Cr	SmX	SmC	SmA _L	SmA _H	I				
3/9	•	173 [46.1]	—	—	•	224 [12.0]	•	252 [4.9]	•	
4/9	•	190 [47.3]	—	•	232 [3.9]	—	•	271 [7.7]	•	
5/9	•	137 [36.7]	—	—	•	232 [5.8]	•	254 [5.9]	•	
6/9	•	171 [32.8]	—	•	205 [5.4]	—	•	252 [5.9]	•	
7/9	•	156 [42.7]	•	168 [3.6]	—	• ^(b)	170 [1.1]	•	238 [5.0]	•
3/7	•	146 [33.9]	—	—	•	224 [13.7]	•	236 [5.3]	•	
4/7	•	167 [38.6]	—	•	211 [2.1]	—	•	250 [10.0]	•	
5/7	•	99 [23.0]	—	—	•	233 [4.9]	•	238 [9.0]	•	
6/7	•	153 [34.2]	—	•	189 [5.2]	—	•	230 [8.7]	•	
7/7	•	130 [41.9]	—	—	•	159 [4.7]	•	210 [5.5]	•	
3/3	•	156 [15.9]	—	—	•	187 [17.7]	—	—	•	
5/3	•	132 [27.7]	—	—	•	182 [16.3]	—	—	•	

^a *m* = spacer length, *n* = length of the perfluorinated chain.

^b The low temperature SmA phase of compound **7/9** was found to be different from SmA_L.

Table 3. The phase behaviour of the compounds **4** with modified alkylene spacers.

<i>m/n</i> ^a	Cr	SmA _L	SmA _H	I			
5_F/9	•	172 [54.3]	—	•	207 [7.9]	•	
5_O/9	•	110 [41.0]	•	245 [7.6]	•	268 [8.2]	•
5_F/7	•	146 [42.4]	—	•	180 [7.3]	•	
5_O/7	•	113 [44.7]	•	249 [21.7]	—	•	
5_F/3	•	180 [50.5]	—	—	—	•	
5_O/3	•	139 [46.2]	•	200 [20.6]	—	•	

^a **5_O** = -CH₂-CH₂-O-CH₂-CH₂; **5_F** = -CH₂-CF₂-CF₂-CF₂-CH₂.

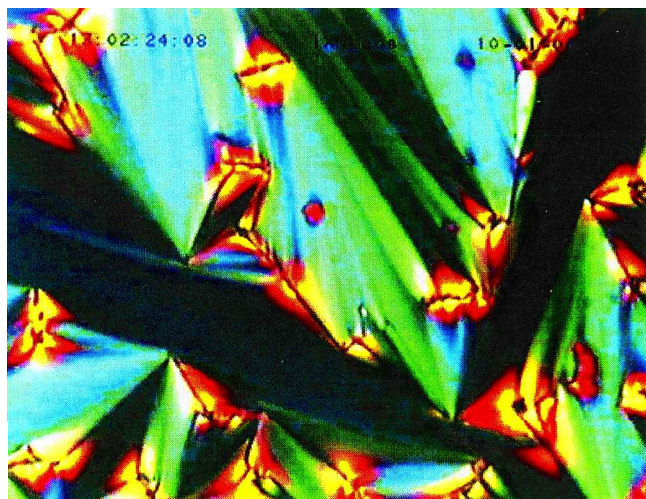
In the compounds with dimorphic SmA phases, the transition from the high temperature SmA_H phase into the low temperature SmA_L phase is indicated by a minor change in the double refraction. On further cooling, strings of some small elliptical domains appear, giving rise to an unusual fan-shaped texture, figure 1 (b). As can be seen from air bubbles within a microscopic preparation,

the transition SmA_H → SmA_L is accompanied by a discontinuous volume contraction. On the other hand, the transition between the two phases is clearly detected by DSC (figure 2).

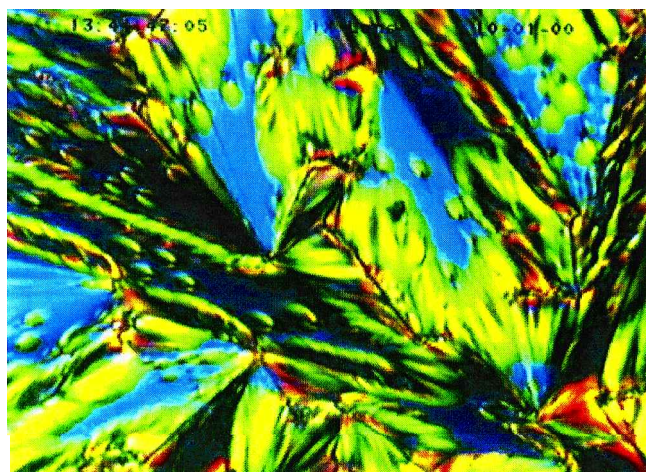
In the case of homologues with the short perfluorinated chains (**3/3** and **5/3**), the SmA phase preferably grows in the form of circular domains. In these domains the smectic layers are more or less perpendicular to the substrate and form circles around the centre of the domain. This is indicated by a black extinction cross which coincides with the direction of the crossed polarizers, figure 3 (a). On the other hand, unusual rosette-like textures also appear, figure 3 (b).

