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Smectic layering in polyphilic liquid crystals : X-ray diffraction and infra-red dichroism study

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Abstract. — We present X-ray diffraction measurements of lamellar ordering for a new class of mesogens — polyphilic compounds — which were reported to form achiral ferroelectrics. Two phases called smectic X and X′ manifest polar properties. Analysis of the scattering profiles parallel and perpendicular to the smectic layers provides detailed data on the structure of smectic A, smectic X and X′ phases of these compounds. Smectic X′ phase corresponds to a strongly defective layered structure of the smectic C type with longitudinal correlation length $\xi_{\parallel} \leqslant 200$ Å. The molecules are in a zigzag conformation and are tilted with respect to the layer normals. Infra-red dichroism data show that the biphenyl moiety and the polyfluorinated chain of molecules form angles of 56° and 26° with respect to the layer normals. In the smectic X phase, three types of layering coexist : (i) polar layers with tilted molecules, (ii) a modulated structure of the same type consisting of layers periodically shifted with respect to each other and (iii) the orthogonal smectic A layers with a spacing of 41 Å incommensurate with period 35 Å of the polar smectic layers. The coexistence of such incommensurate structures is only possible in a strongly disordered medium. Infra-red dichroism data are consistent with this picture. The in-plane structure factor in smectic X, X′ phases reveals two features of polyphilic compounds : a dramatic increase in the short-range positional correlations ($\xi_{\perp} \approx 35 \div 40$ Å or approximately 7 or 8 molecules in the local in plane order) and splitting of the intensity profiles into three peaks. The latter corresponds to the appearance of nearest-neighbour molecular stacking at different distances. The formation of polar, either uniform or modulated layered structures in the system of polyphilic molecules is discussed.

1. Introduction.

Smectic A and C mesophases are characterized by a translational order in one dimension and a liquid-like positional order in the two others. In the conventional smectic A_1 phase, rod-like molecules are randomly oriented up and down within each layer ; this corresponds to a quadrupolar symmetry of the medium. The bilayer smectic A_2 phase with antiferroelectric

ordering of permanent dipoles and the partly bilayer smectic A_d formed by the antiparallel dimers are known to form when asymmetric mesogens possessing strongly polar end groups are used [1]. These layered structures all belong to nonpolar groups of symmetry. There is no fundamental reason for the non-existence of polar phases (pyroelectric, ferroelectric) with a $C_{\infty v}$ symmetry [2] ; however, until recently only the chiral smectic C*, F*, I* phases have been shown to be ferroelectric [3]. Calculations taking into account dispersive, dipolar and steric interactions for the case of simple rod-like mesogens show that a polar smectic A phase with a finite macroscopic polarization is strongly destabilized almost independently of the location of molecular dipoles [4]. It means that additional chemical and (or) steric forces are required to overcome the unfavourable parallel arrangement of the dipoles. From this point of view, a significant interest is generated by the recent observation of polar properties in a new class of non-chiral mesogens — polyphilic compounds [5-7]. These are made up of a sequence of chemical moieties differing in their chemical nature, for example : perfluoroalkyl chain — hydrocarbon chain — rigid biaryl core — and again perfluoroalkyl chain, figure 1. The basic idea stimulating the synthesis of these compounds was that in polyphilic mesogens three or more chemically different fragments (e.g. A, B, C, A′) can segregate favouring a noncentrosymmetric arrangement of molecules within the smectic layers. If this type of order continues throughout the stack of the layers, the corresponding phase is polar. Similar ideas about the appropriate design of constituent molecules which may form the nonchiral polar liquid crystalline phases were also discussed theoretically [8-10].

X-ray scattering provides valuable information on the structure of smectic phases in the direction both parallel and perpendicular to the smectic planes. To elucidate the structure and to relate it to the observed polar behaviour of polyphilic mesogens we have initiated X-ray diffaction studies of smectic ordering on well-oriented samples of the compounds manifesting polar properties. To have information on the conformation of molecules forming polar smectic layers we also measured the linear dichroism for various vibrational bands. The two techniques have provided valuable data on the molecular structure of polyphilic compounds relevant to their ferroelectric behaviour.

2. Experimental technique.

2.1 SUBSTANCES. — The molecular structure of polyphilic compounds I and II are shown in figure 1. Compounds I and II have been synthesized according to the method described earlier [7]. These mesogens differ from each other by the direction of their longitudinal dipoles since the ether and ester linkages have been exchanged. Pure compound I and a mixture of the two derivatives M70 (70 %I : 30 %II), both showing polar properties [6, 7], have been investigated. The mesomorphic behaviour was investigated by DSC, optical microscopy and X-ray diffraction. The phase sequence for M70 is :

$$X' \underset{84\,^\circ C}{\overset{87\,^\circ C}{\rightleftarrows}} A \overset{106\,^\circ C}{\rightleftarrows} I .$$

The smectic X′ phase which has been reported to be polar is enantiotropic and can be overcooled down to room temperture. The A → X′ phase transition is strongly first order with a temperature hysteresis of ≈ 3 °C. In contrast to M70, pure compound I demonstrates a fairly complicated sequence of phases :

$$K \xrightarrow{96\,^\circ C} A \overset{113\,^\circ C}{\rightleftarrows} I$$

$$76\text{-}92\,^\circ C \quad \uparrow \quad X \quad \downarrow \quad 88\,^\circ C$$

The monotropic smectic X phase has a tendency to crystallize in the temperature range 76-92 °C, however, it may be overcooled down to room temperature.

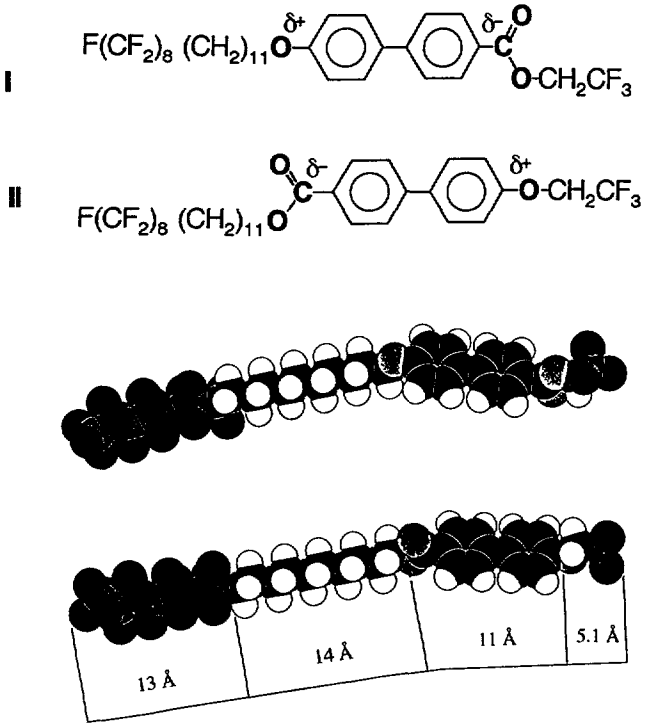

Fig. 1. — Structure and molecular models of polyphilic compounds I and II.

