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X-ray diffraction study of smectic A layering in terminally fluorinated liquid crystal materials

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We report an X-ray study of smectic A layering for mesogenic compounds with fluorinated substituents in terminal positions. The measurements were carried out using diffractometers with one- and two-coordinate proportional chambers. It was found that in contrast to $-CN$ or $-NO_2$ terminated smectics, the polar $-OCF_3$ compounds form only a monolayer smectic A_1 phase. The ratio of the intensity of the second harmonic to the first in smectic A phases formed by molecules with lengthy perfluorinated chains was found to be two orders of magnitude higher than is commonly reported for low molar mass thermotropic mesogens, indicating deviations of the density distribution function $\rho(z)$ from a pure sinusoidal form. The layer periodicity d for these mesogens exceeds the molecular length L: $d/L \simeq 1{\cdot}1$, which corresponds to a smectic A_d phase consisting of parallel or antiparallel dimers. We have observed that lateral fluorine substitution in the benzene ring adjacent to the perfluorinated chain leads to the disturbance of uniform smectic A layering and to the formation of a defect-modulated smectic A structure of a chequer-board type. For polyphilic compounds containing both hydrogenous and perfluorinated units in the terminal chain, the in-plane structure factor displays double-peaked liquid-like profiles indicating the existence of nearest-neighbour molecular stacking at different distances. The peculiarities of smectic A layering in fluorinated mesogens are discussed in terms of steric coupling and enhanced conformational rigidity of fluorine containing moieties.

1. Introduction

Recent studies of thermotropic liquid crystals display a remarkable sensitivity of smectic A layering to details of molecular architecture [1–3]. Among the factors exerting their influence on the structure of smectic layers, the most noticeable are the polar and sterical asymmetry of the constituent molecules. The polar asymmetry of mesogens is associated with the presence of permanent dipole moments at one of the ends of the molecule, as well as with differences in the number and the type of cyclic fragments or terminal groups of the molecules. The steric asymmetry is determined by the spatial configuration of the fragments of the molecular rigid cores as well as with the presence of the end groups of different nature. The difference in the flexibility of the terminal chains also affects the packing possibilities of molecules in the layers [4–5].

A variety of particular smectic A phases has been found to occur with the asymmetric molecules. In addition to the classical monolayer smectic A_1 phase in

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which the molecules are oriented randomly up and down within each layer and interlayer spacing d_1 is approximately equal to the molecular length L, there are also bilayer smectics A_2 having a period $d_2 \simeq 2L$, as well as partly bilayer smectics A_d whose layer spacing is incommensurate with the length of the individual molecules $d_2 \simeq L'$ ($L < L' < 2L$) [6,7]. Among terminally polar mesogens, the antiphase ($\tilde{A}$) and the ribbon phase ($\tilde{C}$) were detected in which a bilayer density wave is modulated in the plane of the layers [8,9]. Smectic A phases with incommensurate layering and two-dimensional (modulated) structures have also been found among non-polar compounds with a complicated spatial configuration [10–12].

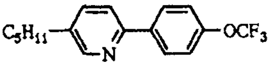
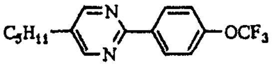
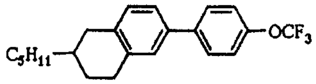
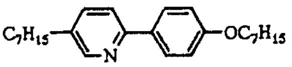
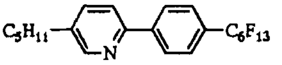
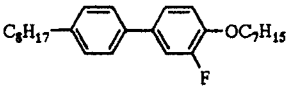
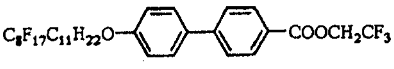
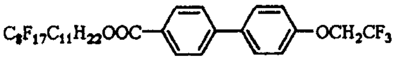
We can suggest different ways of imparting polar and sterical asymmetry to mesogenic units. One of the possible approaches in modifying the properties of smectic layers consists of the partial or total substitution of hydrogen atoms by fluorine atoms, that possess a larger van der Waals radius and electronegative properties, at one of the end fragments of the molecules [13–15]. Earlier work by several groups on mesogenic compounds with perfluoroalkyl (alkyloxy) tails indicated that smectic mesophases are usually enhanced [13–17]. However, the effects of fluorination, that leads to a large terminal dipole moment, as well as to conformational rigidity of alkyl chains, on the structure of smectic A layers have not been examined in detail. Mesogens incorporating fluorine atoms frequently show interesting characteristics for display devices, including ferroelectric liquid crystal device applications and their development is currently of great interest [18–20]. An additional interest in mesogenic molecules containing perfluorinated chains is generated by the recent observation of ferroelectricity for a new class of non-chiral mesogens, the so-called polyphilic compounds [21,22].

Here we present X-ray studies of smectic A layering for mesogenic compounds differing in the structure and the length of perfluorinated terminal chains. X-ray diffraction directly probes the smectic layering by measuring the Fourier transform of the density wave along the normal to the layers. X-ray patterns in low molar mass thermotropic mesogens usually display only the lowest order reflection (001) resulting from the smectic A layering. The intensity of the second order reflection (002) is three to four orders of magnitude less [23–27]. This is in sharp contrast to lyotropic lamellar liquid crystals [28,29] and high molar mass smectics A [30], where higher harmonics may be quite intense. In this sense, low molar mass thermotropic smectics A are as a rule essentially 'soft' layered systems, with a nearly sinusoidal density wave $\rho(z)$. Our X-ray data indicate that the packing of molecules in smectic layers becomes more rigid for mesogens with perfluorinated terminal chains, resulting in deviation of the density distribution function $\rho(z)$ from a pure sinusoidal form. The layer periodicity in these cases exceeds the molecular length L: $d/L \simeq 1{\cdot}05$–$1{\cdot}10$, which corresponds to the formation of the smectic A_d phase, consisting of parallel or antiparallel dimers. In other cases, the formation of strongly defective layers with an alternating packing of central cores and perfluorinated chains has been observed.

2. Experimental technique

The molecular structure and phase sequences of the perfluorinated compounds under study are shown in table 1. The space-filling models for two molecules are presented in figure 1. Note that the last two mesogens in table 1 belong to a new class of liquid crystalline substances—polyphylic compounds which were reported to be achiral mesomorphic ferroelectrics in their low temperature smectic X, X′ phases [22]. The transition temperatures (°C) were determined using the characteristic features of X-ray diffraction patterns and by optical microscopy.