The compounds with an even-numbered spacer exhibit the polymorphism SmC–SmA. It is remarkable that the transition enthalpy is relatively high which points to the transition being of first order (table 2). The SmC phase of these compounds forms a characteristic schlieren texture or a broken fan-shaped texture.

Miscibility studies performed with compounds **6/7** and **7/7** revealed complete miscibility of the SmA phase of compound **6/7** (SmC–SmA) with the SmA_H phase of compound **7/7** figure 4 (a). In contrast miscibility investigations of compound **7/7** with **5/3** confirm the presence of the SmA_L phase for the compounds with short spacers (*m* = 3), figure 4 (b).



(a)



(b)

Figure 1. Textures of (a) the SmA_H and (b) the SmA_L phases (compound 5/9).

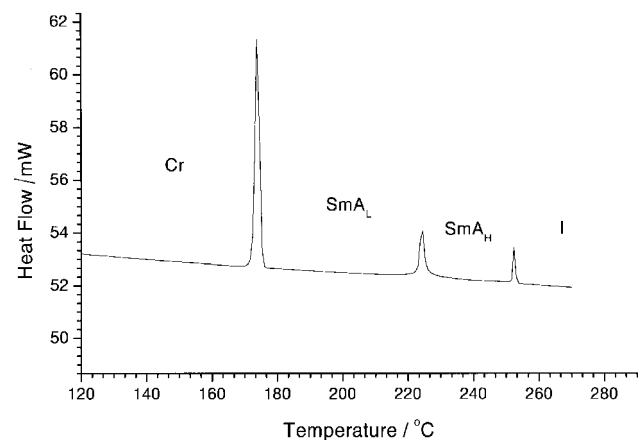
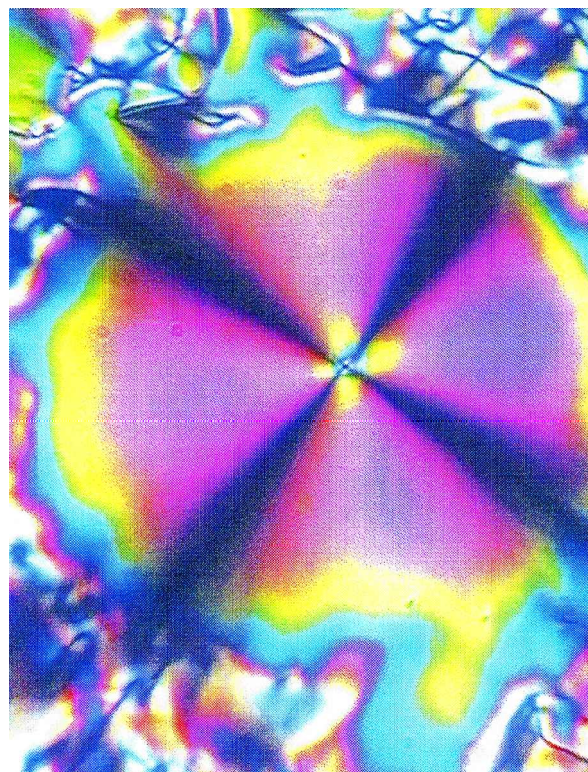
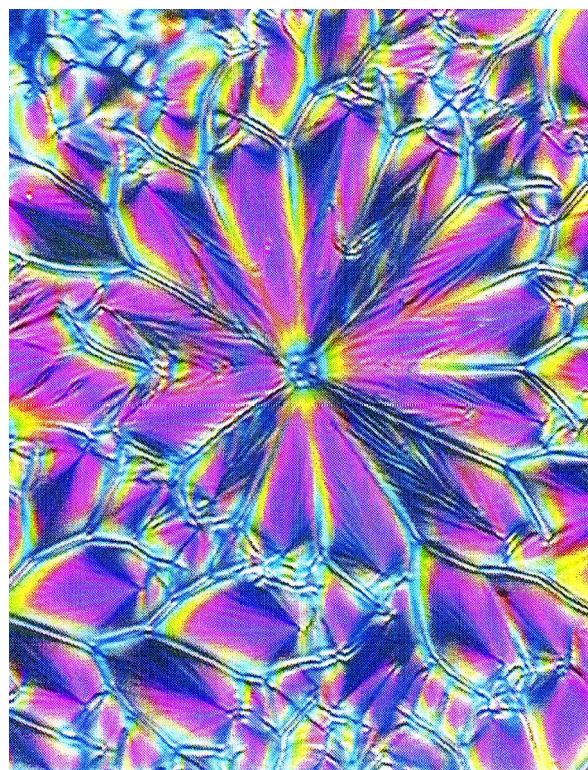


Figure 2. DSC curve for compound 3/9 showing the phase transitions indicated in table 2.