2.2 X-RAY ANALYSIS. — X-ray investigations were carried out using CuK_α radiation and two types of computer controlled diffractometers. The intensity profiles in the small scattering angles region were determined using a linear position-sensitive detector and a three slit collimation scheme with a nickel filter or a graphite monochromator [11]. The longitudinal resolution thus obtained was $\Delta q_\parallel = 2 \times 10^{-3}$ Å^{-1} (full width at half maximum, FWHM). The components of the scattering wave vector $q_\parallel$ and $q_\perp$ are parallel and perpendicular to the director **n** respectively ($q = \frac{4\pi}{\lambda} \sin\theta = \frac{2\pi}{d}$, d is a layer spacing). Thus, measurements of the longitudinal correlation lengths were limited to $\xi_\parallel = 2/\Delta q_\parallel \approx 900$ Å. the actual width of profiles in the $q_\perp$ direction was limited by the sample mosaic.

Two dimensional diffraction patterns in the wide scattering angle region were studied using a KARD diffractometer with a two-coordinate detector and pinhole collimation of the incident radiation [12]. The detector is based on a planar proportional chamber with fast delay lines and has 256 × 256 pixels of the size 1.3 × 1.3 mm (FWHM). With a sample-detector distance of 800 mm, the resoltion $\Delta q \approx 10^{-2}$ Å^{-1} was achieved. Intensities in each channel were measured in one scale, i.e. space angle and nonuniformity in any point did not exceed 0.6 %. In our data analysis, intensity profiles were modelled by simple Lorentzian line shapes. The complicated spectra were analyzed with the least-squares fits by a sum of up to three Lorentzian peaks, each to be characterized by the intensity, position and width.

The absence of the nematic phase in the compounds under study makes impossible the effective orientation of the director in a magnetic field : on slow cooling down from the

isotropic phase in capillaries, an applied magnetic field of 1.2 T has provided the mosaicity of the order of 10° FWHM, this geometry was used to characterize the M70 compound. This mosaicity was not sufficient to resolve the arrangement of the off-axis diffraction spots characterizing the modulated states in compound I [13]. In order to study well aligned samples, we used the tendency of mesogenic molecules with certain terminal groups for homeotropic alignment on clean polished substrates [14]. In our experiments, oriented films of thicknesses 10-100 μm were obtained by inserting the substance between two thick polished beryllium plates (Fig. 2). On cooling down from the isotropic phase, spontaneously oriented films form in which smectic planes lie parallel to the substrate surface. The mosaicity thus obtained was typically of about 1 ÷ 2° FWHM.

2.3 INFRA-RED DICHROISM. — The ability of polyphilic compounds to form (spontaneously) homeotropically oriented films on NaCl substrates was used for measuring the infra-red dichroism. The films were prepared by melting a small amount of substance on a heated

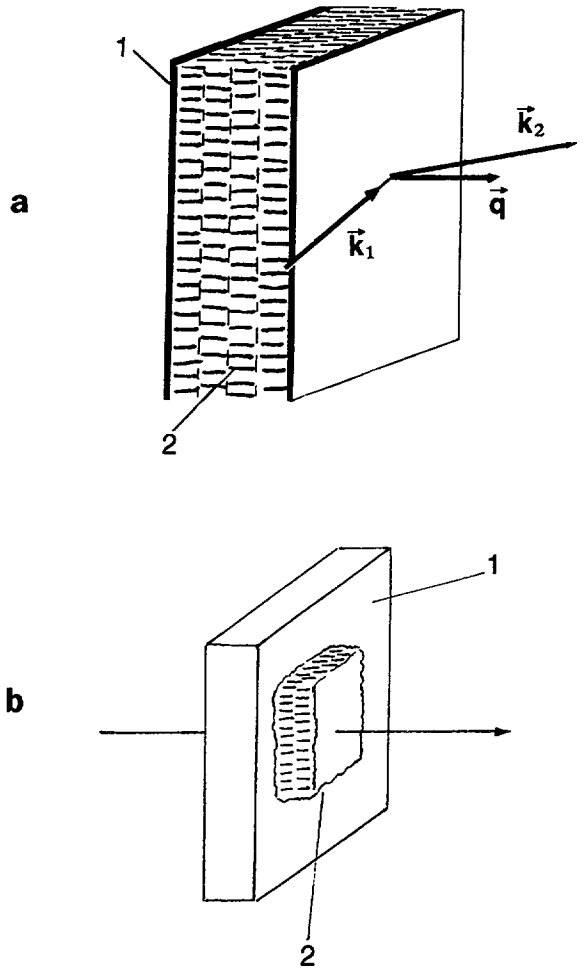

Fig. 2. — (a) X-ray diffraction geometry with the momentum transfer **q** parallel to the layer normal. 1) beryllium plates ; 2) smectic liquid crystal in homeotropic alignment. (b) experimental geometry used for infrared dichroism : 1) NaCl plate ; 2) smectic liquid crystal in homeotropic alignment.

substrate with a subsequent spreading of drops over the surface with a teflon blade. The upper surface of the layer was free.

The well known technique [15] of comparison of the absorbance (optical density) in the isotropic phase (D_i') with that of a homeotropically oriented smectic phase (D_h'), figure 2b, was modified to take into account the regular (isotropic) part of the temperature dependence of the vibrational band intensities. The latter was measured on the same substances incorporated in KBr pellets. For certain bands of the polyphilic compounds studied such a dependence is very strong and can dramatically influence the results of the dichroism study. Thus, at each temperature, all intensities of dichroic vibrational bands in mesophases were normalized to the corresponding band intensities in KBr pellets.

The apparent « order parameter » for each vibrational oscillator of interest was calculated using the formula :

$$S^* = 1 - (D_h/D_i) \tag{1}$$

where D_h and D_i are normalized optical densities. The angles of orientation of vibrational oscillators (ψ) with respect to the normal to smectic layers were calculated according to equation :

$$S^* = SS_\psi = S[1 - (3/2)\sin^2\psi] \tag{2}$$

where S is the true orientational order parameter of a smectic phase.

