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Evidence of Tilted Dimeric Mesophase for Terminally Polar Polyphilic Mesogens

B.I. Ostrovskii ⁽¹⁾, F.G. Tournilhac ⁽²⁾, L.M. Blinov ⁽¹⁾ and W. Haase ⁽³⁾

⁽¹⁾ Institute of Crystallography, Academy of Sciences of Russia, Leninsky pr. 59, Moscow 117333, Russia

⁽²⁾ Ecole Supérieure de Physique et Chimie Industrielles, 10 rue Vauquelin, 75231 Paris Cedex 05, France

⁽³⁾ Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraße 20, 64287 Darmstadt, Germany

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Abstract. — We report an X-ray diffraction and infra-red dichroism study of the structure and phase transitions for a new homologous series of cyanoterminated polyphilic liquid crystals. Analysis of the X-ray scattering profiles in the direction parallel and perpendicular to the smectic layers provides detailed data on lamellar ordering in smectic phases of polyphilics. The infra-red dichroism measurements allow molecular conformations and the tilt of various molecular moieties in smectic phases to be determined. In addition to the partly bilayer smectic A_d phase composed of antiparallel dimers, its tilted analogue-smectic C_d phase has been detected. The temperature variations of the interlayer spacing in the smectic C_d phase are very small as compared to the classical smectic A–smectic C transitions. This unusual behaviour results from the fact that both the tilt angle for different molecular moieties and the relative displacement of molecules in dimers vary with temperature. The enhanced stability of dimeric smectic C_d phase and the features of smectic A_d –smectic C_d phase transition are discussed in terms of sterical coupling of molecules with differently tilted fragments.

1. Introduction

The smectic phases of liquid crystals are described as one-dimensional stacking of liquid-like layers. In the smectic C phase the molecules are tilted with respect to the normal to the layers. The structure and properties of smectic C phases, as well as the origin of tilting of molecules have been the subject of extensive experimental and theoretical studies during the last decades [1–4]. In the early eighties new types of tilted phases were detected among so-called frustrated smectics composed of mesogenic molecules with strongly polar terminal groups [5]. In addition to the classical smectic C_1 phase in which the molecules are oriented randomly up and down within each layer, the bilayer tilted smectic C_2 phase with antiferroelectric ordering of permanent dipoles and two-dimensional \bar{C} phase were observed. At the same time only a

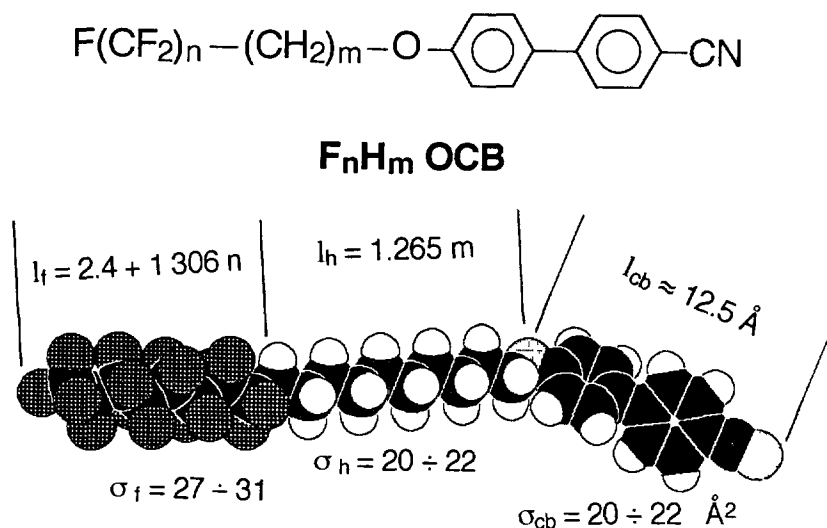


Fig. 1. — Chemical structure and molecular model of the cyanoterminated polyphilic compounds. The lengths and lateral cross sections of the various fragments are indicated.

few examples of the tilted analogue of partly bilayer smectic A_d phase (i.e., C_d), whose layer periodicity is incommensurate with the length of individual molecules have been detected [6–8]. The C_d phase is usually unstable and can be observed in individual compounds only on cooling (monotropic phase). The enantiotropic smectic C_d phase was shown to exist in a very narrow temperature and concentration range in the binary mixture of three-ring terminally polar mesogens [7]. This is of course not incidental: in the smectic A_d phase, due to strong dipole-dipole correlations between neighbouring molecules a significant part of the molecules are joined in suitable antiparallel pairs (dimers) [9]. The transverse dimensions of the central parts of such dimers considerably exceeds that of alkyl chains. This leads to an unfavourable decrease in the entropy of packing and makes the smectic A_d highly unstable (this is one of the reasons for the delicate stability and multiple reentrance in frustrated smectics [10]). On the other hand, the tilt of molecules in smectic layers is disadvantageous since, in this case, the average area per molecule increases and hence the entropy of packing diminishes. Specific additional interactions are therefore required to overcome the unfavourable tilted arrangement of dimers in the smectic C_d phase.

From this point of view, new possibilities appear in the case of terminally polar polyphilic compounds, made up of molecular fragments differing in their chemical nature, namely, chemically attached cyanobiphenyl moiety and sequenced hydrocarbon-perfluoroalkyl chain (Fig. 1) Recently it was shown that polyphilic mesogens with perfluorinated chains at both ends of the molecule form new types of smectic C-like polar multilayer structures with tilted molecules in a strongly zig-zag conformation [11]. We can expect that the presence of molecular moieties with very different properties in lengthy terminal chain may stabilize smectic C_d phase due to specific sterical and polyphilic effects [11–13].

Here we present X-ray diffraction and infra-red dichroism studies of the structure and phase transitions for a new homologous series of cyanoterminated polyphilic mesogens. In addition to the partly bilayer smectic A_d phase the tilted dimeric C_d phase has been detected over a broad temperature range for a number of compounds. X-ray diffraction provides detailed

data on lamellar ordering in smectic A_d and C_d phases of polyphilics. The infra-red dichroism measurements allow the molecular conformations and the tilt of various molecular moieties to be determined. These two techniques have provided mutually complementary data on the structure and thermodynamic behaviour of terminally polar polyphilic mesogens that is essential for the elaboration of a realistic structure model of the smectic C_d phase.

2. Experimental Technique

2.1. SUBSTANCES AND MESOMORPHIC BEHAVIOUR. — The molecular structure of terminally polar polyphilic mesogens is shown in Figure 1. The compounds of general formula: $F(CF_2)_n-(CH_2)_m-O-\Phi-\Phi-CN$ (F_nH_mOCB for short) were synthesized according to the method described earlier [14]. The final substances were purified by liquid chromatography and recrystallization from heptane. Due to the large amount of fluorine atoms, the elemental analysis systematically showed a weak defect in C, H and N atoms, while 1H NMR and IR spectroscopy were consistent with the expected chemical structure.

The mesomorphic behaviour was investigated by DSC, optical microscopy, X-ray diffraction and IR-spectroscopy. Upon cooling from the isotropic phase, all compounds form a smectic A phase, as indicated by focal conics or homeotropic texture. On further cooling the smectic C phase becomes visible for the major part of the members of the series through a *schlieren* texture in initially homeotropic domains and a broken fan shaped texture in the other areas. The presence of the smectic C phase in the phase diagram of F_nH_mOCB series was confirmed in experiments where polyphilics were doped ($\leq 1\%$) with chiral dipolar substances. The addition of a chiral component to an initial matrix of a tilted smectic "removes" the center of inversion of the system, resulting in the formation of the ferroelectric smectic C^* [15]. The tilted phases were identified through the appearance of the helix fringes and the linear electrooptical response in alternative field. In addition, the latter technique enabled us to measure directly the optical tilt angle in the smectic C_d phase. The phase transition to the smectic C_d phase was also detected through the nonmonotonic thermal behaviour of the interlayer spacing and apparent orientational order parameter as measured by X-ray diffraction and IR dichroism, respectively

The regions of stability of the various phases as a function of the molecular parameters are represented in Figure 2 and Table I. From the above experimental data we can arrive at the following conclusions:

(1) In contrast to their fully hydrocarbon counterparts (8OCB, 12OCB) the F_nH_mOCB compounds have a very broad smectic A_d range (from 40 to 60 °C, up to 100 °C including the monotropic range). A broad range of smectic A_d phase has also been observed for cyanobiphenyls bearing a bulky pentamethyldisiloxane end group [17].

(2) The presence of both alkyl and perfluoroalkyl moieties are sufficient for stability of smectic A_d phase formed by F_nH_mOCB mesogens with lengthy terminal chains: $m + n \geq 13$ (compare, for example, $F_8H_{10}OCB$ with the nonpolyphilic compound $H_{18}OCB$ which has the same number of carbon atoms in the terminal chain; the latter shows only a crystalline smectic phase).

(3) A requirement for stability of the C_d phase is that both alkyl and perfluoroalkyl chains contain more than four carbon atoms (compare, for example, $F_4H_{11}OCB$ and F_7H_1OCB compounds which have only the A_d phase with $F_8H_{11}OCB$ and F_8H_5OCB , which form the C_d phase).