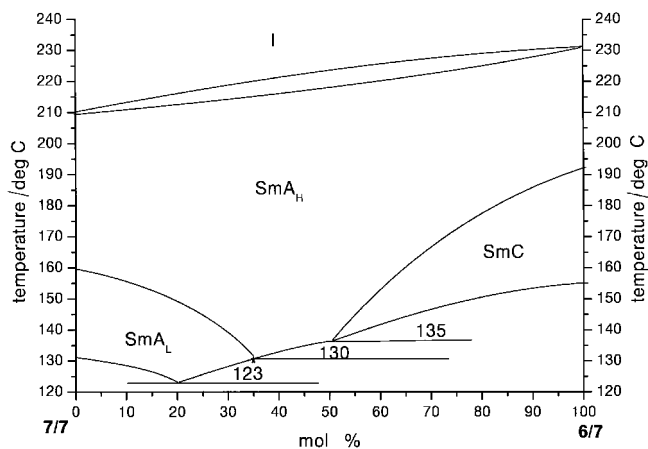


(a)

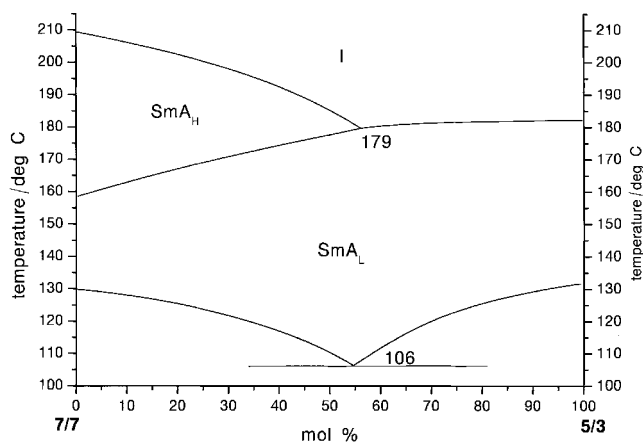


(b)

Figure 3. (a) Circular domain with an extinction cross and (b) rosette-like texture of the SmA_L phase of the compound 3/3.



(a)



(b)

Figure 4. Phase diagrams of mixtures of the compounds (a) 6/7 and 7/7, (b) 7/7 and 5/3.

The phase behaviour of compounds with modified spacers is not markedly changed in comparison with the compounds with an alkylene spacer. The spacers $-(\text{CH}_2)(\text{CF}_2)_3(\text{CH}_2)-$ and $-(\text{CH}_2)_2\text{O}(\text{CH}_2)_2-$ (denoted as $\mathbf{5}_F$ and $\mathbf{5}_O$, respectively) can be considered to be analogous of $-(\text{CH}_2)_5-$. According to the texture observations, the liquid crystalline phase of the compounds $\mathbf{5}_F/9$ and $\mathbf{5}_F/7$ was SmA_H . The compounds $\mathbf{5}_O/3$, $\mathbf{5}_O/7$ and $\mathbf{5}_O/9$ form SmA_L phases, and the compound $\mathbf{5}_O/9$ gives additionally an SmA_H phase.

On cooling the homeotropic SmA_L phase of the compound 7/9, an additional phase (designated SmX) appears. This phase forms circular and oval domains which coalesce to a weakly birefringent mosaic texture (figure 5). If the SmX phase arises from a fan-shaped texture, figure 6(a), the smooth fan-shaped texture is transformed into a kind of broken fan-shaped texture, figure 6(b).