The measurements of infra-red spectra were carried out within the wavenumber range from 400 to 4 000 cm^{-1} using a Perkin-Elmer (model 1600) FTIR spectrometer equipped with a thermal jacket controlling the temperature of a liquid crystal cell.

3. Experimental results.

We start the description of our experimental results with a mixture of polyphilic compounds M70 as its structure is simpler than that of pure compound I.

3.1 Mixture M70.

Interlayer spacing. — Figure 3 shows the temperature dependence of the interlayer spacing in the smectic A and X′ phases. The diffraction patterns in the high temperature smectic phase show up to three orders of resolution limited peaks $\mathbf{q}_{1n} = (0\,;\,0\,;\,nq_{\parallel 1})$ resulting from the smectic A order ($q_{\parallel 1} = 2\pi/d_1$; n = 1-3). The interlayer periodicity, d_1 = 42.7-44.5 Å in dependence of temperature, slightly exceeds the maximum molecular length (43 Å in the fully extended conformation). The ratio of intensity of the second harmonic to the first is about $I(2q_0)/I(q_0) \approx 1.5 \times 10^{-1}$ that is two orders of magnitude higher than in conventional smectics A.

In the X′ phase, the X-ray diffraction in the small scattering angles region shows three orders of reflections $\mathbf{q}_{2n} = (0\,;\,0\,;\,nq_{\parallel 2})$ corresponding to a lamellar structure with the period $d_2 = 2\pi/q_{\parallel 2} \approx 35$ Å (Fig. 3). The latter is significantly less than the molecular length. These peaks are not resolution limited ; the correlation length in the direction parallel to the director is $\xi_{\parallel 2} = 2/\Delta q_{\parallel 2} \leqslant 200$ Å (Fig. 3). Thus, the one dimensional lamellar structure in the smectic X′ phase appears to have no true long-range translational order. The interlayer spacing which is less than the length of individual molecules corresponds to a tilted arrangement of molecules or their moieties. We can conclude that the smectic X′ phase is an example of the strongly defective periodic structure in which smectic C-like layers are not correlated in space.

The infra-red dichroism studies allowed a fairly precise determination of the molecular shape both in the smectic A and X′ phases. We have measured the angles of orientation of the

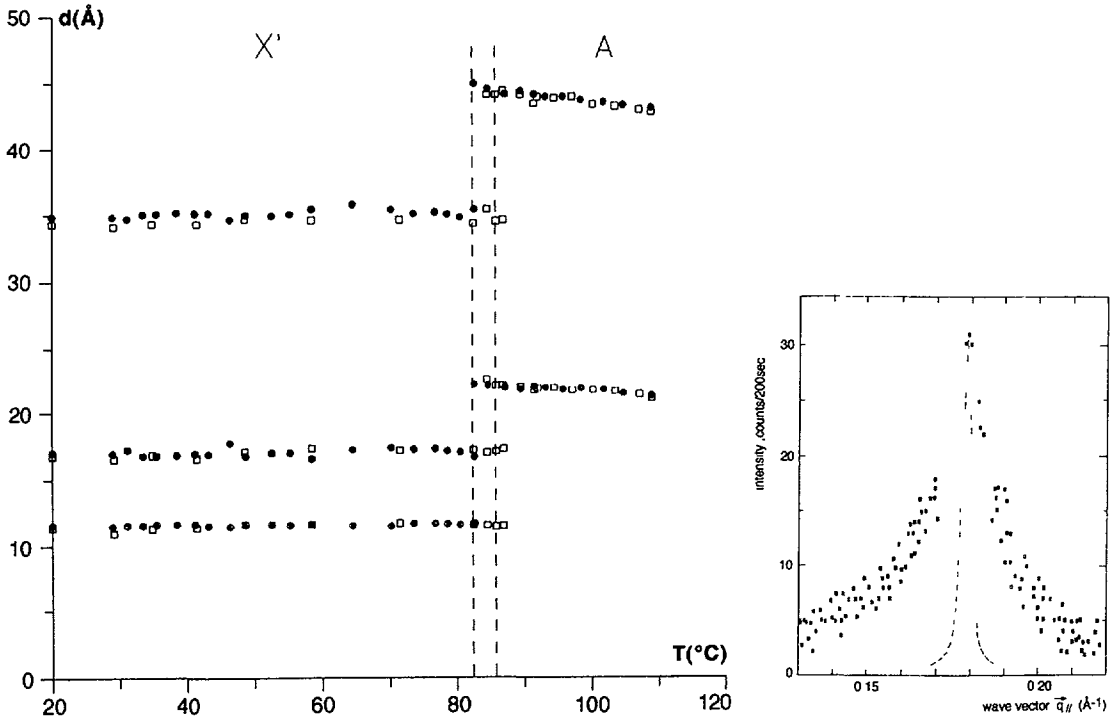

Fig. 3. — Temperature dependence of the layer spacing d in the smectic A and X′ phases for the mixture M70 ; (•) and (□) denote the data measured on cooling and heating respectively ; broken lines indicate the thermal hysteresis region. The inset shows X-ray scattering profile of the q_{21} peak in comparison with the instrumental resolution (represented by the q_1 diffraction peak in A phase-broken curve ; T = 73.6 °C.

most important molecular fragments : the biphenyl moiety (by measuring the dichroism on the aromatic stretching C-C vibration band, ν = 1 605 cm^{-1}), the hydrocarbon chain (dichroism of the C-H asymmetric stretching vibration band, ν = 2 859 cm^{-1}) and the perfluorinated tail (dichroism on the C-F stretching vibration band, ν = 1 241 cm^{-1}). A typical infra-red spectrum of the X′ phase of M70 (T = 70 °C) is shown in figure 4. For the band assignment and further details on dichroism studies see [16].

The temperature dependence of the apparent « order parameter » for the oscillators of the vibrational bands mentioned is shown in figure 5. The angle of deviation of the biphenyl oscillator from its p-p' axis (ψ = 6°) has been measured in a separate experiment on 4-octyl-4′-cyanobiphenyl [16]. Thus, the true orientational order parameter of the smectic A phase can be calculated from the $S^*(T)$ dependence for band 1 605 cm^{-1} from equation (2). It was found to be S = 0.62 within the range of T = 80-90 °C.

Having determined the S value, one can calculate the deviation angles for C-H (ψ = 79.4°) and C-F (ψ = 59.5°) oscillators. Assuming that both of them are perpendicular to the hydrocarbon and the perfluorinated chains, several possible conformations of molecules (both I or II) in the smectic A phase of M70 can be displayed (Fig. 6a). For such a molecular shape the interlayer distance in the smectic A phase is within the range of 41.8-43.2 Å in good agreement with our X-ray data.