Table 1. Structural formulae, phase transition temperatures (°C), molecular length L, layer thickness d and intensity ratio I_{002}/I_{001} in the smectic A, A_d phases for the compounds investigated.

N	Structural formula and abbreviation	Phase sequence	L/Å	d/Å	$\frac{I_{002}}{I_{001}}$
1	 1Py5OF	$C \xleftrightarrow{23} S_B \xleftrightarrow{37} A_1 \xleftrightarrow{51\cdot7} I$	19·2	18·7 (A_1) 19·2 (S_B)	0·011
2	 Pyr5OF	$C \xleftrightarrow{30} A_1 \xleftrightarrow{44\cdot5} I$	19·2	18·6	$\leqslant 0\cdot003$
3	 5F3O5CHB	$C \xleftrightarrow{54} A_1 \xleftrightarrow{63} I$	21·2	20·5	0·015
4	 1Py7OF7	$C \xleftrightarrow{76} A_d \xleftrightarrow{113} I$	26·8	28 (T = 110°C) 28·7 (T = 80°C)	0·09
5	 1Py5F6	$C \xrightarrow{<20} S_B \xrightarrow{81\cdot5} I$ $S_B \xleftarrow{70\cdot2} A_d \xleftarrow{76\cdot5} I$	22·5	23·9	0·10
6	 PF7OF8B	$C \xleftrightarrow{53} \tilde{A}_1 \xleftrightarrow{64\cdot2} I$	28	14	
7		$\begin{tikzcd} C \arrow[r, "96"] & A_d \arrow[r, leftrightarrow, "113"] \arrow[d, dash] & I \\ {} & S_X \arrow[l, "88"'] \end{tikzcd}$	40·5 –42·5	44	0·15
8					
	M70 (7 : 8 = 70% : 30%)	$\leftarrow Sm_{X'} \underset{84}{\overset{87}{\rightleftarrows}} A_d \xleftrightarrow{106} I$	40·5 –42·5	43·5	0·15

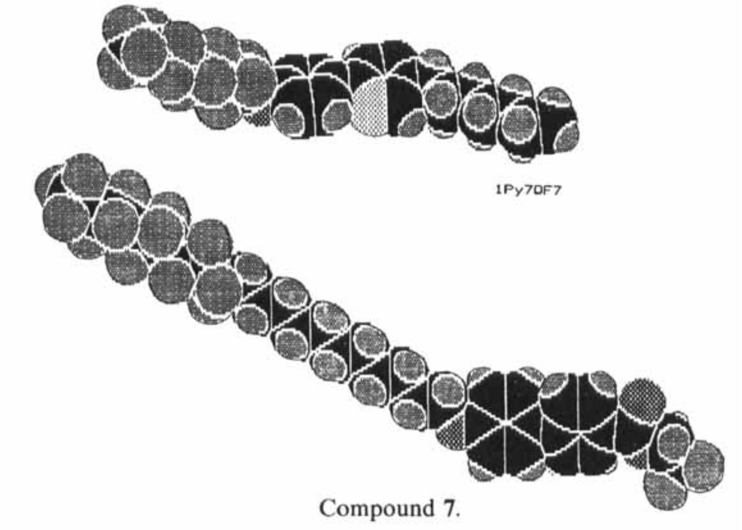


Figure 1. Molecular models of perfluorinated 1Py7OF7 and polyphilic compound **7**.

X-ray investigations were carried out using Cu–K_α radiation and two types of computer controlled diffractometers. The first set-up includes a three slit collimation scheme with a nickel filter or graphite monochromator and a linear position-sensitive detector for data collection [31]. The longitudinal resolution so obtained was $\Delta q_{\parallel}=2\times10^{-3}\,\text{Å}^{-1}$ full width at half maximum (FWHM). The components of the scattering wavevector $q_{\parallel}$ and $q_{\perp}$ are parallel and perpendicular to the director **n**, respectively ($q=(4\pi/\lambda)\sin\theta$). Thus, measurements of the longitudinal correlation lengths were limited to $\xi_{\parallel}=2/\Delta q_{\parallel}\approx900\,\text{Å}$. The transverse out of plane resolution was determined by the illuminated sample height of 4 mm to be $0{\cdot}04\,\text{Å}^{-1}$ (FWHM). The actual width of profiles in the $q_{\perp}$ direction was limited by the sample mosaic. In our data analysis, peak shapes were modelled by lorentzian line shapes, yielding peak intensity, position and width.

The out of plane reflections and wide angle scattering region were studied using a KARD diffractometer with a two-coordinate detector and point collimation of the incident radiation [32]. The detector is based on a planar proportional chamber with fast delay lines and has 256×256 channels of size $1{\cdot}3\times1{\cdot}3$ mm (FWHM). With the sample–detector distance of 800 mm the resolution $\Delta q\simeq10^{-2}\,\text{Å}^{-1}$ was achieved. Intensities in each channel were measured in one scale, i.e. space angle and non-uniformity of efficiency were taken into account. The mean non-uniformity in any point did not exceed 0·6 per cent.

The absence of the nematic phase in compounds **1–8** (see table 1) presents a major problem for the effective orientation of the liquid crystalline director. We have used two different techniques to achieve a uniform alignment of samples. In the first, mesogens in thin-walled quartz capillaries of 2 mm diameter were cooled down from the isotropic phase in an applied magnetic field of 1·2 T providing a mosaicity of the order of 10° (FWHM). The second method utilized the tendency of mesogenic molecules with terminally polar (fluorinated) groups to form homeotropically aligned films on clean, polished substrates [33]. In our experiments, oriented films of thickness 10–100 μm were obtained by insertion of the substance between two thick, polished beryllium plates. On cooling down from the isotropic phase, this forms spontaneously oriented films in which the molecular planes lie parallel to the substrate surface. The mosaicity thus obtained was typically about 1–2° (FWHM).