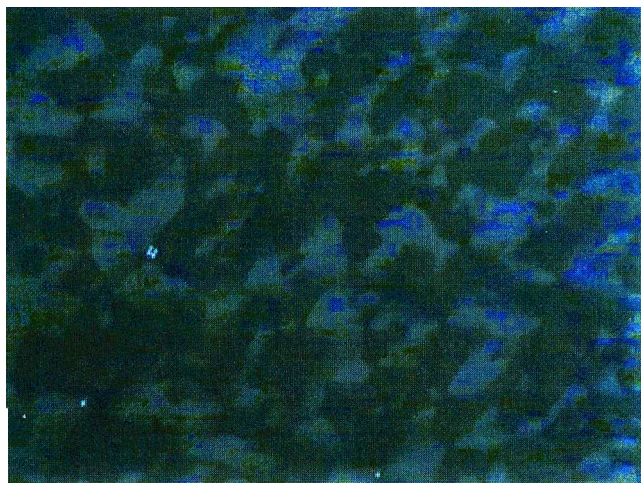


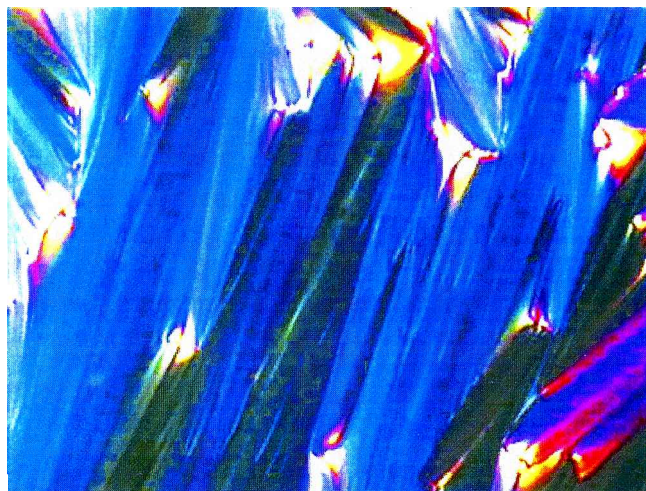
Figure 5. Weakly birefringent mosaic pattern of the SmX phase of compound 7/9.

It should be noted that the transition between the dimorphic SmA phases and also the transition $\text{SmX}-\text{SmA}_L$ are clearly detected by the calorimetric measurements (see the transition enthalpies in table 2).

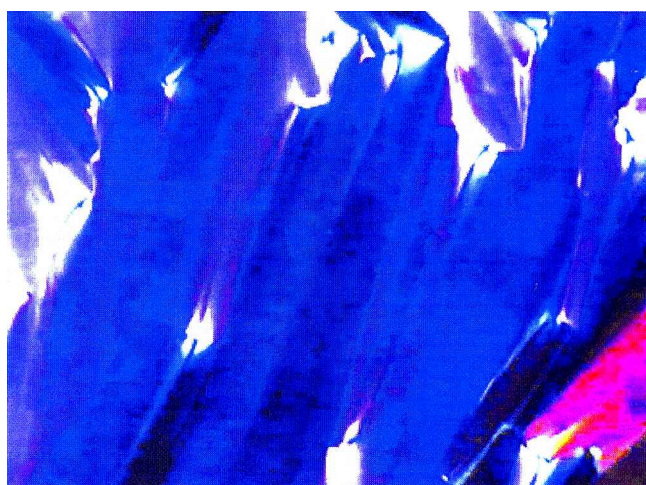
4.2. X-ray investigations

First we should emphasize that the XRD measurements were made difficult because of the relatively high temperature ranges of the smectic phases of most of the compounds studied. For this reason, only for selected materials were measurements on oriented samples possible. However, for all the compounds listed in tables 2 and 3, the layer spacing d could be determined by measurements on powder-like samples. It was found that the d values are nearly temperature-independent in the SmA phases. In table 4 the d values for all the compounds are presented, together with the molecular lengths L , which were obtained for the most stretched conformations of the molecules. Comparing the d values of the different compounds outlined in table 4 one can infer the following:

- (1) For a given spacer length m the d values increase with increasing terminal chain length.
- (2) Passing from the compounds with odd-numbered spacers to the compounds with even numbered spacers the d values significantly increase.
- (3) The d values for both SmA phases—the high temperature phase SmA_H and the low temperature phase SmA_L —are less than the molecular length L in the most stretched conformation, but clearly higher than half of the molecular length.
- (4) The d value of the SmA_H phase is higher by 0.4–0.8 nm than that of the SmA_L phase of the same substance. An exception is compound 7/9



(a)



(b)

Figure 6. Textures of (a) the SmA_H and (b) the SmX phase of compound 7/9.

where the d value of the SmA_L phase is somewhat higher than that of SmA_H.

- (5) Compound 7/9 exhibits three mesophases: two SmA and another liquid crystalline phase, designated SmX, which has an unusual X-ray pattern with some out of meridian reflections (figure 7).
- (6) Within the group of compounds with an odd-numbered spacer on the one hand and with an even numbered spacer on the other hand, the d values are nearly independent of the length of the spacer (except for compound 7/9).
- (7) The d values of the compounds with modified spacers (**5_O**, **5_F**) are not very different from those of the analogous compounds with alkylene spacers.

Table 4. The layer spacings (d) of the smectic phases of all the compounds under investigation, where L is the molecular length in the most stretched conformation.

m/n	d/nm			L/nm
	SmC	SmA _L	SmA _H	
3/9	—	3.74	4.14	5.8
4/9	4.50	—	4.73	5.9
5/9	—	3.61	4.16	6.0
6/9	4.50	—	4.95	6.1
7/9	—	5.24*	4.90	6.2
3/7	—	3.20	3.79	5.3
4/7	4.20	—	4.55	5.4
5/7	—	3.26	3.78	5.5
6/7	4.30	—	4.92	5.6
7/7	—	3.28	4.11	5.7
3/3	—	2.46	—	4.2
5/3	—	2.47	—	4.4
5 _F /9	—	—	4.36	6.0
5 _O /9	—	3.67	^a	6.0
5 _F /7	—	—	3.66	5.6
5 _O /7	—	3.27	—	5.6
5 _O /3	—	2.44	—	4.4

^a Could not be measured because of the high temperature range.