At the smectic A-X′ transition the orientation of the biphenyl moiety changes dramatically. Now, from the apparent « order parameter » $S^* = -0.024$, we obtain ψ = 55.7° or 56.5° assuming the orientational order parameter magnitude equal to 1 or 0.62, respectively. In any case the value of $\psi \approx 56°$ is very close to the « magic » angle 54.7° at which an optically

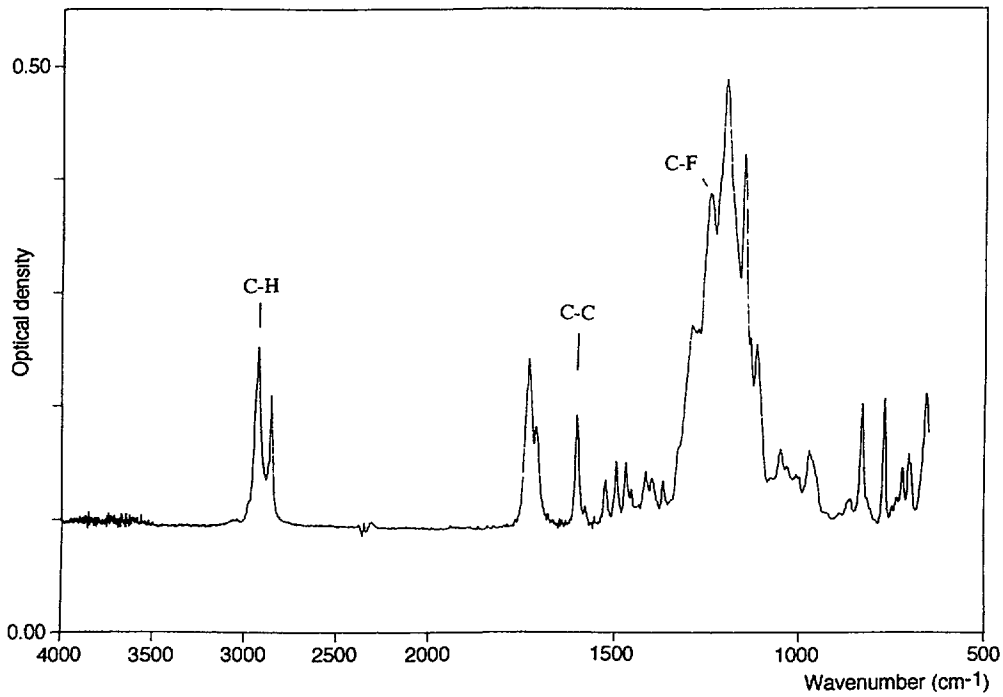

Fig. 4. — The infra-red spectrum of M70 in the smectic X′ phase (T = 70 °C).

uniaxial medium becomes optically isotropic. This explains the very low birefringence of the X′ phase of the mixture observed under a polarizing microscope.

The angles of deviation of the C-H and C-F oscillators are within the ranges of 60.2°-63.9° and 63.5°-69.9°, respectively, for the range of the order parameter of $1 > S > 0.62$. The latter figure is that found for the smectic A phase. Having considered the dichroism of the other vibrational bands we concluded that the condition $S = 1$ better fitted the experimental data. Thus, in figure 6b, we display the shapes of molecules I and II for $S = 1$. Such molecular structures correspond to the interlayer distance in the X′ phase equal to $\approx$ 34.5-38.9 Å (with the most probable value of 34.5 Å, again in good agreement with our X-ray data).

The in-plane order. — Now, let us consider the peculiarities of positional order in the plane of smectic layers. Figure 7 shows X-ray scans in both the smectic A and X′ phases with diffraction vector directed along $q_\perp$ which probes the intermolecular correlations in the plane of smectic layers ; more precisely, in our experiment, we probe the density profile along the line perpendicular to the beam incidence plane (Fig. 2a). In conventional smectics A, similar scans in the wide scattering angle region ($q_\perp > 1$ Å^{-1}) usually show a broad, liquid-like peak centered at $q_{\perp 0} \approx 1.4$ Å^{-1} corresponding to an average intermolecular distance of $\approx$ 4.5-5 Å. The angular width of this peak corresponds to the intralayer positional correlation length of $\xi_\perp \leqslant 16$ Å [17-19]. The situation is quite different in the case of polyphilic compounds. Even in the smectic A phase, the scattering is not of the single peak form, indicating the existence of two different nearest neighbour molecular distances in the plane of layers (Fig. 7a). For the smectic X′ phase, a rather complicated scattering profile with three peaks has been observed (Figs. 7b, c). The width of these peaks indicates a liquid-like short-range positional order in the plane of layers and suggests that an appropriate functional form to characterize the