3. Experimental results and interpretation

Let us start with a description of the types of layering for the compounds **1–3** (see table 1). These compounds are analogues of cyano-substituted pyridines (pyrimidines) and possess a fairly large longitudinal terminal dipole moments ($\mu \simeq 2$–3 D [34, 35]). In contrast to the cyano-derivatives, we have detected in compounds **1–3** only a monolayer A_1 phase with an interlayer spacing d_1 which is, as usual, slightly less than the molecular length L ($L-d_1 \simeq 0{\cdot}5$–1 Å). An analysis of the X-ray diffraction spectrum in the small angle region indicates that even on the level of fluctuations, there were no signs of any dimeric type of layering. X-ray diffraction studies of the fluorine-substituted pyridines 1Py7OF7 and 1Py5F6 (see table 1) containing seven and six carbon atoms in the perfluorinated chains respectively, reveal marked changes in the character of the smectic A layering. Thus, the interlayer spacing exceeds the molecular length: $d/L \simeq 1{\cdot}05$–$1{\cdot}10$. Dependent upon the temperature, this corresponds to the formation of an A_d phase in which the molecules are shifted relative to one another over a distance of 1–2 Å in a parallel or antiparallel configuration. The diffraction patterns for these compounds display up to three orders of resolution-limited peaks $\mathbf{q}_n = (0; 0; nq_{\parallel 0})$ resulting from the smectic A order ($q_{\parallel 0} = 2\pi/d$; $n = 1$–3). The ratio of the second harmonic intensity to the first is $I(2\mathbf{q}_0)/I(\mathbf{q}_0) \approx 10^{-1}$, that is two orders of magnitude higher than in conventional smectic A phases. The intensity of the third harmonic amounts to about 10^{-3} of the first. Similarly to 1Py7OF7 and 1Py5F6, the high temperature smectic phases in the polyphilic compounds **7** and **8** and mixture M70 (see table 1) show Bragg-like peaks at wavevector $\mathbf{q}_n = (0; 0; nq_{\parallel 0})$; $n = 1$–3, corresponding to a smectic A_d layered structure with spacing $d = 2\pi/q_{\parallel 0} \approx 43$–44 Å ($d/L \approx 1{\cdot}05$).

The in-plane X-ray scattering data display interesting features of positional order for these compounds. We show in figure 2 a scan in the smectic A_d phase for polyphilic mixture M70 with the diffraction vector along $q_\perp$ (parallel to the layers) which probes intermolecular correlations in the plane of the smectic layers. The $q_\perp$ scans in perfluorinated compounds 1–6 (see table 1) show, similarly to conventional smectic A phases [25, 3, 36], a broad, liquid-like peak centred at $q_{\perp 0} \approx 1{\cdot}4$ Å^{-1} corresponding to an average intermolecular distance of 4·5–5 Å in the smectic plane, with intermolecular correlation lengths of $\xi_\perp \leqslant 16$ Å. The situation is quite different in the case of polyphilic compounds where the perfluorinated unit is effectively decoupled from the rigid core via a flexible hydrocarbon spacer. The in-plane scattering in these compounds is clearly not single peaked, indicating the existence of two different nearest-neighbour distances. In figure 2, the solid line through the data is the result of a least-squares fit of a sum of two lorentzians:

$$I = \sum_{i=1,2} I_i/1 + \xi^2_{\perp_i}(q_\perp - q_{\perp_i})^2$$

centred at $q_{\perp_1} \approx 1{\cdot}21$ Å^{-1} and $q_{\perp_2} = 1{\cdot}43$ Å^{-1} with in-plane correlation lengths $\xi_{\perp_1} \approx 12$ Å and $\xi_{\perp_2} \approx 17$ Å ($T = 94$°C). The first peak at $q_{\perp_1} = 2\pi/d_1$ ($d_1 \approx 5{\cdot}2$ Å) is due to the liquid structure of the rotationally averaged molecules as a whole, including aromatic core and perfluorinated chains, while the second peak at $q_{\perp_2} = 2\pi/d_2$, $d_2 \approx 4{\cdot}5$ Å most likely arises from short range correlations ($\xi_{\perp_2} \sim 3$ to 4 molecules) of the

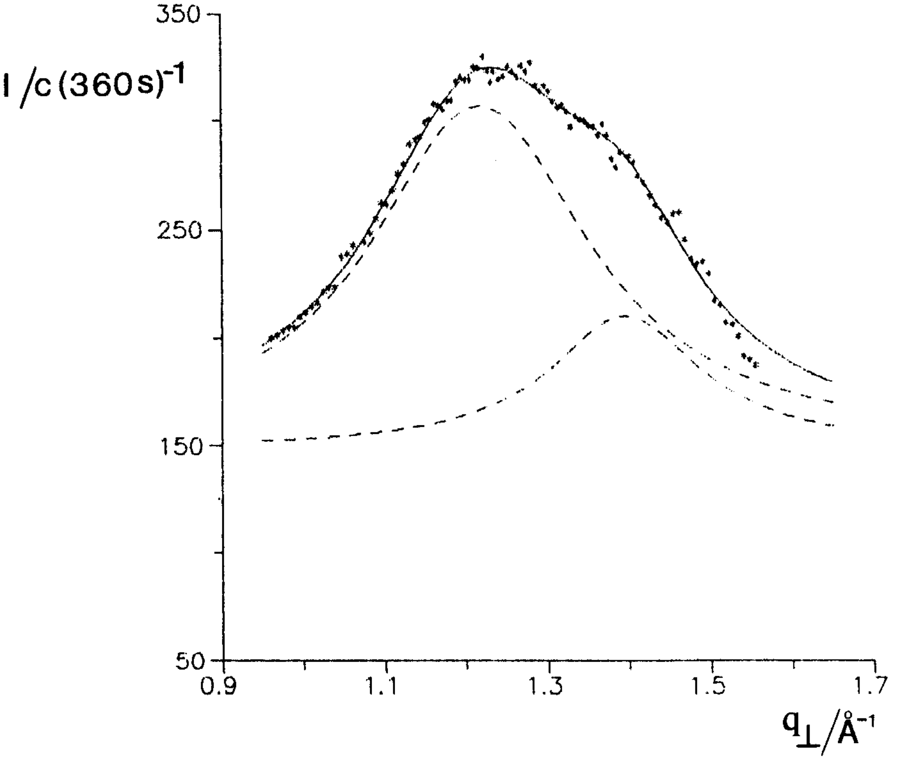


Figure 2. X-ray intensity profile (counts per 360 s), with diffraction vector along $q_\perp$ (in the plane of layers) for the polyphilic mixture M70 in the smectic A_d phase at 93°C. The solid line through the data points is the sum of two lorentzian peaks (described in the text) which are shown by broken curves.