- (8) The transition from the high temperature SmA_H phase to the low temperature SmA_L phase is accompanied by a sudden increase in the number of $00l$ reflections (see figure 8).

5. Discussion

The interpretation of our results and further discussion of the structural models is mostly based on the earlier observed segregation tendencies of perfluoroalkylated moieties and the tendencies to intercalation of the aromatic parts of molecules. Another important point is the steric moment which the molecules possess due to the considerably large difference in cross-sections of the perfluorinated and aromatic parts. The fact that the layer spacings are essentially smaller than the molecular lengths L , and the absence of tilt of the molecules within the layers, point to an intercalated structure for the smectic phases.

To fit the experimentally observed layer spacings we considered two different molecular shapes: U-shaped and stretched form with different extents of overlapping. Our model calculations for the SmA_L phase indicated that only the U-shaped conformation, discussed earlier by other authors for mesogenic dimers [5, 12], yields a structure factor, with sufficiently high values at the positions of $00l$ reflections with $l=2, 3$ and 4, which corresponds to our experimental X-ray pattern in the low temperature SmA_L phase, figure 8(b).

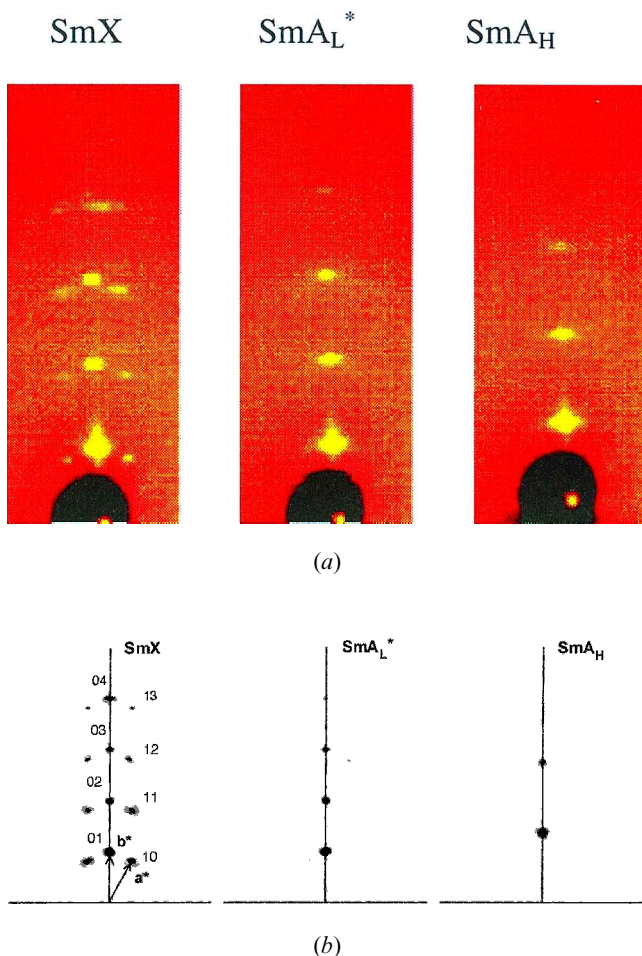
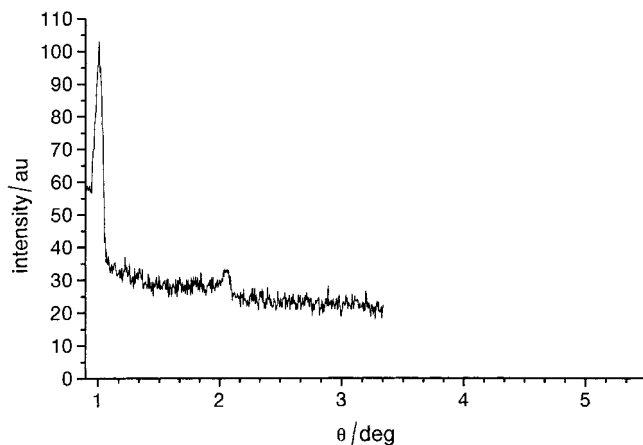


Figure 7. (a) Two dimensional X-ray patterns of surface oriented samples (SmA_H, SmA_L and SmX phases of the compound **7/9**); (b) schematic sketch of the same diagrams.