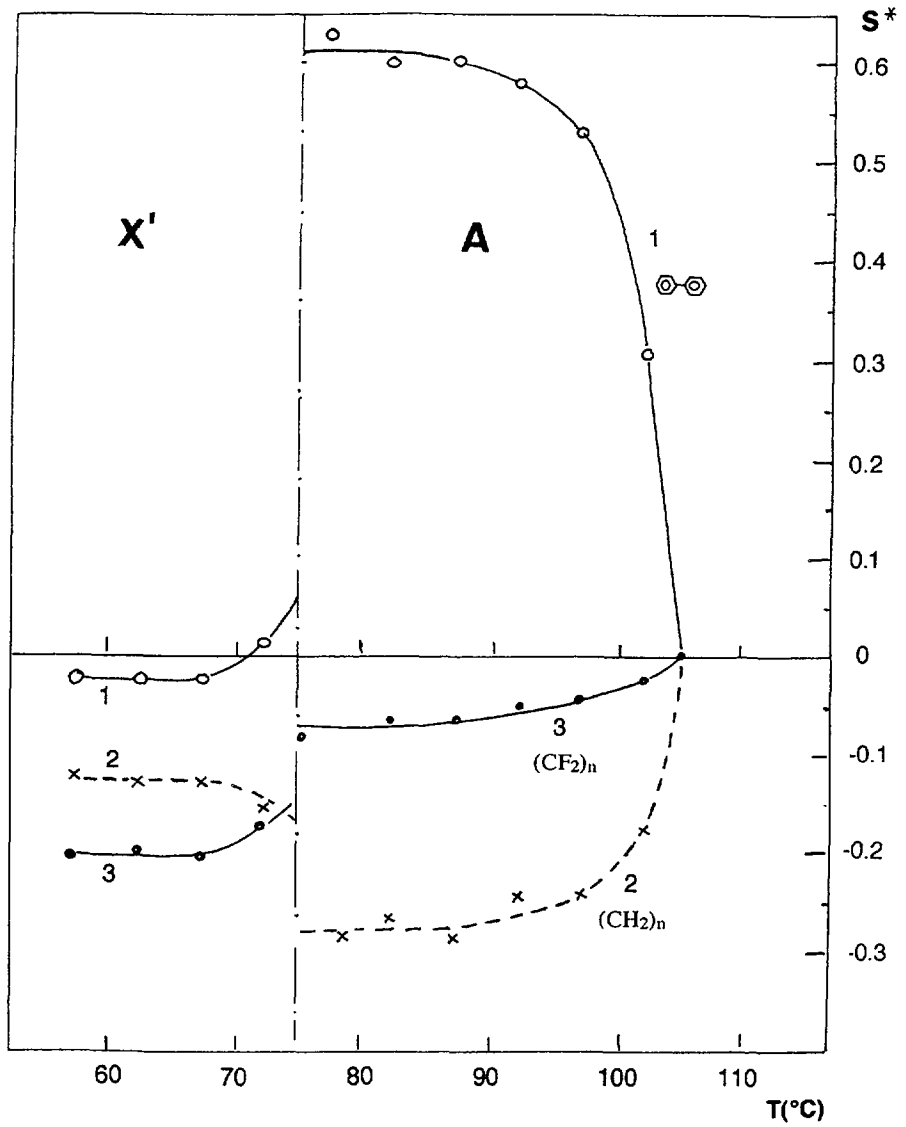

Fig. 5. — Temperature dependences of the apparent « order parameters » for three oscillators : 1) C-C aromatic stretching vibrations ; 2) C-H aliphatic stretching vibration (asymmetric) ; 3) C-F stretching vibration for the perfluorocarbon chain.

scattering intensity is the sum of two or three Lorentzian peaks :

$$I(q_\perp) = \sum_{i=1\text{-}3} \frac{I_i}{1 + \xi_{\perp i}^2 (q_\perp - q_{\perp i})^2} + I_0 \,. \tag{3}$$

Using this expression to fit experimental data we have calculated the intermolecular distances $d_i = 2\,\pi/q_{\perp i}$, intensities I_i and in-plane correlation lengths $\xi_{\perp i}$ presented in table I. The best fit using formula (3) is shown with solid lines in figure 7. The first peak at $d \approx 5.5$ Å, ($q_{\perp 1} = 2\,\pi/d \approx 1.21$ Å^{-1}) most likely is related to the liquid structure of

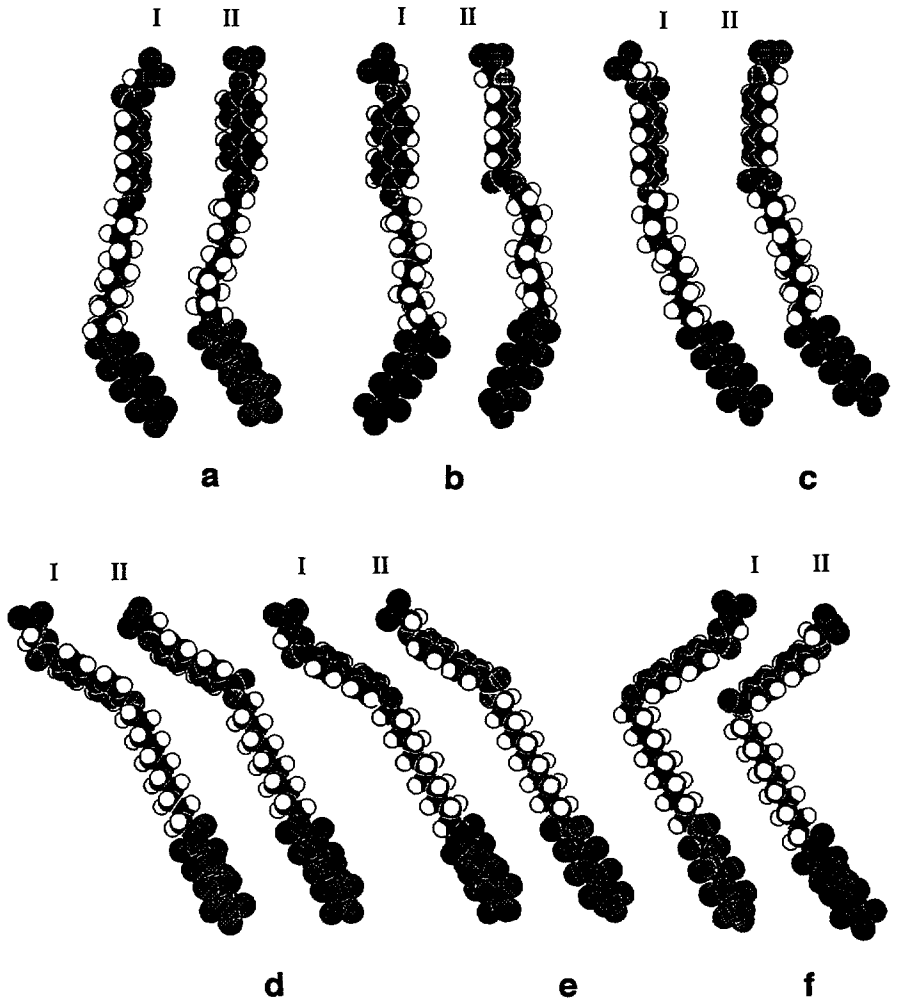

Fig. 6. — Different conformations of molecules I and II in the smectic A (a, b, c) and smectic X′ (d, e, f) phases of mixture M70.

rotationally averaged molecules as a whole. The corresponding correlation length $\xi_{\perp 1} \approx 12 \div 20$ Å slightly increases with decreasing temperature and shows very small changes at the transition to the smectic X′ phase (Tab. I). The scattering peak at $q_{\perp 3} = 2\,\pi/4.5$ Å ≈ 1.38 Å^{-1} (Fig. 7a) most likely arises from short-range correlations of the flexible alkyl chains ($\xi_{\perp 3} \approx 17$ Å corresponding to 3-4 molecules).