flexible alkyl chains. Note, that different mean intralayer distances are only possible in a liquid-like in-plane structure formed by molecules with flexible moieties.†

The lateral substitution of fluorine for hydrogen in the benzene ring adjacent to the perfluorinated chain in compound PF7OF8B (see table 1) radically changes the type of smectic A layering. X-ray diffraction patterns of oriented samples of PF7O8B in the smectic phase display a scattering peak at wavevector $\mathbf{q}_2 = (0; 0; 2q_{\|0})$ corresponding to periodicity $d = 2\pi/\mathbf{q}_2 \approx L/2$ and diffuse off-axis spots at reciprocal space points $\mathbf{q} = (\pm q_{\perp 0}; 0; q_{\|0})$, $q_{\|0} = 0{\cdot}23\,\text{Å}^{-1}$; $q_{\perp 0} \approx 0{\cdot}13\,\text{Å}^{-1}$, see figure 3. In fact, these off-axis spots originate from the ring of scattering with wavevector $\tilde{\mathbf{q}} = (q_{\|0}\cos\phi;\ q_{\perp 0}\sin\phi;\ q_{\|0})$ located in the reciprocal plane $(0;\ 0;\ q_{\|0})$ (ϕ is an azimuthal angle, $0 \leqslant \phi \leqslant 2\pi$). The angular width of the diffraction peak $\mathbf{q}_2$ slightly exceeds the instrumental resolution of our diffractometer which corresponds to a correlation length in the direction parallel to the director $\xi_{\|2} = 2/\Delta q_{\|2} \leqslant 800\,\text{Å}$. The diffuse spots at the wavevector $\tilde{\mathbf{q}}$ are due to scattering from the fluctuations of a monolayer smectic density wave modulated in the plane of the layers. The period of modulation $a = 2\pi/q_{\perp 0} \approx 50\,\text{Å}$ corresponds to a group of approximately ten molecules in a layer. The correlation length corresponding to that

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† A detailed description of smectic A layering both in smectic A_d and low temperature polar smectic X phases for polyphilic compound **7** and mixture M70 is presented in [37].

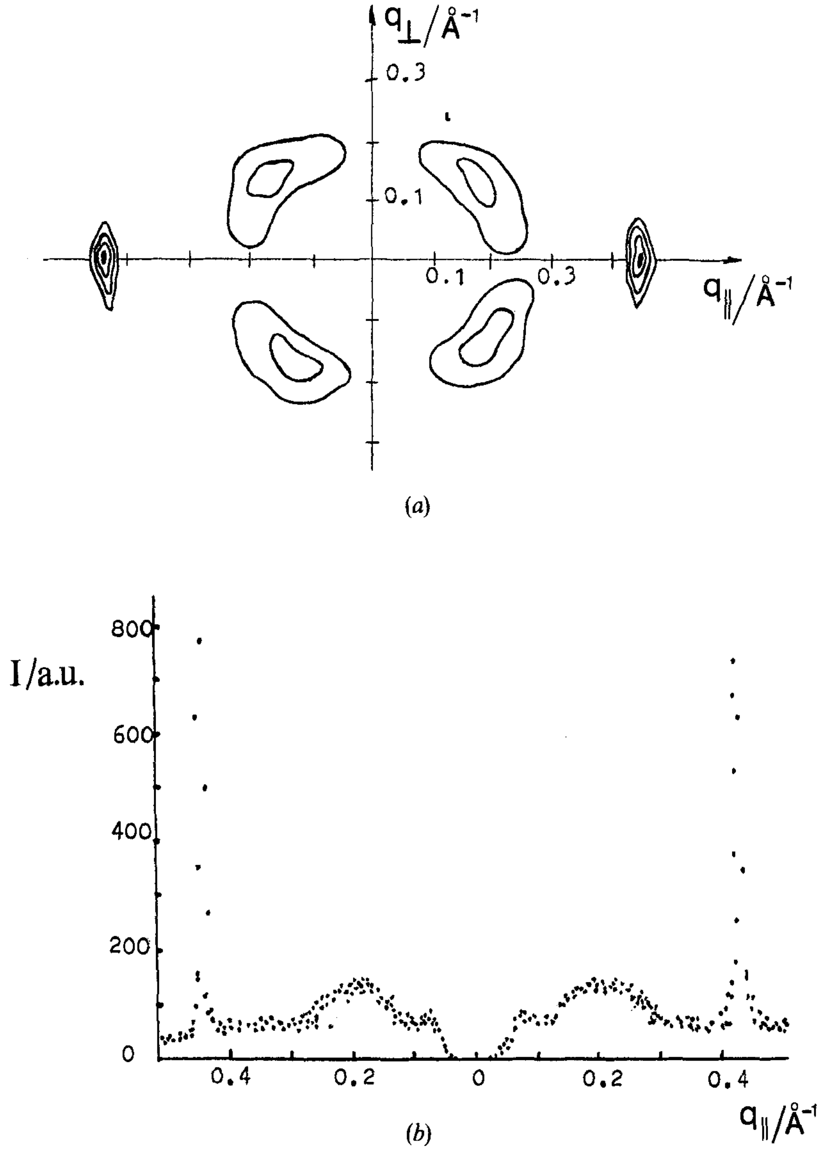


Figure 3. (*a*) The intensity contours of X-ray small-angle scattering in the $q_{\parallel}$–$q_{\perp}$ plane for the smectic $\tilde{A}_1$ phase of PF7OF8B. (*b*) The intensity profiles with diffraction vector along $q_{\parallel}$.

type of periodicity is determined from the angular width of the $\tilde{q}$ peaks: $\xi = 2/\Delta\tilde{q}$ and is also about $\xi \approx 50$ Å. The appropriate structural model of the smectic A phase in PF7OF8B is represented in figure 4. In accordance with a model, the regions of monolayers are shifted relative to one another by a half of the molecular length, thereby forming an alternating structure of a chequerboard type. Taking into account the diffuse character of the modulation peaks, one can conclude that in the case of perfluorinated compound PF7OF8B we have to deal with a strongly defective modulated structure of the type smectic $\tilde{A}_1$, where the positions of the areas of shifted layers are not correlated in space.