2.2. X-RAY DIFFRACTION. — X-ray measurements were carried out using $Cu K_\alpha$ radiation and two types of diffractometers with linear position-sensitive detectors (LPSD) for data col-

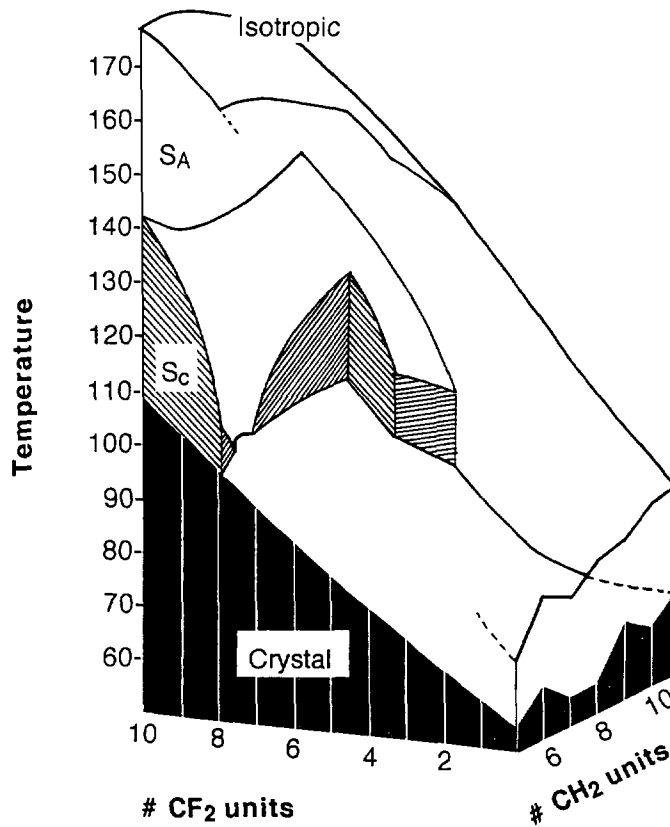


Fig. 2. — Phase diagram for the $F_n H_m$ OCB homologous series.

lecting. The first set-up includes a focusing two-circle STOE diffractometer with a curved Ge monochromator [18]. The second set-up utilizes a three slit collimation scheme with Ni filter [19]. The longitudinal resolution was at the level of $\Delta q_{||} = 3 \times 10^{-3} \text{ \AA}^{-1}$ and $\Delta q_{\perp} = 2 \times 10^{-3} \text{ \AA}^{-1}$ (full width at half maximum, FWHM) respectively. The components of the diffraction vector $q_{||}$ and q_{\perp} are parallel and perpendicular to the director \mathbf{n} : $q = (4\pi/\lambda) \sin \Theta$ (Θ is the scattering angle, and λ is the wavelength of the X-rays, 1.54 \AA). The LPSD was placed in the detection plane in a way which allowed the registration of the scattered radiation along the $q_{||}$ coordinate in reciprocal space (2Θ profiles). In our data analysis peak shapes were modelled by Lorentzian line shapes, yielding peak intensity, position and width. The layer spacing d can be calculated from 2Θ profiles by the Bragg equation

$$d = (\lambda/2) / \sin \Theta \quad (1)$$

where 2Θ corresponds to the peak maximum. The measurements of the longitudinal correlation lengths were limited to $\xi_{||} = 2/\Delta q_{||} = 900 \text{ \AA}$. The width of diffraction profiles in the q_{\perp} direction was limited by the sample mosaic. The q_{\perp} profiles (rocking curves) were obtained by rotation of sample around an axis orthogonal to the director and the scattering plane.

The X-ray measurements in the wide scattering angle region ($q_{\perp} \geq 1 \text{ \AA}^{-1}$) provide data on the intermolecular positional correlations in the plane of the smectic layers. These studies were

Table I. — Phases and transition temperatures for some members of the F_nH_mOCB series. Notice that the compounds with a sequenced chain have a tendency for smectic phases to be overcooled.

N	Mesogens	Phase sequence; T°C	Ref.
1	8OCB (H_8OCB)	54.5 67 80 Cr \Leftrightarrow A _d \Leftrightarrow N \Leftrightarrow I	[16]
2	F_7H_1OCB	75 144 Cr \Rightarrow A _d \Leftrightarrow I	
3	12OCB (H_{12OCB})	69 89 Cr \Leftrightarrow A _d \Leftrightarrow I	[16]
4	F_8H_5OCB	97 106 162 Cr \Rightarrow C _d \Leftrightarrow A _d \Leftrightarrow I	
5	$F_4H_{11}OCB$	70 113 Cr \Rightarrow A _d \Leftrightarrow I	
6	$F_6H_{11}OCB$	84 96 131 Cr \Rightarrow C _d \Leftrightarrow A _d \Leftrightarrow I	
7	$F_6H_{11}OCB + 8OCB$ (9:1)	74 131 Cr \Rightarrow A _d \Leftrightarrow I	
8	$F_8H_{10}OCB$	100 121 150 Cr \Rightarrow C _d \Leftrightarrow A _d \Leftrightarrow I	
9	18OCB (H_{18OCB})	83 91 Cr1 \Rightarrow Cr2 (smectic) \Leftrightarrow I	
10	$F_{10}H_{10}OCB$	114 136 160 Cr \Rightarrow C _d \Leftrightarrow A _d \Leftrightarrow I	
11	$F_{10}H_{11}OCB$	112 135 158 Cr \Rightarrow C _d \Leftrightarrow A _d \Leftrightarrow I	

performed using a diffractometer with LPSD and a KARD diffractometer with a two-coordinate detector [20].

The absence of the nematic phase in the compounds under study makes impossible the effective orientation of the liquid crystalline director in a magnetic or electric field. Hence the systematic measurements of the interlayer spacings for the members of homologous series were fulfilled on nonoriented samples (powder diffraction). The mesogens for these experiments were placed in thin-walled quartz capillaries of 1.5–2 mm in diameter.

The precise X-ray measurements in the vicinity of the smectic A_d-smectic C_d phase transition in the model compound ($F_8H_{11}OCB$) were carried out on well oriented samples. The oriented films of thickness 10 – 100 μm were obtained by insertion of the substance between polished beryllium plates [11]. On cooling down from the isotropic phase, spontaneously oriented films with the smectic planes lying parallel to the substrate surface were formed. The mosaicity was on the level 2 – 4° (FWHM).

Table II. — *Characteristic bands for the IR dichroism study.*

Wavenumber (cm ⁻¹)	Assignment	Polarization with respect to the longitudinal axis
2932	CH <i>asymm.</i> stretching	⊥
2859	CH <i>symm.</i> Stretching	⊥
2224	CN stretching	∥
1604	Aromatic CC stretching	∥
1149	CF stretching	⊥
658	CF ₂ wagging	∥

2.3. INFRA-RED DICHROISM. — The infra-red (IR) dichroism is a powerful method for the determination of orientational order parameters for various molecular fragments and the evaluation of the molecular conformations in different types of mesophases. Recently the IR dichroism technique has successfully been applied to study the conformations of polyphilic compounds with perfluoroalkyl chains at both ends of the molecule [11]. The measurements of the IR spectra of cyanoterminated polyphilics were carried out within the wavenumber range from 4000 to 400 cm⁻¹ using a Perkin-Elmer (model 1600) FTIR spectrometer. The films were prepared by melting a small amount of substance in a cleavage of a KBr single crystal. The homeotropically oriented smectic films were obtained (spontaneously) after cooling down from the isotropic phase. In all the measurements unpolarized light was used, the optical beam being perpendicular to the layer planes.

Dichroic ratios were obtained by comparison of the absorbance (optical density) in the isotropic phase (D_i) with that of a homeotropically oriented smectic phase (D_h). According to the method previously described [21] the regular (isotropic) part of the temperature dependence of the vibrational band intensities was taken into account. The latter was measured on the same substances incorporated in KBr pellets.

The apparent "order parameter" for each vibrational oscillator of interest was calculated using the formula.

$$S^* = 1 - (D_h/D_i).(1/f) \quad (2)$$

where f is the thermal correction factor. In the smectic A phase of rodlike molecules, S^* is related to the true order parameter S through the equation:

$$S^* = SS\psi = [(1/2) < 3 \cos^2 \beta - 1 >].[1 - (3/2) \sin^2 \psi] \quad (3)$$

where β is the deviation angle of the main molecular axis from its average orthogonal position, ψ is the angle between the longitudinal molecular axis and the oscillator under consideration. Hence, in the smectic A phase, S can be conveniently measured by recording the dichroic ratios for either parallel ($\psi = 0$) or perpendicular ($\psi = \pi/2$) bands. For complicated and flexible molecules, S and S^* are not expected to have the same values for all oscillators. In order to describe the molecular conformations of the main molecular fragments: perfluoroalkyl, alkyl and cyanobiphenyl units, we have investigated the dichroism for a number of characteristic bands which are represented in Table II.

In the smectic C phase, two angles are necessary to describe the position of a rigid molecule or molecular fragment with respect to the layer frame. Two other angles are needed to locate a given oscillator with respect to the molecular frame. However, in the geometry of our experiment, using unpolarized light and an azimuthally disordered texture, the apparent order

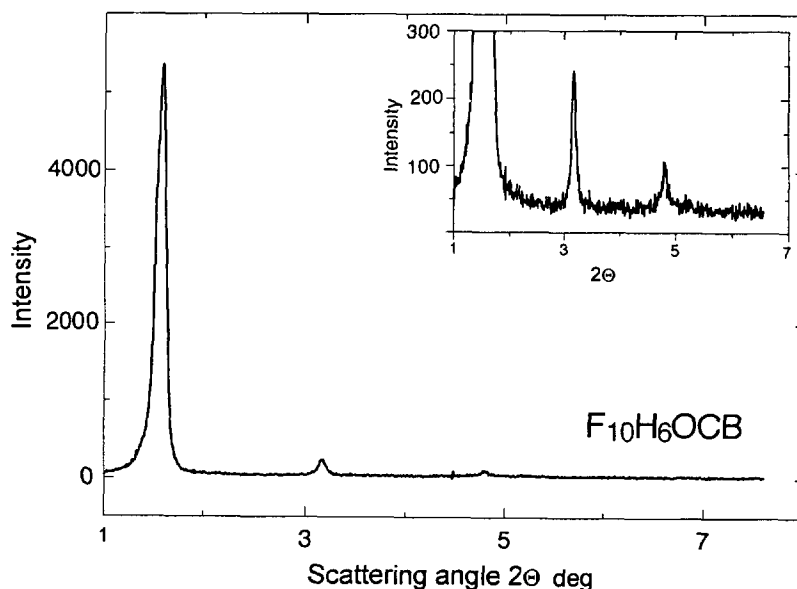


Fig. 3. — X-ray diffraction pattern in the small scattering angle region for the $F_{10}H_6OCB$ compound (smectic A_d phase). The inset shows the higher order harmonics on an enlarged scale.