The additional scattering peak at $q_{\perp 2} = 2\,\pi/4.8$ Å ≈ 1.31 Å^{-1} occurs at the phase transition to the smectic X′ phase (Fig. 7b and Tab. I). At lower temperatures the $q_{\perp 2}$ and $q_{\perp 3} = 2\,\pi/4.4$ Å peaks dominate in the intensity profiles (Fig. 7c) and a dramatic increase in the short-range correlations corresponding to the mean distances $d_3 = 4.4$ Å and $d_2 = 4.8$ Å is observed. The correlation lengths $\xi_{\perp 2}$ and $\xi_{\perp 3}$ reach the value ≈ 35-40 Å, that is approximately seven or eight molecules are involved in the local in-plane order (Tab. I).

The whole picture looks as if the peak of $d = 5.2$ Å is related to the smectic A in-plane ordering whereas the two others, 4.4 and 4.8 Å are due to the short-range positional correlation in the smectic X′ phase.

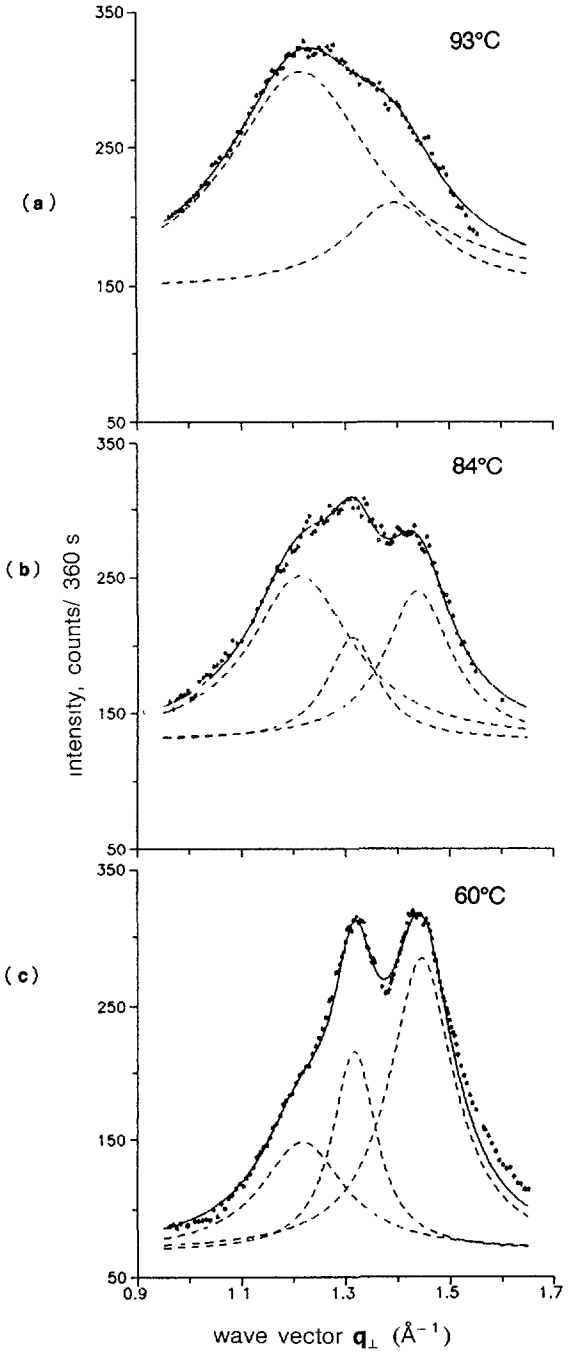

Fig. 7. — X-ray intensity profiles with diffraction vectors along $\mathbf{q}_\perp$ (in the plane of layers for mixture M70). The solid lines through the data points are the sum of two (a) and three (b, c) Lorentzian peaks (described in the text) which are shown by broken curves. (a) smectic A ; (b) phase transition region A $\leftrightarrow$ X′ ; (c) smectic X′.

Table I. — *The values of various parameters characterizing the short-range positional order in the plane of smectic layers determined from the best fits to equation* (1).

T (°C)	I_0 $\left(\frac{\text{counts}}{360\text{ s}}\right)$	d_1 (Å)	I_1 $\left(\frac{\text{counts}}{360\text{ s}}\right)$	$\xi_{\perp 1}$ (Å)	d_2 (Å)	I_2 $\left(\frac{\text{counts}}{360\text{ s}}\right)$	$\xi_{\perp 2}$ (Å)	d_3 (Å)	I_3 $\left(\frac{\text{counts}}{360\text{ s}}\right)$	$\xi_{\perp 3}$ (Å)	phase
Mixture M70											
94	148	5.18	158	12	—	—	—	4.52	61	17	A_d
85	129	5.19	122	16	4.79	76	33	4.39	110	26	$A_d \leftrightarrow$ SmX′
60	108	5.19	80	19	4.80	148	39	4.38	216	27	SmX′
Compound I											
95	160	5.25	157	12	—	—	—	4.55	35	20	A_d
87	85	4.98	150	15	4.76	124	46	4.49	70	33	SmX

3.2 Compound I.

Interlayer spacing. — Let us now consider specific features of the smectic layering for pure polyphilic compound I. The temperature variations of its interlayer spacings are presented in figure 8. Similarly to mixture M70, the high temperature smectic phase of I shows Bragg-like peaks at the wave vector $\mathbf{q}_{1n} = (0\ ;\ 0\ ;\ nq_{\parallel 1})$, n = 1-3 corresponding to the smectic A structure with spacing $d = 2\ \pi/q_{\parallel 1} = 42.5\text{-}43.6$ Å.

The infra-red dichroism data yield the following values for deviation angles of different molecular fragments in the smectic A phase : $\psi = 0°$ for the biphenyl moiety, $\psi = 17.6°$ for the hydrocarbon chain and $\psi = 32.5°$ for the perfluorinated tail. The interlayer distance calculated is 41.5-42.8 Å which almost coincides with our X-ray data. Thus, the molecular conformations in the smectic A phase of compound I are very similar to those shown in figure 6a.

Within the instrumental resolution of $\xi_{\parallel} \leqslant 900$ Å, the smectic A phase has long-range translational order.