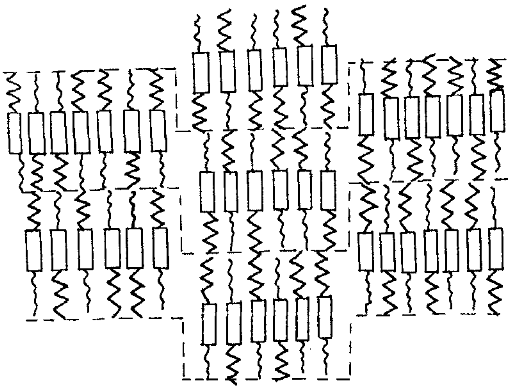


Figure 4. The real space model of the $\tilde{A}_1$ phase of PF7OF8B.

4. The structure of smectic A layers

In this section we will start with the well-known results for X-ray diffraction by the smectic A phase, which will serve as a reference point for the later discussion. In a perfectly oriented smectic A phase, the reciprocal space is the nodal line with spacing $q_{\parallel}=q_z=2\pi/d$ along the layer normal and a diffuse spot in the perpendicular direction at $q_{\perp}\approx 2\pi/4{\cdot}5\ \text{Å}^{-1}$, that reflects the short range order within layers. We will describe the smectic A layering with the electron density distribution $\rho(z)$ along the layer normal. The function $\rho(z)$ for the smectic domain of finite size may be represented in the form [38]

$$\rho(z)=\rho_{\mathrm{M}}(z)*f(z)*T(z)\cdot S(z) \tag{1}$$

where $\rho_{\mathrm{M}}(z)$ is the z projection of the electron density profile of a molecule in the most probable configuration averaged in accordance with the up–down distribution of molecules in the layers; $f(z)$ is the molecular centre of mass distribution within the layers, $T(z)$ is a function which describes the set of points of a one-dimensional lattice, $T(z)=\Sigma\delta(z-nd)$, $S(z)$ is the domain shape function, which is defined to be unity inside the domain of size R and zero elsewhere, and the asterisk denotes the convolution operation. Using the Fourier transform of the expression (1) and the convolution theorem, we arrive at the following expression for the scattering intensity

$$I(q_z)=F_{\mathrm{M}}^2(q_z)f^2(q_z)\sum\delta\left(q_z-\frac{2\pi n}{d}\right)*\frac{\sin^2 Rq_z/2}{(q_z/2)^2}, \tag{2}$$

where the molecular form factor $F_{\mathrm{M}}(q_z)$ and $f(q_z)$ are the Fourier transforms of the functions $\rho_{\mathrm{M}}(z)$ and $f(z)$, respectively. The traditional approach in describing the properties of smectic layers consists in expanding the distribution function $f(z)$ into a Fourier series:

$$f(z)=\sum_n \psi_n \cos(nq_{\parallel 0}z),$$

where the coefficients ψ_n are the de Gennes–McMillan translational order parameters of the smectic A phase. According to equation (2), the intensities (I) of the (00n) reflections from the smectic layers are directly proportional to the square of order parameter ψ_n: $I_n\sim F_{\mathrm{M}}^2(q_n)\psi_n^2$, and the ratio of the second harmonic intensity to the first is given by

$$I_2/I_1=\frac{F_{\mathrm{M}}^2(2q_{\parallel 0})}{2F_{\mathrm{M}}^2(q_{\parallel 0})}\cdot\frac{\psi_2^2}{\psi_1^2}, \tag{3}$$

where the factor 1/2 comes from the lorentz correction factor. Once the wavelength dependence of the molecular form factor $F_M(q_{\parallel})$ is known from reasonable molecular models, the ψ_2/ψ_1 ratio may be estimated. For typical values $F(2q_{\parallel 0})/F(q_{\parallel 0}) \simeq 1\text{–}10^{-1}$ and $I_{002}/I_{001} = 10^{-3}\text{–}10^{-4}$ [23–27], the corresponding ratio of the first two translational order parameters is $\psi_2/\psi_1 \leqslant 10^{-1}$. These estimates are basic for the de Gennes–McMillan description of the nematic–smectic A phase transition in terms of a single order parameter ψ_1. However, for particular types of layering, the ratio ψ_2/ψ_1 may be much higher, leading to the necessity of taking into account the higher order terms in the Fourier expansion of the distribution function $f(z)$.

From expression (3), only the relative values ψ_2/ψ_1 may be calculated. Further progress can be made by assuming some analytical form for the function $f(z)$ [23]. The simplest form, which seems to be a good approximation, is a normalized gaussian distribution with width σ. The Fourier transform of $f(z)$ is also a gaussian: $f(q_z) \sim \exp(-\sigma^2 q_z^2)$. According to equation (2), the intensities of high-order reflections will be reduced by a factor $\exp(-\sigma^2 q_z^2)$ analogous to the Debye–Waller factor of crystals. The ratio of intensities of two successive harmonics in these cases is given by:

$$I_2/I_1 = \frac{F_M^2(2q_{\parallel 0})}{2F_M^2(q_{\parallel 0})} \exp(-3q_{\parallel 0}^2 \sigma^2). \tag{4}$$

For typical values of parameters cited in equation (4) $I_2/I_1 = 10^{-3}\text{–}10^{-4}$; $F^2(2q_0)/F^2(q_0) \simeq 10^{-1}$, $q_0 \simeq 0{\cdot}2\,\text{Å}^{-1}$ the corresponding width $\sigma \simeq 6\,\text{Å}$. Note that according to equations (3) and (4) the translational order parameter ψ_n is simply a Debye–Waller factor: $\psi_n \sim \exp(-\sigma^2 q_n^2/2)$. The physical sense of parameter σ^2 is readily apparent—it is the mean square amplitude of the layer displacements u in the direction along the layer normal: $\sigma^2 = \langle u^2(r^2) \rangle$. One can point out different contributions to the thermal displacement of the molecules or groups of molecules relative to their average positions, which give rise to a broadening of the gaussian distribution function $f(z)$ [39]. In addition to layer fluctuations corresponding to collective motions of molecules and existing on a time scale of 10^{-6} s (long-wave fluctuations σ_{lw}) there are individual motions of molecules having a liquid-like random diffusive nature with characteristic times of 10^{-11} s (σ_{i}) and static displacements of layers caused by elastic fields of defects σ_{d}. One can include the aforesaid contributions in the expression for the combined square displacement amplitude [38, 39]: $\sigma^2 = \sigma_{\text{lw}}^2 + \sigma_{\text{i}}^2 + \sigma_{\text{d}}^2$. The σ_{lw} value in smectic A phases may be as much as $\sigma_{\text{lw}} \simeq 5\text{–}7$ Å, reflecting the large scale layer fluctuations which are characteristic of systems with reduced dimensionality of translational order (Landau–Peierls theorem) [40]. The value of σ_{i} was determined by Leadbetter and coworkers [41] using quasi-elastic neutron scattering to be $\sigma_{\text{i}} \simeq 1\text{–}2$ Å. Point defects (for example, impurities) usually lead to a small values of $\sigma_{\text{d}} \leqslant 1$ Å [42]. From the above estimations, it is clear that the long-wavelength contribution usually dominates in the total displacement amplitude of smectic A layers.