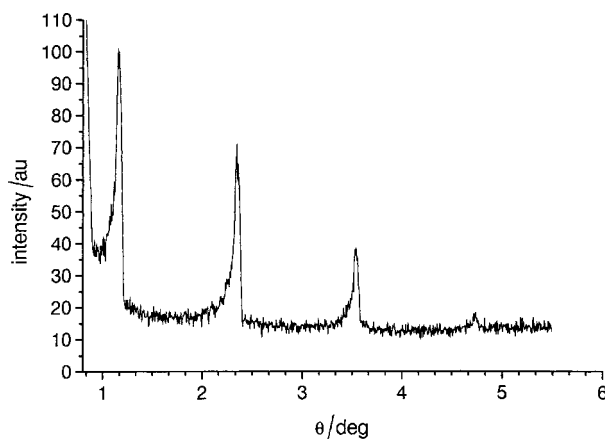
The model assumed for the SmA_L phase with a U-shaped conformation of the molecules is shown in figure 9. In this model the aromatic parts and the spacers of the adjacent antiparallel aligned molecules are overlapped. Then in the sub-layer of perfluorinated chains, two chains have to fill the area of the cross-sections of four aromatic moieties. The difference can be equalized by an average tilt of the chains of about 40–45° with respect to the aromatic parts. The d values in this model can be expressed in the form

$$d = a + 2L_f \cos \alpha + \varepsilon$$

where a (1.4 nm) is the length of the aromatic part of the monomer, L_f is the length of the perfluorinated chain, α is the tilt angle between the aromatic part and the perfluorinated chain (see figure 10), ε reflects a contribution of the spacer which is independent of its length and did not exceed ~ 0.4 nm in our experiments. The independence of the layer spacings on the length



(a)



(b)

Figure 8. X-ray powder pattern of the compound **3/9** (a) SmA_H (230°C) and (b) SmA_L (200°C).

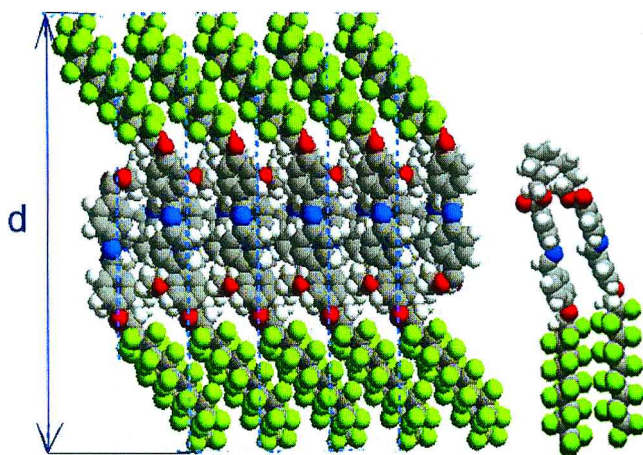


Figure 9. Structural model of the SmA_L phase.

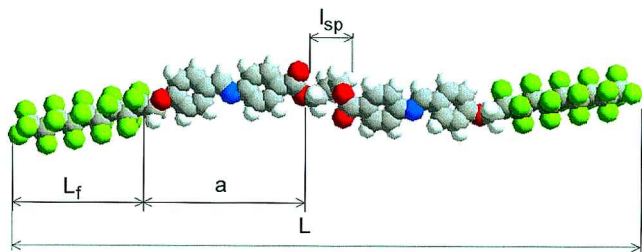


Figure 10. Scheme of the mesogenic dimer in its stretched conformation. (L = the molecular length, a = the length of the aromatic part, l_{sp} = the length of the spacer, L_f = the length of perfluorinated chain).

of the spacer for most compounds indicates that the spacer is bent and its projection on the molecular axis is small.

The d value of the SmA_L phase of compound **7/9** falls out of this sequence because it is found to be much greater. The higher proportion of aliphatic spacers in conjunction with the high proportion of perfluorinated chains could be the reason for this different behaviour. It prevents intercalation of the aromatic parts as assumed in the above-described model. Obviously, in this case the three parts of the molecule (perfluorinated chains, aromatic parts and aliphatic spacer) segregate in separated sub-layers (figure 11). Assuming the same (U-shaped)

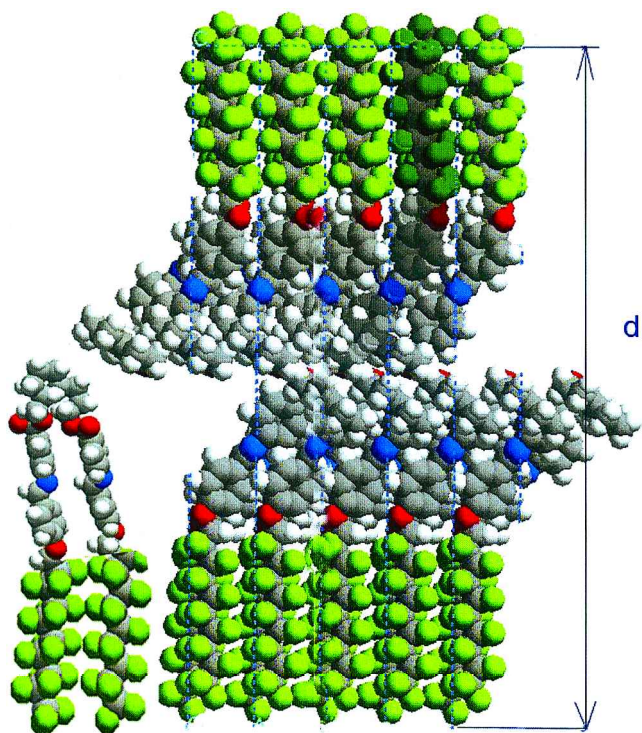


Figure 11. Structural model of the SmA_L* phase of the compound **7/9**.