parameter can be written in a simple form for a longitudinal oscillator:

$$S_{\parallel}^* = SS_{\theta} = 1/2 S(3 \cos^2 \theta - 1) \quad (4)$$

where θ is the tilt angle. Knowing the value of the order parameter S , it is therefore possible to determine the tilt angle from dichroic data. For a transverse oscillator, the same is true only if the polarization is degenerated in the transverse plane or if the free rotation of the molecular fragment around its long axis (uniaxial approximation) is assumed. Under these conditions, the following relation can be used:

$$S_{\perp}^* = SS_{\pi/2-\theta} = 1/2 S(3 \sin^2 \theta - 1) \quad (5)$$

It is worth noting that the order parameter S can be easily determined if dichroic data for two oscillators, one parallel and one perpendicular to the same fragment are known:

$$S = 2(S_{\parallel}^* + S_{\perp}^*) \quad (6)$$

3. Experimental Results and Interpretation

3.1. X-RAY DIFFRACTION AND ELECTROOPTICAL MEASUREMENTS. — The diffraction patterns in the high temperature smectic phases for F_nH_mOCB series display up to three orders of resolution limited peaks $\mathbf{q}_n = (0; 0; nq_{\parallel 0})$ resulting from the lamellar ordering ($q_{\parallel 0} = 2\pi/d$; $n = 1 - 3$), Figure 3. The smectic C phase is formed by cooling down the A phase, hence the orientation of the smectic planes is fixed and determined by the smectic A texture, whereas inside the layers the molecules or their flexible fragments tilt through certain angles. Since in the X-ray experiment we deal with orientation of planes and not molecules, the scattering

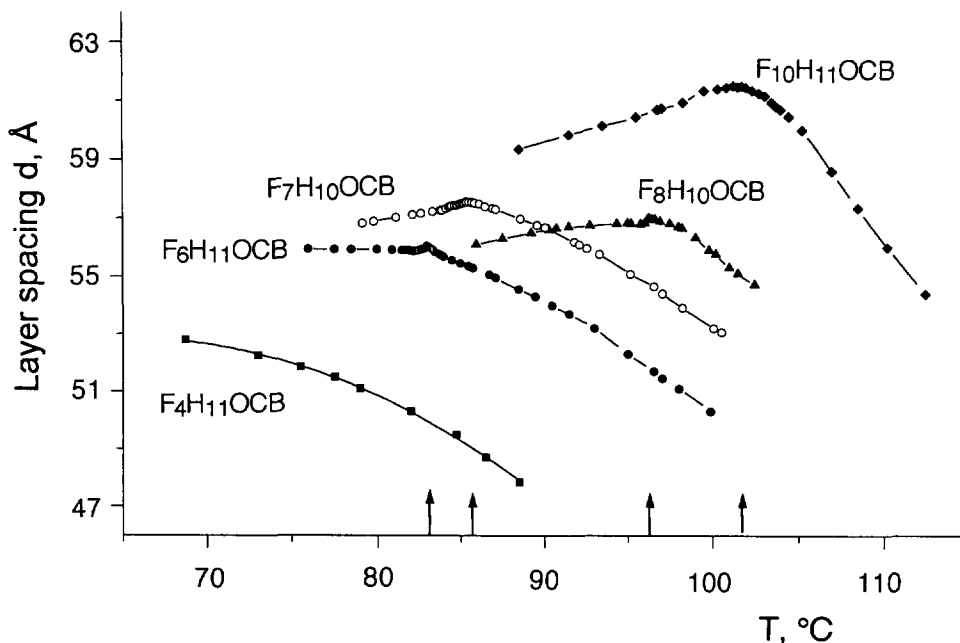


Fig. 4. — Temperature dependences of the layer spacing d in the smectic A_d and C_d phases for $F_4H_{11}OCB$ (■), $F_6H_{11}OCB$ (●), $F_7H_{10}OCB$ (○), $F_8H_{10}OCB$ (▲) and $F_{10}H_{11}OCB$ (◆) compounds. Data for the $F_7H_{10}OCB$ mesogen are shifted up by 1 Å for clarity. Arrows indicate the smectic A_d -smectic C_d phase transition points.

geometry remains the same (as that of the A phase), whereas the diffraction peaks are shifted along the coordinate axis $q_{||}$ due to the variation in spacing d

$$d_C = d_A \cos \theta_r \quad (7)$$

where d_A and d_C are interlayer spacings in the smectic A and C phases and θ_r is an average tilt angle of molecules. The temperature dependences of the interlayer periodicity in the smectic A and C phases for a number of mesogens are shown in Figure 4. The interlayer spacing significantly exceeds the molecular length: $d/L = 1.35 - 1.65$ in temperature dependence and homolog number (the stereomodel predicts, for example, $L \approx 35$ Å for the fully extended molecular conformation of $F_6H_{11}OCB$). This corresponds to the formation of the smectic A_d (C_d) phases in which molecules are shifted relatively to one another by a certain distance. The intensities of higher order reflections from the smectic layers are highly influenced by the wavenumber dependence of the molecular formfactor $F_m(q)$, which may be very different for the members of homologous series with various lengths of perfluoroalkyl tails [22]. As a result the ratio of second harmonic intensity to the first $I(2q_0)/I(q_0)$ differs from 10^{-2} to 7×10^{-2} in the compounds under study. The intensity of the third harmonic amounts to about 10^{-2} of the first, Figure 3.

The temperature behaviour of interlayer spacing, d , for different members of the series is quite similar (Fig. 4). In the smectic A_d phase the layer spacing increases monotonically as the $A_d \leftrightarrow C_d$ transition is approached from above. This behaviour is typical of frustrated smectics

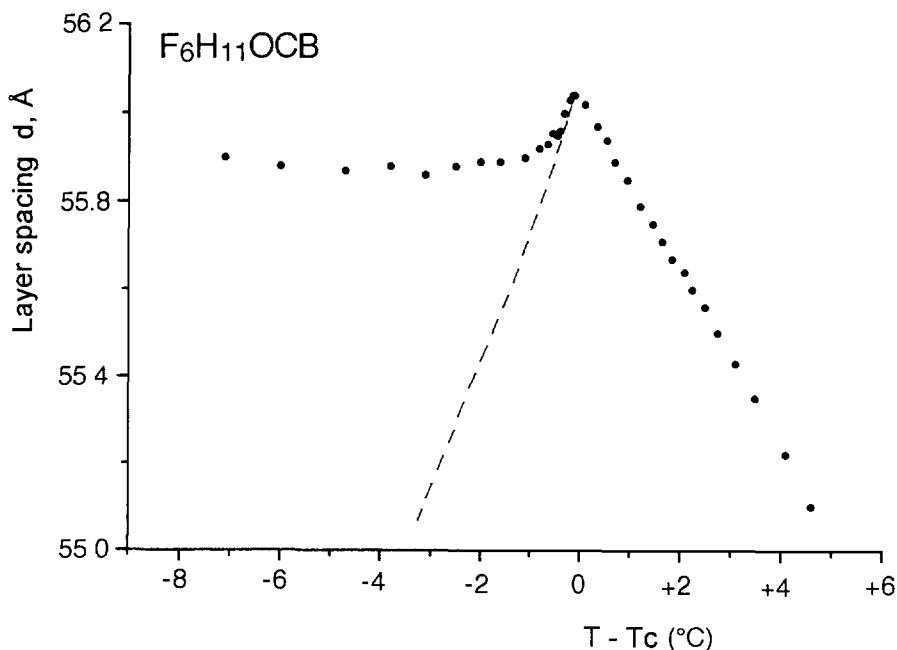


Fig. 5. — Layer spacing *versus* relative temperature in the vicinity of the smectic A_d –smectic C_d transition for $F_6H_{11}OCB$ compound. Dotted line: d -values calculated on the basis of equation (7).

lying on the phase diagram in the upper critical region of the smectic A_d –bilayer smectic A_2 phase transition line [23]. Beyond the critical $A_2 \leftrightarrow A_d$ point the layer spacing evolves continuously from the A_d ($d \approx 1.5L$) to the bilayer $d \approx 2L$ value. From the microscopic point of view, the temperature variations in d are accounted for by a change in either the dimer size or the ratio of monomers and dimers in the system. The layer spacing, d , shows a maximum in the region of smectic A_d –smectic C_d transition (Fig. 4). In the smectic C_d phase the d value remains approximately constant ($F_6H_{11}OCB$) or slightly decreases with decreasing temperature. Precise measurements of the variations of d in the vicinity of the $A_d \leftrightarrow C_d$ transition for the $F_6H_{11}OCB$ compound display a fracture of the curve which is characteristic of the phase transitions to the tilted phases (Fig. 5). However, the temperature variations of the interlayer spacing in the C_d phase are very small as compared to classical smectic A–smectic C transitions. The same is also true for the other compounds (Fig. 4).

The X-ray intensity profiles of the smectic A_d and C_d phases in the wide scattering angle region show diffuse liquid-like peaks centered at $q_{\perp 0} \approx 1.4 \text{ \AA}^{-1}$, corresponding to the average intermolecular distance of $4.5 - 5 \text{ \AA}$ in the smectic planes (Fig. 6). The diffuse character of the in-plane scattering testifies that smectic A_d and C_d phases of cyanoterminated polyphilics really consist of liquid-like layers. We can compare such a behaviour with the intralayer diffraction patterns of the reference nonpolyphilic $H_{18}OCB$ compound that only displays a crystalline smectic phase (Fig. 6).