The study of higher order reflections from smectic layers may be complicated by multiple scattering effects [25–27]. Because the mosaicity of the samples is of the same order of magnitude as the (001) Bragg angle ($\theta_{\text{B}} \simeq 1{\cdot}5\text{–}2°$), it is possible that X-rays are diffracted by two successive scattering processes with a momentum transfer $q_{\parallel 0}$. Depending on the sample alignment and thickness, this event may be indistinguishable from scattering of the second harmonic of the smectic density wave with component $2q_{\parallel 0}$. To eliminate the possible influence of multiple scattering, we have prepared samples from different compounds with the same thickness. Mesomorphic compounds having approximately the same Bragg angles and similar mosaic profiles show intensity ratios $I(2q_{\parallel 0})/I(q_{\parallel 0})$ varying by a factor of 10–10^2 (see table 1). This circumstance proves that the large values of the second harmonic intensity are due not to a double scattering process, but are intrinsic properties of smectic A layering.

In accordance with equation (2), finite size effects broaden the delta-function diffraction peaks (0; 0; *n*), but have no influence on the intensity ratio $I(2q_{\parallel 0})/I(q_{\parallel 0})$. The situation may be different if the smectic ordering is of the short-range character, leading to the gradual broadening of successive diffraction peaks [43]. In these cases, it is necessary to correct the peak intensities with the aid of integrated intensity data. Within instrumental resolution ($\xi_{\parallel} \leqslant 900$ Å), smectic A phases in our experiments show long-range translational order. Therefore, any broadening of diffraction peaks is small enough and corrections are not required.

As mentioned above, the molecular form factor $F_M(q_{\parallel})$ from equations (2)–(4) may be calculated on the basis of some model for layer organization. For the smectic A_1 phase, in which the molecules are randomly distributed up and down, an appropriate model is to use the *z* coordinates for two molecules in a head to tail arrangement so as to fit within the known layer spacing. In the case of the smectic A_d phase, we place two molecules in the parallel or antiparallel arrangement and shift them relative to one over a certain distance. In the calculation of the molecular form factor $F_M(q_{\parallel})$, the molecules were assumed to be in their fully extended configuration, with bond angles and lengths taken from space-filling models. The electron density projected on the *z* direction was approximated by a superposition of gaussians:

$$\rho(z) = \sum_i \rho_i(\sqrt{(2\pi\mathscr{H})})^{-1} \exp\left[-(z-z_i)^2/2\mathscr{H}^2\right]$$

centred at the different atomic positions z_i, with a prefactor ρ_i equal to the atomic number [44]. The width of the gaussian was taken to be $\mathscr{H} = 1$ Å. In figure 5 we show the $F_M^2(q_{\parallel})$ dependence for 1Py5F6 and 1Py7OF7 containing six and seven carbon atoms in their perfluorinated chains, respectively, in comparison with the hydrogenous analogue 1Py5H6 of the first of the two mesogens.

It should be noted that the $F_M(q_{\parallel})$ calculations are generally complicated by orientational disorder and many equivalent tail configurations of molecules at finite temperatures. In the case of the smectic A_d phase, not all nearest neighbour molecules form parallel or antiparallel pairs (dimers) [1, 45]. The monomers interact very weakly with dimers and can occupy different positions inside the layer. Furthermore, if we consider as a zeroth order approximation a model in which scattering centres are uniformly distributed inside a cylinder with dimensions equal to the molecular length *L* and diameter *D*, then we arrive at the well-known expression in diffraction theory for $F_M(\mathbf{q})$ [46]

$$F_M(\mathbf{q}) \sim \frac{\sin q_{\parallel}L/2}{q_{\parallel}L/2} \cdot \frac{J_1(q_{\perp}D/2)}{q_{\perp}D/2},$$

which has minimal values in the $q_{\parallel}$ direction just at reciprocal space points $q_{\parallel} = 2\pi n/L \simeq nq_{\parallel 0}$. This means that the $F_M(q_{\parallel})$ dependence is very sensitive to details of the molecular models in the vicinity of the wavevectors where $q_{\parallel} = nq_{\parallel 0}$, (see figure 5). From the above reasoning it is clear that calculated values of the molecular form factor $F_M(q_{\parallel})$ must be treated with some caution. Nevertheless, we may estimate the upper limits for the ratio ψ_2/ψ_1 (lower limits for σ) from the measured ratio $I(2q_{\parallel 0})/I(q_{\parallel 0})$ (see table 2).

Table 2. Intensity ratio I_{002}/I_{001}, the ratio of the squares of the molecular structure factors $F^2(2\mathbf{q}_0)/F^2(\mathbf{q}_0)$ and the ratio of the translational order parameters ψ_2/ψ_1 for the fluorinated materials numbered N. Compound abbreviations are as in table 1.

N	Compound	T/°C	I_{002}/I_{001}	$F^2(2\mathbf{q}_0)/F^2(\mathbf{q}_0)$	ψ_2/ψ_1	σ/Å
1	1Py5OF	46	1×10^{-2}	8×10^{-1}	0·15	3·8
2	1Py7OF7	80	9×10^{-2}	1·0	0·40	3·5
3	1Py5F6	74	1×10^{-1}	2	0·30	3·4
4	M70	106	$1{\cdot}5\times10^{-1}$	6·0	0·25	6·0