molecular conformation as that discussed above, the d value can be expressed by

$$d = 2[(\varepsilon + a) \cos \alpha + L_f]$$

where ε is the contribution of the spacer and α is the tilt angle of the aromatic moieties with respect to the perfluorinated chains which are now parallel to the layer normal. The tilt angle, was estimated according to space filling conditions and was found to be about 45° . It could not be measured straight from the X-ray pattern because the maximum of the outer diffuse scattering is on the equator, giving an averaged orientation of the molecules along the layer normal. This structure is stable over only a small temperature interval. After that it passes over into the two-dimensional structure of the SmX phase.

During the transition to the SmX phase, the X-ray pattern of the SmA phase turns into the pattern of the SmX phase where some out of meridian satellite reflections appear (figure 7). However, having indexed them as $1k$ reflections on the basis of an oblique cell, we cannot observe $-1k$ reflections. To clarify the reasons behind these phenomena further research is required. As a preliminary suggestion it may be that $1-1k$ reflections are not seen because of their low intensity and the X-ray pattern itself corresponds to a superstructure with an oblique cell. Because the outer diffuse scattering maximum is on the equator, the molecules within the cells are oriented perpendicular to the a -axis. In order to prevent neighbouring lattice units being identical, we must assume that either the conformations or the positions of the two adjacent groups are different. One possible ordering is represented in figure 12. The cell parameters are $a = 11.62$ nm, $b = 5.42$ nm and $\gamma = 154^\circ$.

The model of the SmA_H phase deduced from our experimental data is much more speculative. In this case we have also observed a rather weak dependence of the d values on the length of the spacer for the compounds with an odd-numbered spacer (table 4) and the experimental d values for the SmA_H phase can be expressed in the form

$$d = 2a + L_f + \varepsilon$$

where a is the constant length of the aromatic part (see figure 10) and L_f is the length of the perfluorinated chain; ε is the contribution of the spacer which is assumed to be in a compact form, so that its projection on the molecular long axis is small. This kind of behaviour may result from intercalation of the terminal chains of the molecules in a stretched conformation, as shown in the structure model in figure 13.

It should be stressed that the transition enthalpies for SmA_L–SmA_H are comparatively high. Therefore, we can

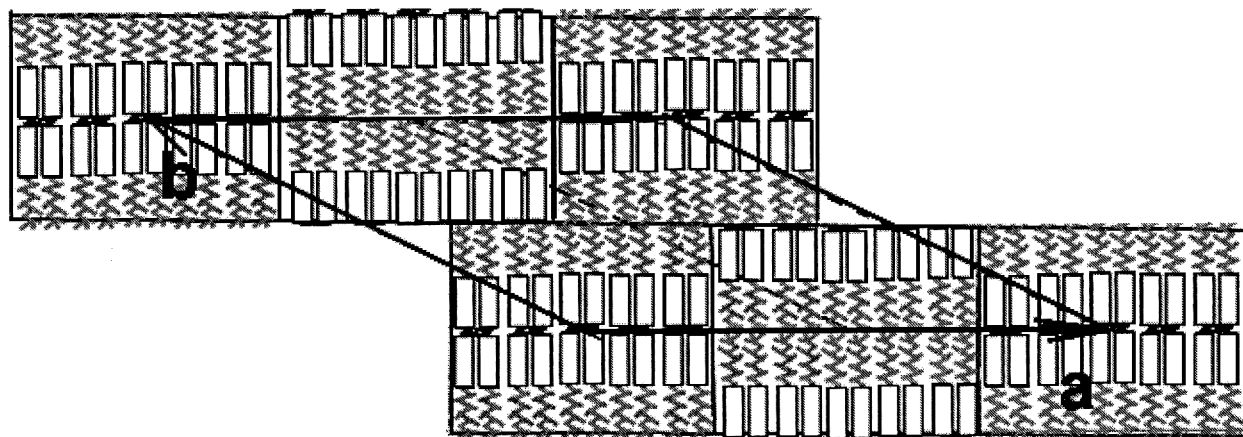


Figure 12. Possible two-dimensional arrangement of the molecules in the superstructure of the SmX-phase.