In order to have more information about molecular conformations and to prove directly that F_mH_nOCB compounds form a tilted mesophase, we have initiated experiments with doping certain members of the series with a chiral additive of relevant molecular structure. As mentioned above, the addition of a chiral component to an initially tilted smectic matrix leads to

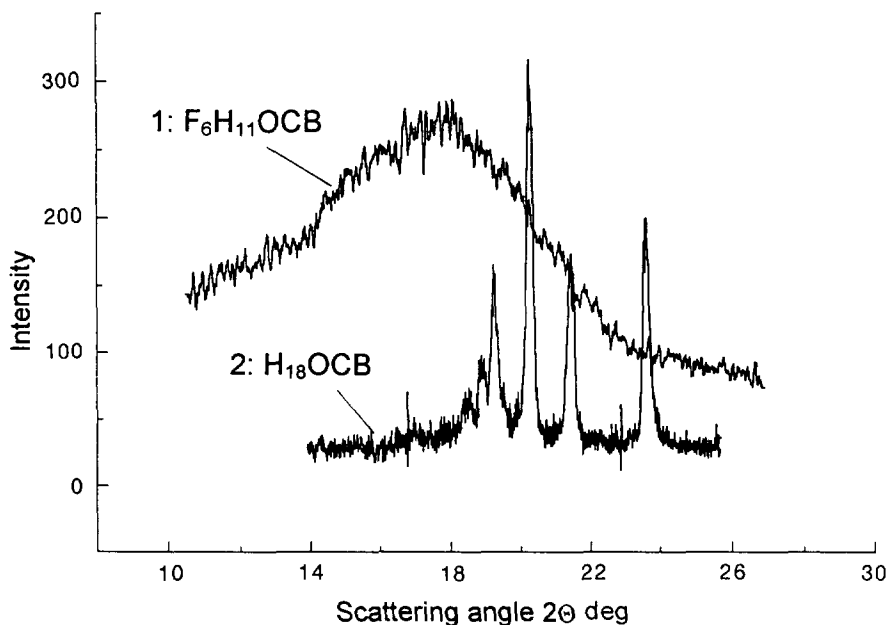


Fig. 6. — X-ray diffraction patterns in the wide scattering angle region for the $F_6H_{11}OCB$ (1) and $H_{18}OCB$ (2) compounds illustrating the smectic A in-plane layering and crystalline smectic structure, respectively.

the appearance of the chiral smectic C^* phase possessing ferroelectric properties [15]. This enables us to measure the tilt angle θ_{opt} of highly polarizable moieties by a sufficiently simple method utilizing the electrooptical effect in ferroelectric smectics [24, 25] (the anisotropy of polarizabilities in F_mH_nOCB compounds is due to the conjugated rings in the cyanobiphenyl moiety). The dopants used (diesters of 4,4'-terphenyl dicarboxylic acid) are effective to provide large values of induced polarization [26]. The electrooptical measurements were performed on commercially available standard cells of thickness $10 \mu m$ with planar boundary conditions (E.H.C. Co, Tokyo, Japan). In Figure 7 the θ_{opt} angle is plotted as a function of temperature for the $F_6H_{11}OCB$ compound doped with 0.5% of chiral component. The values of θ_{opt} are relatively small and its temperature dependence saturates at $\theta_{opt} \approx 15 - 16$ deg. The θ_{opt} temperature dependence indicates that the smectic A_d to smectic C_d transition is of second order (continuous) in good agreement with extremely small values of transition enthalpy as detected by DSC. The tilt angle $\theta(T)$ is well fitted by the power law with the critical exponent $\beta \approx 0.4$. Note that the variation of the concentration x of the chiral dopant (from $x = 2\%$ to $x = 0.4\%$) shifts the transition temperature, but does not affect the nature of the $A_d \leftrightarrow C_d$ transition as seen from the $d(T)$ and $\theta_{opt}(T)$ temperature dependences.

Figure 5 additionally shows the interlayer spacing d_C as calculated using equation (7) with $\theta_{opt}(T)$ deduced from the data of Figure 7 and d_A equal to the measured spacing at the smectic A_d to smectic C_d transition point. As is clearly seen, there is a significant discrepancy between the measured and calculated layer spacings. The unusual behaviour of the layer periodicity d reflects the fact that diverse molecular moieties in the smectic C_d phase are very differently tilted with respect to the layer normals and their tilt angles have different temperature dependences. Notice that transition to the tilted phase cannot be attributed

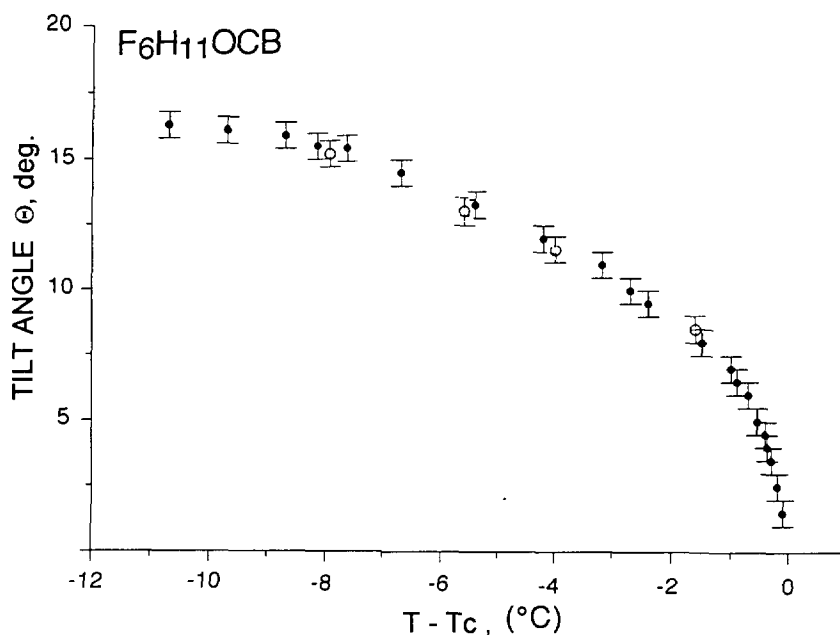


Fig. 7. — Optical tilt angle *versus* relative temperature in the smectic C_d phase for the $F_6H_{11}OCB$ compound doped with a chiral substance, filled and open circles correspond to different series of measurements.

to the formation of the bilayer tilted C_2 phase because of the substantially lower values of molecular tilt (Fig. 7). In order to understand the measured d values in the smectic C_d phase it is necessary to have reliable information about molecular conformations for the F_nH_mOCB compounds comprising sequenced hydrocarbon-perfluoroalkyl chains. Furthermore a change in the size of dimers which seems to be a common feature of smectic A_d and C_d phases may also influence the layer spacing variations in the smectic C_d phase.

3.2. INFRA-RED DICHOISM. — The dichroic ratios measured for $F_4H_{11}OCB$, $F_6H_{11}OCB$ and $F_{10}H_{10}OCB$ are plotted in Figure 8.

The $F_4H_{11}OCB$ compound with a short perfluoroalkyl chain only shows the smectic A_d phase (see Tab. I and Fig. 2). The apparent order parameter $S_{||}^*$ recorded for the cyano (2225 cm^{-1}) and aromatic (1606 cm^{-1}) oscillators abruptly increase at the transition from the isotropic to the smectic A_d phases and remains almost stable (from 0.55 to 0.68) over the whole smectic A_d range. Such high values are typical of smectics and can be regarded as magnitudes of the true order parameter. It can therefore be reasonably postulated that the cyano group and the aromatic core are on average not tilted in the smectic A_d phase. If the whole molecule behaved like a rigid rod, one would find the same value $S_{||}^* = S$ for all other longitudinal oscillators and $S_{\perp}^* = -S/2$ for transverse ones. This is not the case for the two characteristic absorption bands of the perfluoroalkyl chain: the orthogonal CF stretching vibration (1134 cm^{-1}) with $S_{\perp}^* = -0.09$ and the longitudinal CF_2 wagging band (650 cm^{-1}) for which $S_{||}^* = 0.45$, Figure 8a. The apparent order parameter for these two oscillators is much weaker than expected for a rodlike molecule, however the true order parameter obtained from the data using equation (6) is again as high as 0.7. This testifies that the perfluoroalkyl fragments are not in a more disordered conformation than the rigid cores but on average