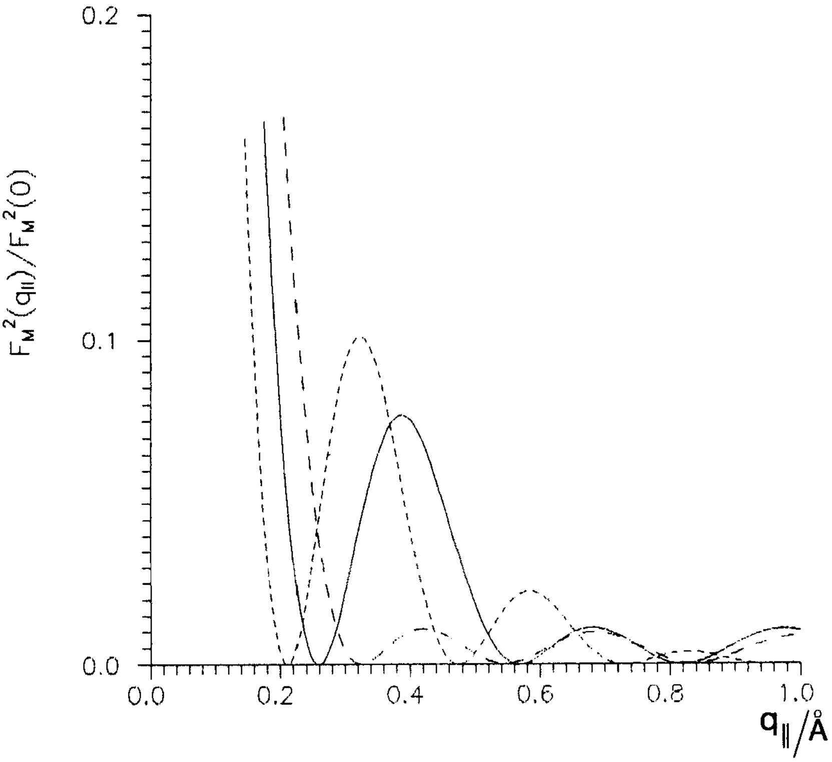
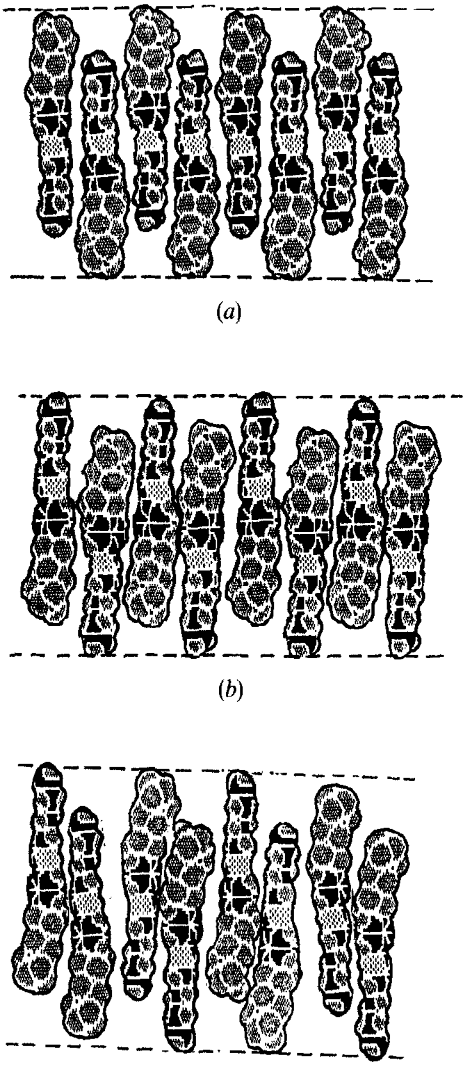


Figure 5. The wavelength ($q_\|$) dependences of the square of the molecular form factor (normalized to the $F_M^2(0)$ values) calculated for 1Py5F6 (——), 1Py7OF7 (- - -) and 1Py5H6 (– – –). The corresponding layer wavenumbers $q_{\|0}=0{\cdot}26\,\text{Å}^{-1}$ (—— and – – –) and $q_{\|0}=0{\cdot}22\,\text{Å}^{-1}$ (- - -).

From figure 5 it is readily seen that terminal fluorination leads to the transfer of the molecular scattering intensity from the position of the first harmonic to the second. However, the enhanced values of the ratio $F_M^2(2q_{\|0})/F_M^2(q_{\|0})$ in lengthy perfluorinated mesogens are not enough to explain the observed increase in the intensity ratio $I(2q_{\|0})/I(q_{\|0})$ by two orders of magnitude as compared with mesogens containing only hydrocarbon tails. As a result, the ratio of the first two translational order parameters ranges up to about $\psi_2/\psi_1 \leqslant 0{\cdot}3$–$0{\cdot}4$ ($\sigma \geqslant 3{\cdot}5$ Å), (see table 2). The smectic layers are thus


(a)

(b)

(c)

Figure 6. Different types of antiparallel (*a*; *b*) and parallel (*c*) molecular packings for mesogenic molecules with lengthy perfluorinated chains.

more rigid than in conventional smectic A phases, and the density distribution function $\rho(z)$ deviates from a pure sinusoidal form.

Now, consider the structure of the smectic A_d layers in mesogens 1Py5F6, 1Py7OF7 and the polyphilic compounds. Different types of dimeric organization can exist in these smectics, (see figure 6). They include two types of centro-symmetric antiparallel arrangement of molecules differing in the position of the perfluorinated chains relative to the layers (see figures 6 (*a*) and (*b*)), and one type of parallel arrangement (see figure 6 (*c*)). Note that because smectic A_d layering is neither ferroelectric nor antiferroelectric, the parallel dimers are oriented randomly up and down within the layers. The molecular form factor calculations for the aforesaid types of layer organization give wavelength dependences with similar behaviour in the vicinity of the first and second harmonic. Together with the limited number ($n \leqslant 3$) of reflections resulting from the smectic layering, this makes impossible an accurate determination of the preferential types of molecular arrangement in the smectic phases along the layers.