In the smectic X phase, the X-ray diffraction in the small scattering angles region shows a number of spots, including the off-axis reflections that are characteristic of modulated structures (Fig. 9). Reflections 2 and 3 with wave vectors $\mathbf{q}_{22} = (0\ ;\ 0\ ;\ 2\,q_{\parallel 2})$ and $\mathbf{q}_{23} = (0\ ;\ 0\ ;\ 3\,q_{\parallel 2})$ respectively correspond to the same layered structure with tilted molecules and spacing $d_2 = 2\ \pi/q_{\parallel 2} \approx 35$ Å that was earlier described for mixture M70 (Fig. 3). In addition, the off-axis reflections 1 with wave vector $\mathbf{q}_{21} = (\pm q_{\perp 1}\ ;\ 0\ ;\ q_{\parallel 2})$ can be seen on the diffraction patterns ($q_{\perp 1} = 0.125$ Å^{-1}). These spots originate from the ring of scattering with the wave vector $\mathbf{q}_{21} = (q_{\perp 1} \cos \varphi\ ;\ q_{\perp 1} \sin \varphi\ ;\ q_{\parallel 2})$ located in the reciprocal plane $(0\ ;\ 0\ ;\ q_{\parallel 2})$ ($0 \leqslant \varphi \leqslant 2\ \pi$ is an azimuthal angle). The combination of spots 1 and 2 corresponds to the two-dimensional (modulated) structure in which smectic C layers are periodically shifted with

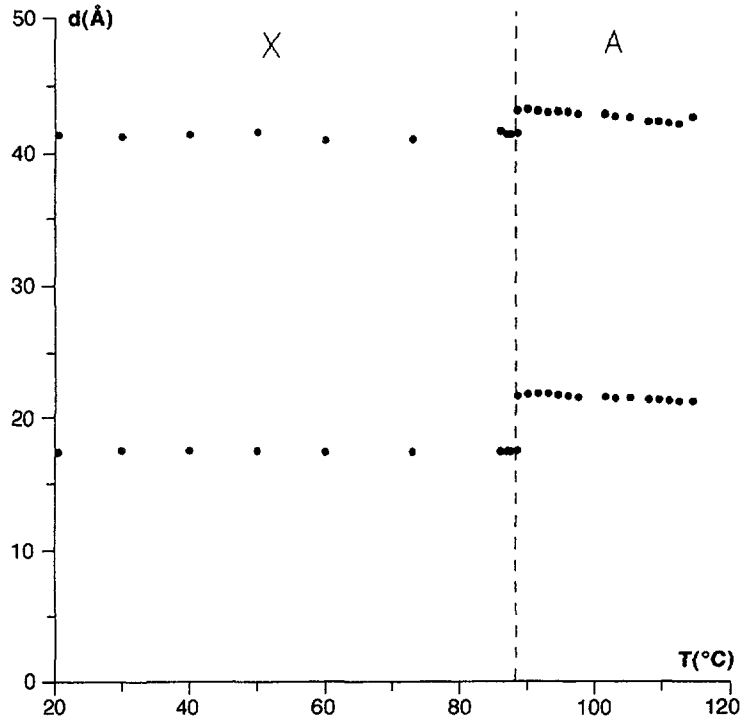

Fig. 8. — Variation of layer spacing in the smectic A and X phases of compound I. The data in smectic X phase correspond to the position of the incommensurate $q_4 = 2\ \pi/41$ Å and $q_{22} = 2\ \pi/17.5$ Å diffusion peaks.

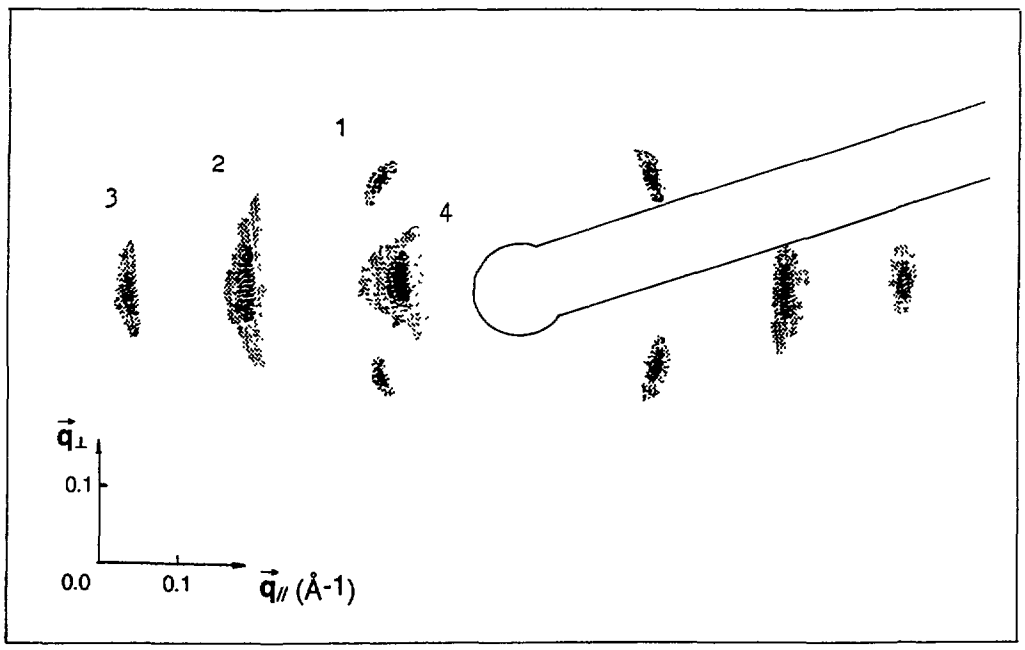

Fig. 9. — Intensity contours in the $q_{\parallel} - q_{\perp}$ scattering plane in the smectic X phase for the compound I. The spots 1-4 are described in the text. $T = 80$ °C.

respect to one another by a half of the interlayer spacing [13]. This structure resembles the smectic $\tilde{A}$ antiphase [2] observed in mesogens with strongly polar terminal groups [1, 13]. The period of the transverse modulation in the smectic X phase, $a = 2\pi/q_{\perp 1} \approx 50$ Å corresponds to the intralayer stacking of approximately 10 molecules.

Surprisingly, in the temperature range of the smectic X phase, we have also found the spot 4 at wave vector $\mathbf{q}_4 = (0\ ;\ 0\ ;\ q_{\parallel 4})$ which is collinear to vector $\mathbf{q}_{2n}$ but incommensurate with it (Fig. 9). The $q_{\parallel 4}$ peak corresponds to the smectic A structure with interlayer spacing $d = 2\pi/q_{\parallel 4} \approx 41$ Å which is slightly less than the value found in the high temperature region.

Similar to the smectic X′ phase of mixture M70, peaks 1-4 are not resolution limited. The correlation length for the translational order in the direction parallel to the layer normals does not exceed $\xi_{\parallel} \approx 300$ Å (Fig. 10). Thus, smectic X demonstrates another example of strongly defective periodic structure where three different types of layering coexist : (i) the lamellar structure with a tilt of molecules, (ii) the modulated structure with tilted molecules and the layers periodically shifted with respect to one another and (iii) the orthogonal smectic A layers the period of which is incommensurate with those of structures (i) and (ii). It is evident that the coexistence of such structures is only possible in strongly disordered media.