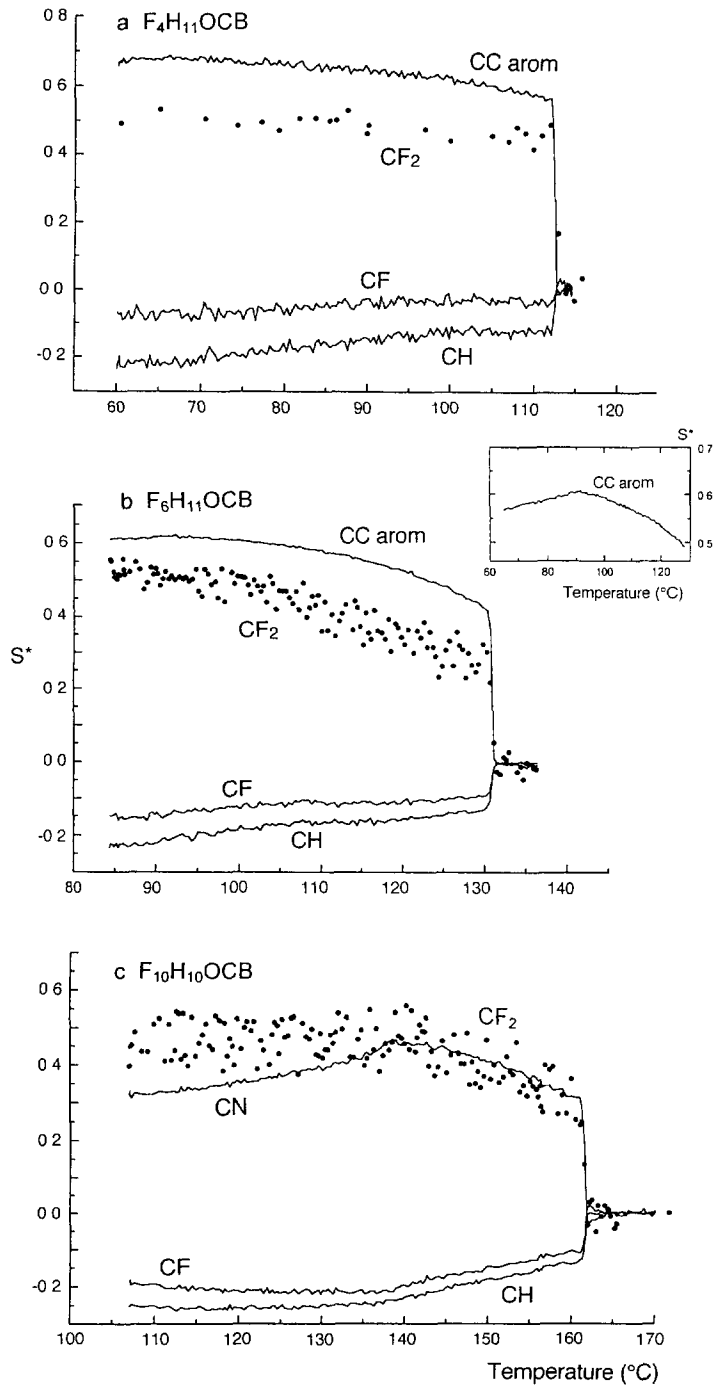


Fig. 8. — Temperature dependences of the apparent order parameter S^* for a) $\text{F}_4\text{H}_{11}\text{OCB}$, b) $\text{F}_6\text{H}_{11}\text{OCB}$ and c) $\text{F}_{10}\text{H}_{10}\text{OCB}$, as measured by IR dichroism for four different oscillators: the C-C aromatic, C-H asymmetric, C-F stretching vibrations (—) and the CF_2 wagging band (\bullet). The inset shows the S^* behaviour of the aromatic C-C band in the vicinity of the $\text{A}_d\text{-C}_d$ phase transition for $\text{F}_6\text{H}_{11}\text{OCB}$.

Table III. — *Thermal variation of the absorption maximum wavenumber for the CH stretching vibrations (F₆H₁₁OCB, KBr pellets).*

T(°C)	Phase	CH <i>asymm.</i>	CH <i>symm.</i>
25	Crystal	2923.4	2852.5
71	Smectic A	2927.7	2856.4
91	Smectic A	2928.1	2856.8
122	Isotropic	2928.8	2856.7

are tilted. This is not in contradiction with the uniaxial character of the smectic A_d phase, provided that the tilted fragments are azimuthally disordered. For alkyl chains the wagging band lies in the range 1420 – 1300 cm⁻¹ where it is hidden by stronger absorption bands, so we have no S_{\parallel}^* at our disposal to know if the same high order parameter is also relevant for alkyl chains. Insight into the chain conformation is given by the position of the CH stretching absorption maxima (Tab. III). As is known, the CH stretching resonance is observed at a higher frequency for gauche conformers [27]. When going from crystal to smectic A_d both symmetric and asymmetric CH stretching absorption maxima are shifted toward higher wavenumbers, a much less pronounced shift is observed when passing from the smectic A_d to the isotropic liquid, hence indicating that gauche conformers are already present in the smectic A_d phase. For both symmetric and asymmetric CH stretching vibrations, the apparent order parameter S_{\perp}^* is in the range from -0.13 to -0.2 (Fig. 8a) again much weaker in absolute value than expected for a rodlike molecule. For lack of S values relevant to the alkyl chains, we have used the values determined for perfluoroalkyl chains to calculate the tilt angle.

In addition to the smectic A_d phase, the F₆H₁₁OCB compound shows a region of tilted C_d phase. The transition to the C_d phase is scarcely detected by a smooth change in slope of the S_{\parallel}^* curves as seen for the bands related to the rigid core (inset to Fig. 8b). In order to calculate the tilt angle of the rigid core in the smectic C_d phase it is essential to know the value of the true orientational order parameter S . In the smectic A_d phase S coincides with the apparent order parameter S_{\parallel}^* . The proper values of the true order parameter S may be obtained by extrapolation of the S_{\parallel}^* temperature dependence in the region of stability of the C_d phase. For this purpose the S_{\parallel}^* temperature dependence in the smectic A_d phase was fitted to a Landau type model that involves the second, third and fourth-order terms in S . This gives [28]

$$S = S_0 \{1 + [1 - \alpha(T - T^*)]^{1/2}\} \quad (8)$$

where T^* is a temperature slightly lower than the temperature T_c of the phase transition to the isotropic liquid, S_0 and α are constants. Good fits were found in the whole temperature range of the smectic A_d phase, moreover, in the zero Kelvin approximation the order parameter S goes to the value which is very close to unity. Note that the power law with tricritical exponent ≈ 0.25 which is relevant for the description of $S(T)$ dependences in the vicinity of the nematic - isotropic phase transition [29], does not work in the case of strong first order smectic A-isotropic transition in polyphiliacs

Table IV summarizes our data on tilt angles of various fragments for the three members of the series. The temperature dependence of the tilt angle θ_{cb} for the cyanobiphenyl moiety calculated on the basis of equation (6) and equation (8) is plotted in Figure 9. The θ_{cb} -dependence is in reasonable agreement with θ_{opt} values obtained directly from electrooptical measurements (Fig. 7). For perfluoroalkyl chains the order parameter S calculated on the basis

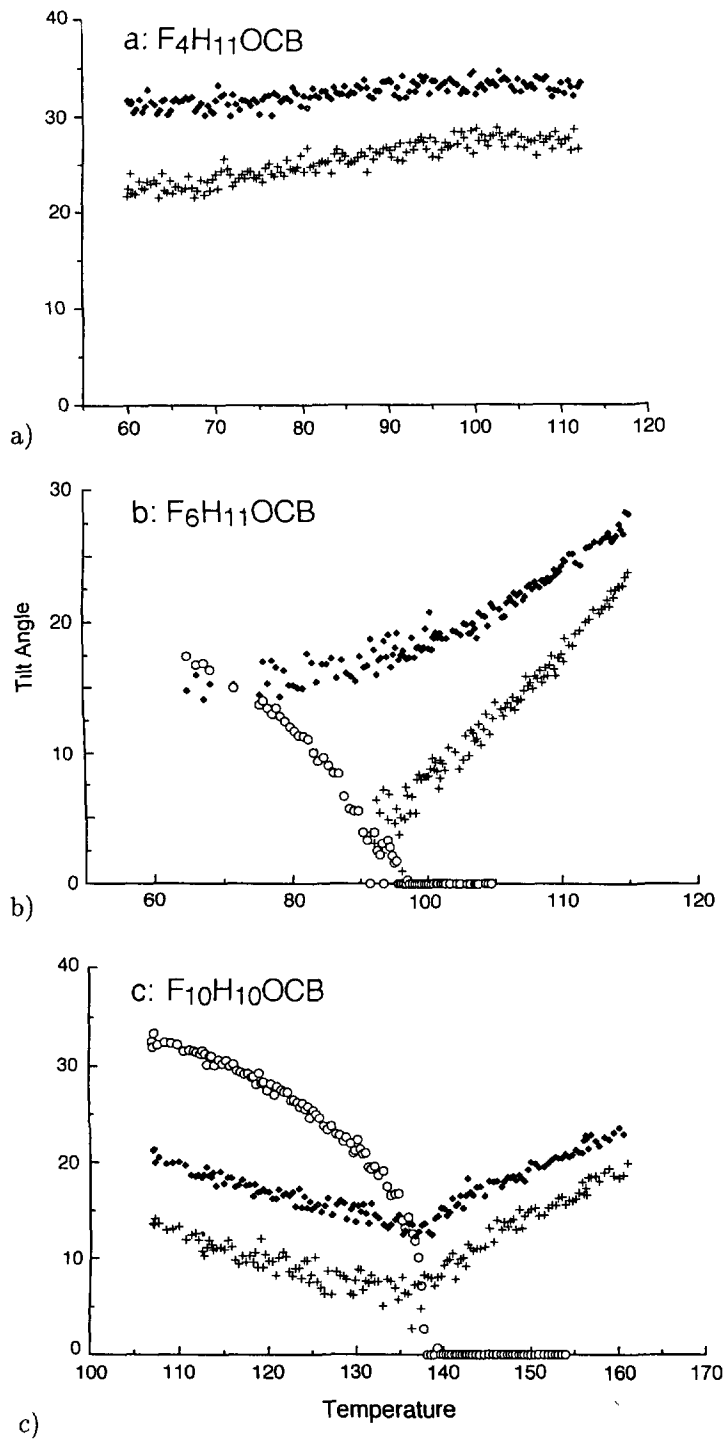


Fig. 9. — Tilt angles of the different molecular fragments as a function of temperature for a) F₄H₁₁OCB, b) F₆H₁₁OCB and c) F₁₀H₁₀OCB: aromatic core (o), perfluoroalkyl chains (◆), alkyl chains (+).