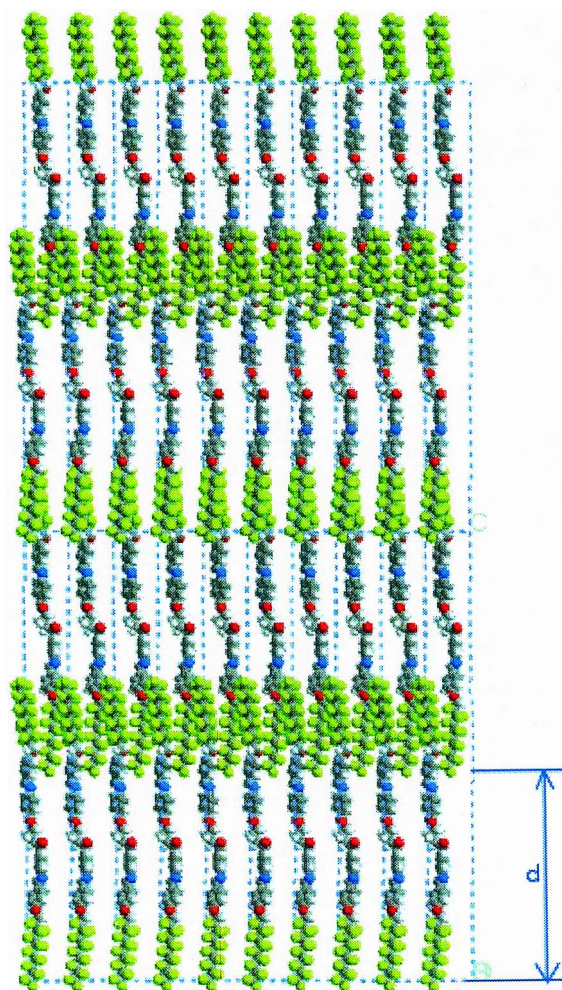
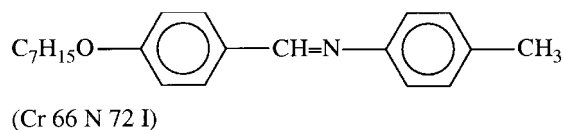


Figure 13. Structural model of the SmA_H phase.

assume that pronounced changes in the molecular shape take place. These changes are in accord with structure factor calculations which favour more a model with

stretched molecular shape and interdigitated chains (figure 13). But the agreement of the calculated intensities with those of only two observed $00l$ reflections cannot be regarded as support for the model. The intercalation of the perfluorinated chains results in a larger free volume in the aromatic sub-layer. Although this free volume difference can be partly equalized by the spacer packing, dense packing cannot be achieved in this model. On the other hand, miscibility studies also support the model. In the mixture of compound **7/7** with a two-ring mesogenic compound of short molecular length



the SmA_H phase is stabilized up to 80 mol% of the admixed compound.

Generally in binary mixtures of smectic A phases the d values behave additively, meaning that

$$d \approx x_1 d_1 + x_2 d_2$$

where x_1 , x_2 are the molar fractions of compounds 1 and 2; d_1 , d_2 are the layer spacings of the pure compounds 1 and 2, respectively. Therefore a linear decrease of d can be expected. In contrast the d values of the mixtures under investigation increase up to $d = 4.8$ nm (d value of the compound **7/7**: 4.1 nm) and remain constant over the whole existence range. A similar behaviour was found in mixtures with laterally branched compounds [13, 14] and is explained by filling out the gaps in the layers built up by the laterally branched molecules. The same process could occur in the case of the SmA_H phase. This would indicate that the aromatic sub-layers in the pure compound are regions of reduced density, which can be filled by the second compound.

6. Conclusions

Here we present for the first time the occurrence of polymorphic SmA phases for symmetric liquid crystalline dimers without terminal polar groups, but with perfluorinated terminal chains. For both SmA phases, the results of X-ray measurements indicate a layer structure with partial overlapping of the molecules which is strongly influenced by the tendency of the perfluorinated chains to segregate. The degree of overlapping is obviously the consequence of a subtle balance between different forces. Besides the van der Waals interaction, steric interaction on the one hand and the separation of chemically incompatible segments on the other are responsible for the structural features of the smectic phases.

On the basis of the experimental data, we have proposed a structural model of the SmA_L phase where the molecules adopt a U-shaped conformation and the aromatic parts are overlapped. For the SmA_H phase we propose a structural model with intercalated perfluorinated chains, but in this case the molecules are more or less stretched. The relatively large transition enthalpies SmA_H–SmA_L also suggest a pronounced change of molecular conformation at this transition. Furthermore, in the homologues with an even-numbered spacer, the SmA dimorphism disappears and the SmA_H and the SmC phases occur and give a phase transition which is also of first order. By introduction of an oxygen atom or three difluoromethylene groups into the spacer, the polarity as well as the flexibility of this connecting unit is changed. It is remarkable that, for example, in comparison with the pentamethylene connected compound **5/7**, which exhibits both the SmA_H and SmA_L phases, the oxygen-containing compound **5_O/7** exhibits only the SmA_L phase, whilst the compound **5_F/7**, with three difluoromethylene units in the spacer, exhibits the SmA_H phase. This can be regarded as support for the

proposed models, because the ethylene glycol fragments in **5_O/7** produce *gauche*-conformers and should therefore favour a U-shape for the molecules. In contrast, three difluoromethylene groups increase the stiffness of the connecting part, which should result in a more stretched conformation, which probably exists in the high temperature SmA_H phase.

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