5. Discussion

It is generally understood that the presence of both rigid central cores and flexible tails is essential for the stability of smectic A order. Additional conformational entropy connected with the aliphatic chains prevents the crystallization of rigid parts of molecules in the smectic layers, thus expanding the range of existence of smectic A phases. Moreover, the presence of molecules with different chain conformations (conformers) in the system stabilizes certain smectic phases due to the denser packing of molecules in the layers [4, 5]. In order to interpret the peculiarities of the smectic A layering in perfluorinated compounds, it is necessary to consider more closely the properties of perfluorinated chains. Firstly, the van der Waals radius of fluorine ($\simeq 1{\cdot}33$ Å) considerably exceeds the corresponding value for a hydrogen atom, the fluorine atoms cover the carbon skeleton as a dense 'fur coat', (see figure 1). Secondly, in accordance with quantum-chemical calculations [47], the activation energy of the *trans–gauche* and *gauche–gauche* rotations in fluorocarbons (decafluorobutane) is a factor of 3 to 4 higher than that in linear hydrocarbons (butane). This practically excludes the possibility of the formation of *gauche*–conformers at finite temperatures. As a result, perfluorinated chains, similarly to polytetrafluoroethylene units, form a rigid rod-like structure featuring a consecutive turning out of the CF_2 moieties through an angle of $\cong 16°$. The appropriate structural model of perfluorinated molecules will be a rigid core built up of a polarizable biphenyl (pyridine) fragment, a flexible hydrocarbon chain at one of the ends of the molecule and a rigid perfluorinated tail (semi-rigid in the case of the polyphilic mesogens) at the other end, (see figure 1). Such properties of perfluorinated chains on the one hand diminish the packing differences between the cores and tails, but on the other hand introduce additional steric hindrance to optimal packing of the molecules. Both these reasons may modify the character of the smectic layering. It should be noted that the presence of the flexible (hydrocarbon) chain in terminally fluorinated mesogens is essential for the stability of mesomorphic order. To the best of our knowledge, rod-like molecules with two terminal perfluorinated chains have never been observed to form mesomorphic states [48, 49].

With the molecular models shown in figure 1, the cross-sections of various molecular fragments may be estimated. For the perpendicularly oriented and cylindrically averaged biphenyl moiety, which is characteristic of the smectic A phase [37, 44], we have $s_B \simeq 22$ Å^2. For the perfluoroalkyl chain tilted at an angle of 0–30°, the typical chain cross-section is about $s_F \simeq 27$–35 Å^2. The alkyl chain has a cross-sectional area close to that of biphenyl $s_H \simeq 20$ Å^2. Comparison of s_B, s_F and s_H clearly indicates that a denser packing in the smectic A_d phase may be achieved for an antiparallel arrangement of neighbouring molecules. Thus, from the pure sterical point of view, the existence of antiparallel dimers is more probably for smectic A phases formed by the perfluorinated molecules.

Let us consider now the dipolar properties of perfluorinated molecules. The $-OCF_3$ and $-CF_3$ molecular groups, as distinct from the $-CH_3$ group, possess a fairly large longitudinal dipole moment ($\mu \simeq 2$–3 D [34, 35]). Quantum-chemical calculations by Shibaev *et al.* [50] indicate that the dipole–dipole interaction for $-OCF_3$ compounds similar to cyano-terminated mesogens has the same order of magnitude

($\simeq -2$ kcal/mol) as the dispersion interaction ($\simeq -6$ kcal/mol) and favours antiparallel arrangement of neighbouring molecules with a relative displacement of the order of $\simeq 5$–6 Å. The observed absence of dimeric layering for $-OCF_3$ terminated mesogens may be caused by purely steric factors. Unlike polar compounds with either the linear $-CN$ or the flat $-NO_2$ configuration of dipole groups, the CF_3 group possesses a bulky tetrahedral arrangement of atoms which sterically hinders the antiparallel dimeric arrangement of molecules. However, for $O(CF_2)_{n-1}CF_3$ compounds with lengthy hydrocarbon chains ($n \geqslant 7$), the dimeric type of smectic layering may exist. In mesogens having lengthy perfluorinated chains with repetitive CF_2 moieties (1Py7OF7, 1PyF56) the charges of opposite signs are spatially distributed along the chain in an alternating way. As a result, the magnitude of the dipole–dipole interaction is reduced as compared with $-OCF_3$ compounds [50], and one can expect the monolayer type of smectic organization in these compounds. However, the effect of local dipolar repulsions between the CF_2 moieties of neighbouring molecules on the smectic A layering cannot be excluded. The minimisation of energy of such local dipolar interactions may lead to stable configurations in which molecules are shifted relative to one another over a distance of the order of one C–C bond length. Such a type of behaviour connected with the formation of the smectic A_d phase has been observed experimentally for mesogens with lengthy perfluorinated chains. Enhanced rigidity of the smectic layers formed by these molecules may be attributed to purely steric factors associated with the increased conformational rigidity of the perfluorinated chains. In the PF7OF8B compound containing a fluorine atom in the lateral position in the benzene ring attached to the perfluorinated tail, additional steric factors appear to disturb the uniformity of the smectic layers. If we consider a stereo-model of PF7OF8B, then it is readily seen that a fluorine atom in the lateral position in the benzene ring prevents the perfluorinated tail from rotating about the C–O bond, thereby setting the rigid chain in a strictly fixed position relative to the plane of the phenyl ring. The enhanced steric hindrance between neighbouring molecules may lead to an increase in the free volume of smectic monolayers, which is a disadvantage from the view of packing entropy, or induce a local bending of the layers. As the sizes of the areas of the bent bilayers increases, an increase in the corresponding elastic energy with some critical curvature makes energetically preferable a transition from uniform monolayers into the modulated $\tilde{A}_1$ phase, where the areas of monolayers with opposite signs of local curvature are separated by antiphase borders (defect walls), (see figure 4). Such modulated states in smectics were theoretically discussed earlier by Longa and de Jeu [51] and Helfrich [52] for terminally polar mesogens. Similar types of defective layer structures were earlier reported for certain comb-like liquid crystalline polymers [53, 54].

As regards specific features of the in-plane positional order for polyphilic compounds as revealed in the scattering profile with two peaks, we associate them with the 'melted' character of the hydrocarbon chains. A large degree of conformational freedom of these chains effectively decouples the ordering of the rigid cores from the perfluorinated chains. As a result, the competition between molecular stacking at different distances: core–core, perfluorinated chain–perfluorinated chain, hydrocarbon chain–hydrocarbon chain may appear. Similar behaviour is also seen in the columnar phases of discotic mesogens, where X-ray diffraction with the momentum transfer parallel to the column axis (along the liquid-like direction) shows two broad peaks which may be attributed to two nearest neighbour molecule–molecule distances: a short core–core distance and a longer tail–tail distance [55, 56]. The presence of both flexible hydrocarbon and rigid perfluorinated moieties in the terminal chain of polyphilic molecules also explains the reduced rigidity of the smectic layers as compared with mesogens in which the perfluorinated chain is directly attached to rigid core (see tables 1 and 2).

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