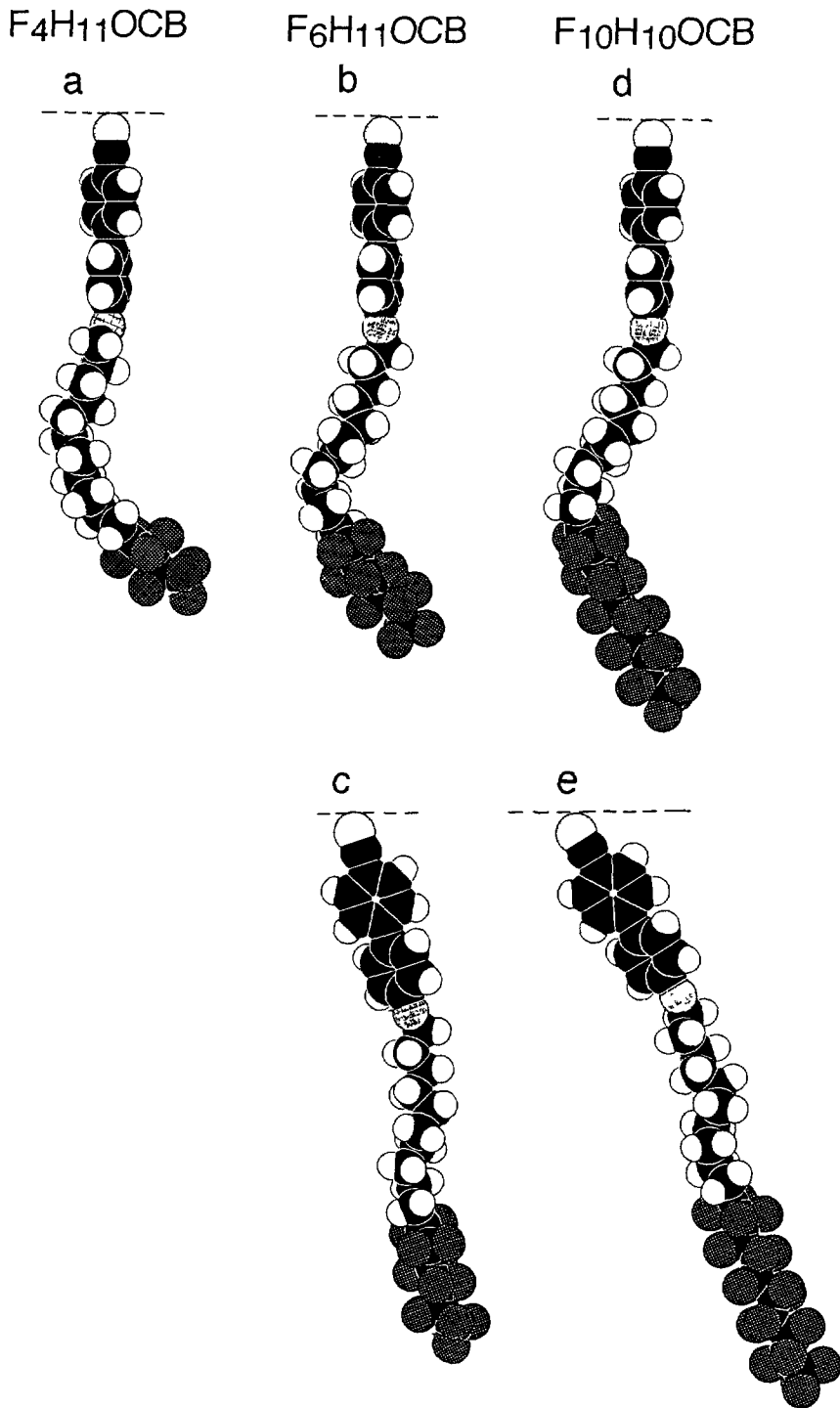


Fig 10. — Preferable molecular conformations in the smectic A_d and C_d phases for a) $F_4H_{11}OCB$; b) and c) $F_6H_{11}OCB$, d) and e) $F_{10}H_{10}OCB$.

Table IV — Summary of tilt angles for the fluoroalkyl (θ_f), alkyl (θ_h) and cyanobiphenyl (θ_{cb}) fragments determined from IR dichroism measurements. Data for the A_d and C_d phases correspond to temperatures close to the transitions to the isotropic and crystalline phases, respectively (compounds 2 and 3).

N	Mesogens	Tilt angles (°)	C_d	$C_d \leftrightarrow A_d$	A_d
1	$F_4H_{11}OCB$	θ_f θ_h θ_{cb}			30 - 34 22 - 28 0
2	$F_6H_{11}OCB$	θ_f θ_h θ_{cb}	15 0 - 5 17	17 0 - 5 0	27 23 0
3	$F_{10}H_{10}OCB$	θ_f θ_h θ_{cb}	20 14 32	13 4 - 6 0	23 19 0

of equation (6) was also fitted to a square root law of the equation (8) type over the whole mesomorphic range. Similarly to the $F_4H_{11}OCB$ compound, in the whole smectic A_d region of $F_6H_{11}OCB$, the apparent order parameter S_{\perp}^* for the orthogonal CF stretching oscillator is less in absolute value than $|-S/2|$ (Fig. 8b) which corresponds to a certain tilt. With decreasing temperature S_{\perp}^* decreases to take a stable value close to $-S/2$ in the smectic C_d range. This means that the average tilt angle θ_f of the perfluoroalkyl moiety gradually decreases when approaching the smectic C_d phase (Fig. 9b). The average tilt angle θ_h of the alkyl fragment behaves in a similar way, attaining the small value about 4-5 degrees at the phase transition point. This situation markedly differs from the behaviour of the perfluoroalkyl and alkyl chains in the $F_4H_{11}OCB$ compound, where the θ_f and θ_h angles remain approximately the same (33 and 25 degrees respectively) over the whole smectic A_d region (Fig. 9a). The $F_{10}H_{10}OCB$ mesogen with equally lengthy perfluorinated and alkyl chains behaves similarly to $F_6H_{11}OCB$ compound (Fig. 9c). The only differences are in the relatively large values of the tilt angle for the cyanobiphenyl moiety ($\theta_{cb} \approx 30$ deg.) and the minimum of the θ_f and θ_h temperature dependences at the phase transition point (Figs. 8c and 9c). The preferable molecular conformations in smectic A_d and C_d phases for the three members of the series are displayed in Figure 10.

Bartolino and coworkers were the first to show that an aromatic rigid core tilts somewhat independently of the lengthy aliphatic end chains within the smectic C layers ("zig-zag" model) [30]. The validity of this model was confirmed later in precise X-ray and optical measurements of the smectic C phase for a number of compounds [31, 32]. The strong "zig-zag" effect has also been observed in the tilted smectic phases of polyphilics with perfluoroalkyl chains at both ends of the molecules [11]. Our present measurements indicate that similar behaviour is also characteristic of the smectic A_d and C_d phases in cyanoterminated polyphilics. On cooling from A_d phase the tilt angles for perfluoroalkyl and alkyl chains diminish and the whole molecule takes a more stretched conformation (Fig. 10). In the smectic C_d phase due to the tilt of cyanobiphenyl moiety the molecule conformations are again of the zig-zag type and characterized by a homogeneous tilt for perfluoroalkyl and biphenyl fragments (Fig. 10).

3.3. INTERLAYER SPACINGS. — Once the preferable molecular conformations for cyanoterminated polyphilics have been determined, the analysis of the layer spacing thermal behaviour may be continued. In the simplest structure model of the smectic A_d and C_d phases the exis-

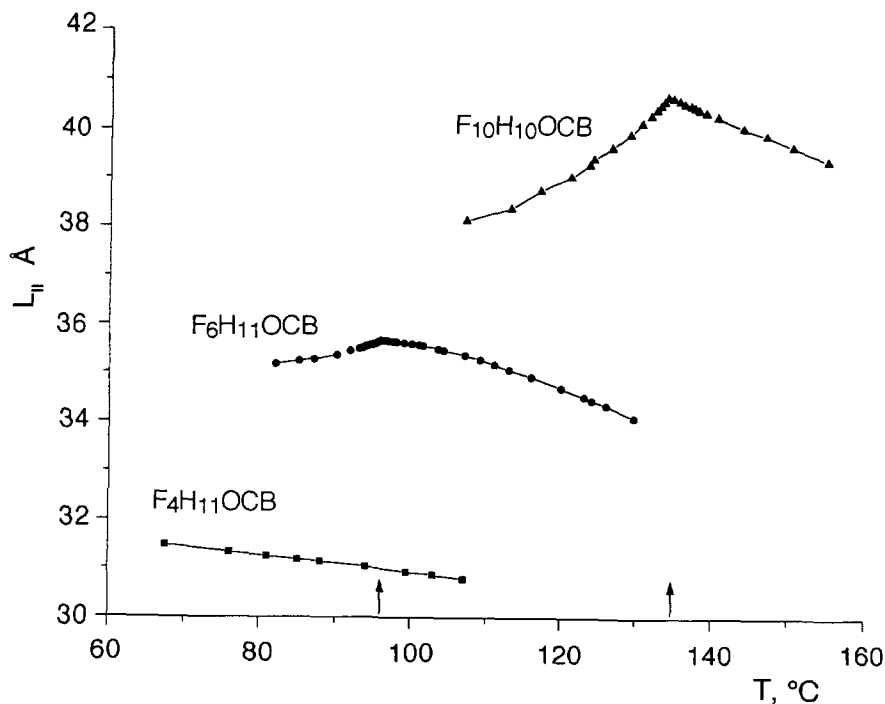


Fig. 11. — Temperature variations of the parameter $L_{||}$ characterising the length of individual molecules for $F_4H_{11}OCB$ (■), $F_6H_{11}OCB$ (●) and $F_{10}H_{11}OCB$ (▲); arrows indicate the smectic A_d -smectic C_d phase transition points.

tence of periodicity which is incommensurate with the molecular length may be attributed to the pairs of overlapping antiparallel molecules (dimers). The expression relating the measured layer thickness d to the size of individual molecules in this case may be written as

$$d = 2(L_{||} - \Delta) = 2L_{||}(1 - \Delta/L_{||}) \quad (9)$$

where 2Δ is a measure of overlapping of molecules ($\Delta/L_{||} = 0.5$ and 0 for the extreme cases of monolayer and bilayer layering respectively) and $L_{||}$ is the sum of the projections of different molecular fragments on the layer normals

$$L_{||} = l_{cb} \cos \theta_{cb} + l_f \cos \theta_f + l_h \cos \theta_h \quad (10)$$

The lengths l_{cb} , l_f and l_h correspond to the cyanobiphenyl, perfluoroalkyl and alkyl moieties of molecules respectively (the molecular model predicts, for instance, $l_{cb} = 12.4$ Å, $l_f = 10.1$ Å, $l_h = 13.7$ Å for the $F_6H_{11}OCB$ compound). With a knowledge of the tilt of various fragments (Fig. 9 and Tab. 4) and the measured d values, on the basis of equations (9) and (10) the temperature dependences of the molecular length $L_{||}$ and parameters Δ , $\Delta/L_{||}$ may be obtained (Figs. 11, 12 and Tab. IV). In the case of $F_{10}H_{11}OCB$ compound we have used the tilt angles determined for its nearest homologous member $F_{10}H_{10}OCB$. As it might be expected the $L_{||}(T)$ dependences display the fracture at the smectic A_d -smectic C_d phase transition point for the $F_6H_{11}OCB$ and $F_{10}H_{11}OCB$ compounds (Fig. 11). In the first case a relatively small decrease of $L_{||}$ with temperature in the C_d phase is mainly related to the tilt of cyanobiphenyl moiety (Fig. 9b). For the $F_{10}H_{11}OCB$ compound the temperature variation of molecular length

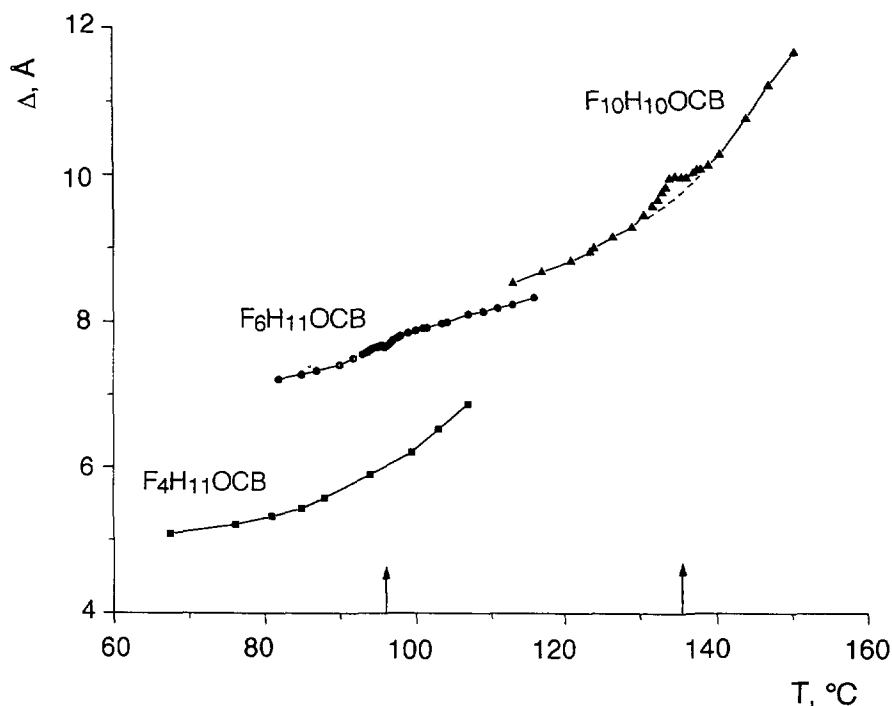


Fig. 12. — Temperature dependence of the parameter Δ describing the average relative displacement of the molecules in dimers for $F_4H_{11}OCB$, $F_6H_{11}OCB$ and $F_{10}H_{10}OCB$ compounds. The broken line indicates a regular temperature behaviour.

Table V. — The values of the various parameters characterising the dimeric structure of the smectic layers determined from equations (9), (10). Data for compounds 2 and 3 correspond to the $A_d \Leftrightarrow C_d$ transition region and to $T = 100$ °C for compound 1.

N	Mesogen	$L_{ }$, Å	d , Å	Δ , Å	$\Delta/L_{ }$	$d/L_{ }$
1	$F_4H_{11}OCB$	30.9	49.4	6.2	0.201	1.60
2	$F_6H_{11}OCB$	35.7	56.1	7.6	0.214	1.57
3	$F_{10}H_{10}OCB$	40.7	61.4	10.0	0.246	1.50

$L_{||}$ in the smectic C_d phase is much more pronounced and is due both to the large tilt of the cyanobiphenyl moiety and to the tilt of the flexible chains (Fig. 9c). Note that $L_{||}$ varies also in the smectic A_d phase of these compounds which is characteristic of the smectic build-up of the conformationally flexible molecules. The temperature dependences of the relative displacement Δ for the three members of the series are more or less similar and reflect the tendency for the formation of the more elongated dimers with decreasing temperature (Fig. 12 and Tab. V). Because both $L_{||}$ and Δ diminish with decreasing temperature in the smectic C_d phase, the temperature dependence of the interlayer spacing d in accordance with equation (9) depends on the relative values of the $L_{||}(T)$ and $\Delta(T)$ derivatives. For example in the $F_6H_{11}OCB$ compound where $L_{||}(T)$ and $\Delta(T)$ derivatives are approximately equal, the $d(T)$

dependence is nearly constant (Figs. 4 and 5). In the common case the layer spacing d in the smectic C_d phase may decrease, be constant or even increase with decreasing temperature in good agreement with the measured $d(T)$ dependences (Fig. 4). One can expect that the tilt of strongly corrugated triphilic molecules may affect the Δ values. Such coupling does occur in vicinity of $A_d \leftrightarrow C_d$ phase transition for the $F_6H_{11}OCB$ and $F_{10}H_{11}OCB$ compounds where the irregularity in the $\Delta(T)$ dependences is readily seen (Fig. 12). Note that because of the dependence on molecular structure the sign of deviation from the regular $\Delta(T)$ behaviour may change. So far we have used the assumption that A_d and C_d layers in polyphilics consist of antiparallel dimers. Actually in the smectic A_d phase not all nearest neighbour molecules form dimers and a peculiar type of equilibrium between a number of monomers, head to head dimers and diverse lateral dimers exists in the system [9, 10, 33]. For example in the spin-gas model [34], well describing the delicate stability of frustrated smectics, approximately one-third of molecules freely permeate through a layer and reverse their dipoles. This means that the relative shift Δ in equation (9) is a result of a statistical averaging over all possible dipole and sterical configurations in the system rather than the characteristic of a certain static object. From this point of view the variations of Δ with external conditions reflect changes in the spectrum of dimers. This can be easily proved for some models. For example the large ratios $d/L = 1.5 \div 1.7$ (layer spacing/ molecular length) for cyanoterminated polyphilics indicate the tendency for the bilayer ordering in the system. In this case the properties of smectic layers depend mainly on the relative number of lateral and head to head dimers and the layer spacing may be written as: $d \approx 2L/(2 - \tau)$ where τ is the proportion of head to head dimers [33]. Thus, the decrease of Δ with temperature (Fig. 12) may be treated as an increase of the relative number of head to head or other elongated dimers. Nevertheless, we believe that a simplified dimeric model can describe the most substantial features of the layer organisation in cyanoterminated polyphilics. Further progress in the understanding of the layer structure in the smectic A_d and C_d phases may be achieved on the basis of the advanced microscopic model which enables one to calculate the temperature variations of parameter Δ .

4. Discussion

4.1. SMECTIC A_d PHASE. — As was shown above, the cyanoterminated polyphilic compounds display a broad range of the smectic A_d phase, the main structural unit of which is the pair of overlapped molecules. The cyano groups at the end of mesogenic molecules are able to achieve π -electron conjugation with the nonsaturated benzene rings of the aromatic core. As a result, delocalization of π -electrons over the entire conjugation chain occurs. On the formation of dimers, the polarized molecules tend to be arranged in such a way that the opposite charges of neighbouring molecules are located at a minimum distance (the quantum-chemical calculations confirm such a tendency [35]). This favours an antiparallel arrangement of neighbouring molecules with an average relative displacement 2Δ of the order of the length of cyanobiphenyl moiety: $\Delta \approx 12 - 14 \text{ \AA}$, Figure 12, Table V. The same situation occurs for the nonpolyphilic fully hydrocarbon analogues of the F_nH_mOCB compounds (8OCB, 12OCB, Tab. I), which form the smectic A_d phase with the values of $2\Delta \approx 12.5 \text{ \AA}$. Thus, we can conclude that the basic structural motive for the cyanoterminated polyphilics has the same origin (i.e., strong dipole-dipole correlations) as for a large variety of mesogens with strong terminal dipoles. The validity of this concept was confirmed in experiments where $F_6H_{11}OCB$ compound was doped with 8OCB mesogen. The smectic C_d phase completely disappears in a mixture with 10% of 8OCB, replaced by a wide region of smectic A_d phase (see Tab. I). 8OCB and cyanoterminated polyphilics possess the same electronic structure and hence are able to form mixed dimers of the 8OCB- $F_6H_{11}OCB$ type with terminal chains of different length and nature. The appear-

ance of a small amount of mixed dimers instead of the initial ones does not affect the stability of smectic A_d phase. In contrast to A_d phase, the smectic C_d phase is much more sensitive to the structure of the terminal chains, which is indicative of the crucial role of packing entropy in the formation of this phase.

The enhanced stability of the smectic A_d phase in cyanoterminated polyphilics may be understood if we take the sterical and conformational degrees of freedom into consideration. Specific features of the sequenced perfluoroalkyl-alkyl chain in polyphilic mesogens have been discussed earlier [11, 21, 22]. The most important of them are the enhanced rigidity of perfluorinated moieties and the fact that they are much bulkier than the aliphatic and aromatic fragments. Thus, for the perfluoroalkyl chain tilted through an angle $\theta_f \approx 20 - 30^\circ$ the typical cross section $\sigma_f = s_f / \cos \theta_f$ is about $32 - 35 \text{ \AA}^2$. For the perpendicularly oriented and cylindrically averaged cyanobiphenyl moiety, which is characteristic of A_d phase, we have $\sigma_{cb} = s_{cb} \approx 22 \text{ \AA}^2$. The alkyl chain has a cross-sectional area close to that of biphenyl $\sigma_h \approx 20 - 22 \text{ \AA}^2$. On the other hand the alkyl chains, due to the relatively small activation barriers for the trans-gauche rotations, are highly flexible and are able to accommodate their conformations to satisfy requirements of optimum packing.

The comparison of σ_{cb} and σ_f clearly indicates that a denser packing in the smectic A_d phase may be achieved with a partial overlap of the rigid biaryl fragments. Furthermore, the bulky fluoroalkyl chains at the ends of flexible alkyl chains may in an optimum way fill the free space in the regions outside the overlapped rigid cores in smectic A_d layers. Thus, the presence of terminal perfluoroalkyl groups in F_nH_m OCB molecules stabilizes the smectic A_d layering, sufficiently expanding the range of its existence. On the other hand the additional conformational entropy related to the sequenced hydrocarbon-perfluorinated chain in polyphilics prevents the crystallization of the aromatic parts of the molecules in the smectic layers as it happens for fully hydrocarbon analogues with the same length of the tail (H_{18} OCB, Tab. I, Fig. 3).

4.2. SMECTIC C_d PHASE. — Let us summarize the most important experimental results concerning C_d phase.

(i) The triphilic character of terminally polar mesogens is crucial for the formation of C_d phase. It appears on the phase diagram of F_nH_m OCB compounds when both hydrocarbon and perfluorinated fragments in sequenced chain are lengthy enough ($n, m \geq 5$).

(ii) The molecular conformations change continuously over the whole temperature range of the smectic A_d and C_d phases. On cooling from the A_d phase the tilt angles for perfluoroalkyl and alkyl chains decrease and the whole molecule takes a more stretched conformation. The tilt angles θ_f and θ_h display minima and relatively low values in the $A_d \leftrightarrow C_d$ phase transition region. The transition to C_d phase is characterized by the tilt of cyanobiphenyl moiety, which continuously varies from zero to $\theta_{cb} \approx 16^\circ$ and $\theta_{cb} \approx 30^\circ$ in F_6H_{11} OCB and $F_{10}H_{11}$ OCB, respectively. The molecules are in zig-zag conformation and characterized by a homogeneous tilt of perfluoroalkyl and cyanobiphenyl moieties.

(iii) The smectic C_d layers similarly to the case of the high temperature A_d phase, mainly consist of antiparallel dimers. The relative displacement of molecules in dimers 2Δ systematically decreases with temperature (except for a small region around $A_d \leftrightarrow C_d$ transition). Both the Δ and molecular length contribute to the layer spacing temperature variations.

An important question arises on whether the above experimental data are sufficient to understand, at least qualitatively, the origin of the formation of the C_d phase. One can find in the literature a number of microscopic models of the smectic C phase on which there is no general agreement (the reader is referred to the discussion in papers [2-4]). At the present time the most advantageous model is that proposed by Van der Meer and Vertogen [3] in which the tilt of molecules is originated from the induction interaction of transverse dipoles and the polar-

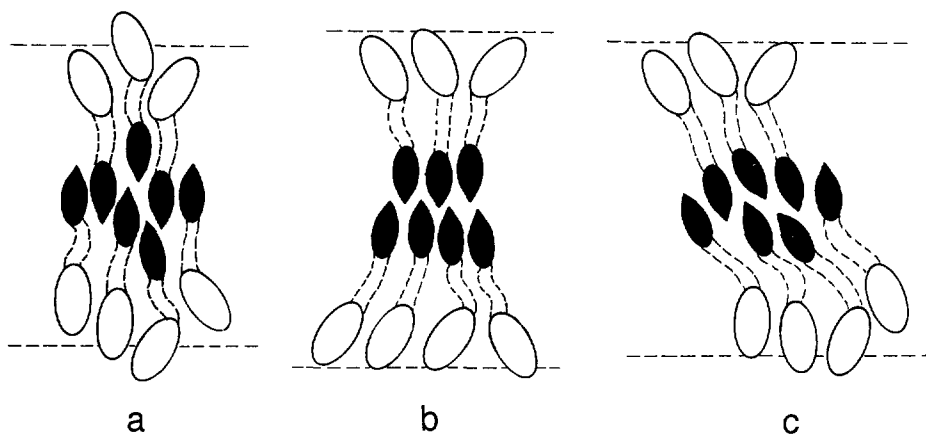


Fig. 13. — Structure of the smectic A_d and C_d layers for $F_6H_{11}OCB$ compound: a) smectic A_d layers; b) sterical mismatch in the limit case of bilayer A_2 layering; c) smectic C_d layers.

izable centres of neighbouring molecules. This interaction in contrast to the dipole model of McMillan [36] or sterical model of Wulf [37], is compatible with the more or less free rotation of the molecules about their long axes which is characteristic of the smectic C phase. Furthermore the induction interaction in the model [3] effectively compensates the decrease of entropy of packing due to the tilt of molecules in the layers. From this point of view the formation of tilted analogues of smectic A phases, i.e., C_1 , C_2 and C_d , is possible for terminally polar mesogens having transverse dipoles. As mentioned above, the absence of smectic C_d phase on the phase diagrams of conventional terminally polar mesogens most likely results from unfavourably low values of packing entropy in the dimeric C_d phase as compared to smectic C_1 and bilayer C_2 phases. The effect of the entropy of packing may be interpreted as follows: in the smectic A_d and C_d phases the transverse dimension of the overlapped cores considerably exceeds that of alkyl chains. This leads to excess free volume in the region of alkyl chains and decreases the entropy of packing. Additionally in the tilted phase there is more excluded area in the layer as compared to smectic A phase and thus less free space for the molecules to jostle around. Thus both the dimeric organization and molecular tilt disfavour smectic C_d structure.

The above reasonings are valid for relatively simple diphilic molecules. In the case of polyphilic mesogens the rigid perfluoroalkyl and cyanobiphenyl fragments at the ends of the flexible lengthy hydrocarbon chain may act together (more or less independently) to stabilize a tilted phase. At relatively high temperatures the presence of gauche bonds in alkyl chains ensures the large tilt angles of perfluoroalkyl moieties thus effectively stabilizing the smectic A_d phase (Fig. 10). With decreasing temperature, the alkyl chains become less and less flexible and the average tilt angle for perfluoroalkyl chains diminishes: the whole molecule takes a more stretched conformation (Fig. 13b). In conventional terminally polar mesogens, such a behaviour leads to an unfavourable decrease of the entropy of packing due to the excess free volume in the region of terminal chains and induces the transition to either the smectic A_1 , A_2 , C_2 phases or the nematic phase (the frustration effect [5,38]). One of the exotic ways to escape frustration is to go over to two-dimensional \tilde{C} phase which has a local bilayer structure [5,38]. The terminally polar polyphilic mesogens show a distinctly different way of escaping the unfavourable packing of dimerized molecules within layers. In the smectic A_d phase composed

of polyphilic molecules, moieties of different chemical nature are forced to coexist in the same regions whereas the polyphilic effect favours the formation of well segregated sublayers. In this respect, the simplest evolution of the system with decreasing temperature would be the formation of a smectic A_2 mesophase. Such a tendency is indeed reflected by the thermal behaviour of the interlayer spacing in the S_{Ad} phase. However, in the extreme case of the bilayer A_2 phase, the sterical mismatch between perfluoroalkyl chains and rigid cores is no longer compensated by overlapping molecules in dimers (¹), Figure 13b. On the other hand, at the transition to the C_d phase, the molecules again accept a zig-zag shape, thus decreasing the packing differences between the central part of dimers and terminal chains. Note that the projection of the cyanobiphenyl cross-section onto the smectic layer plane in the smectic C_d phase amounts only to $\sigma_{cb} = 22 / \cos 30^\circ \approx 25 \text{ \AA}^2$ which is much less than that of the fluorinated chain $\sigma_f \approx 33 \text{ \AA}^2$. Hence, the tilt of cyanobiphenyl moiety by itself cannot destabilize the smectic C_d phase in terminally polar polyphilics. On the contrary, in conventional terminally polar mesogens, the cross-section of hydrocarbon chain is of the order of $\sigma_h \approx 22 - 23 \text{ \AA}^2$ which is compatible with that of the rigid core. This makes the existence of the C_d phase in diphilic mesogens highly unlikely.

In conclusion, the tilted dimeric C_d phase of enhanced stability has been found for a number of cyanoterminated polyphilic mesogens bearing sequenced hydrocarbon-perfluoroalkyl chains. The features of the $A_d \leftrightarrow C_d$ phase transition are determined by the conformational freedom of molecules mainly arranged in dimers as well as the sterical and chemical differences between diverse molecular fragments (polyphilic effect). The conformationally flexible triphilic liquid crystals display a new mechanism of compensation for the changes of packing entropy within the layers related to the tilt of diverse molecular fragments through different angles. This mechanism may play a prominent role in stabilizing various types of tilted phases formed by polyphilic mesogens.

Acknowledgments

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(¹) In reference [39], Nguyen *et al.* report an observation of the smectic A_2 phase for polar mesogens bearing a sequenced polyfluoroalkyl chain. In this case however, the d/L ratio (layer distance/molecular length) was in the range $1.67 \div 1.69$ which again corresponds to a smectic A_d packing.

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