For such coexisting structures, from the infra-red dichroism one may only determine a certain averaged molecular conformation. The average interlayer distance, calculated from the measured « fictitious » angles of vibrational oscillators, was found to be just in the middle between the spacings measured for the smectic A and X′ phases. Thus, one may conclude that percentages of each of the coexisting microphases are approximately equal. In contrast to data on M70, the temperature behaviour of the « order parameters » for various oscillators is very irregular within the range of 10° below the A-X transition, the latter may be accounted for by the coexistence of the microstructures mentioned.

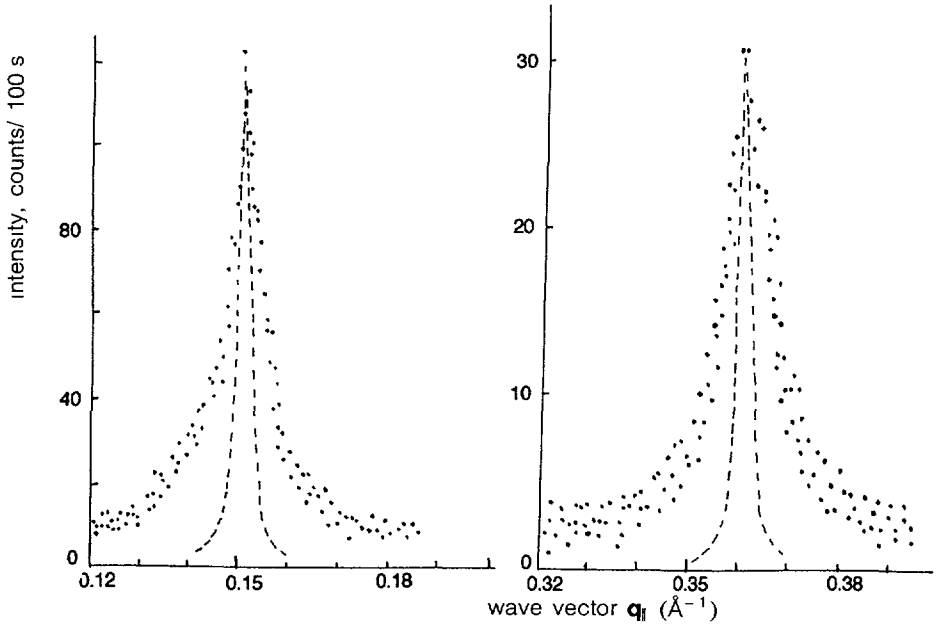

Fig. 10. — X-ray scattering profiles of the incommensurate q_4 and q_{22} peaks in the smectic X phase for compound I in comparison with the instrumental resolution (represented by the diffraction peak in A phase — broken curves). $T = 50$ °C.

In-plane order. — As to the in-plane positional order, compound I shows scattering features similar to those of mixture M70 (Tab. I and Fig. 11). The only difference concerns the relative scattering weights of the two $q_\perp$ peaks. In contrast to the smectic X′ phase, in the smectic X phase of compound I the scattering peak corresponding to the short-range correlations with mean distance $d_2 = 4.8$ Å dominates over the $d_3 = 4.4$ Å peak (Tab. I). The peak attributed to the smectic A phase is even stronger here than the others. This is consistent with the observation of the smectic A type in-plane ordering in the range of the smectic X phase.

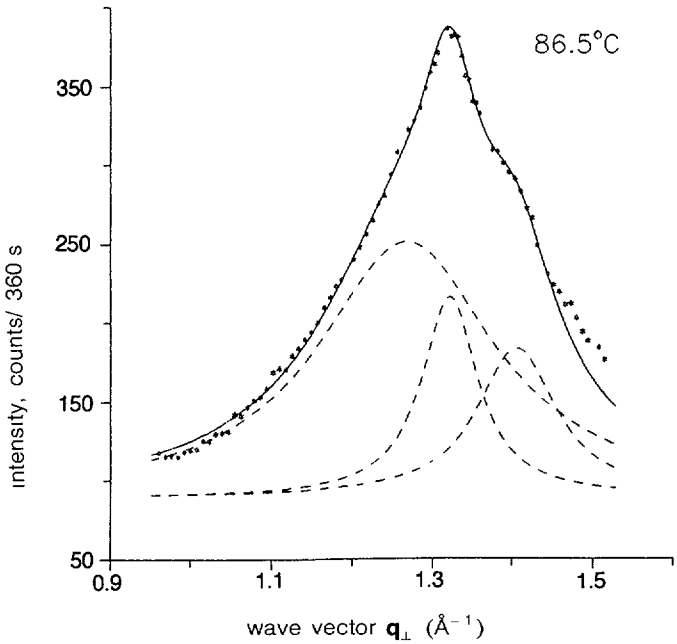

Fig. 11. — X-ray profiles with diffraction vector $\mathbf{q}_\perp$ in the plane of layers in a smectic X phase for compound I. The solid lines through the data points are the sum of three Lorentzian peaks, which are shown by broken curves.

4. Discussion.

Let us briefly summarize the most important experimental results.

(i) In the smectic A phase of both substances, the molecules have a more or less extended form with only the perfluorinated chain markedly deviated from the normal by about 30°. The characteristic in-plane distance is about 5.2 Å and liquid-like positional correlations are strongly influenced by low-temperature smectic X′ or X order.

(ii) The phase transition to smectic X′ is accompanied by a dramatic change in the main molecular conformation. In the smectic X′ phase, the molecules are strongly tilted with respect to the layer normal (especially the biphenyl moiety, ψ is about 56°) in accordance with a considerable decrease in the interlayer distance and very low birefringence observed in M70. The interlayer correlations are rather short-range with only 6-8 layers included. The in-plane structure factor reveals two characteristic distances, 4.8 and 4.4 Å, corresponding to the short-range range positional correlations of the order of 35-40 Å (7-8 molecules in the local in-plane order). Qualitatively the same is true for the smectic X phase of I.

(iii) Additionally, the smectic X manifests a modulated structure and a coexistence of the tilted and orthogonal incommensurate phases.

Now, two questions arise : first, is it possible to understand, at least at the level of a certain qualitative model, all these structural features ? ; and second, is it possible to relate that model to the ferroelectric phenomena observed in these substances ?

4.1 SMECTIC A. — With molecular models shown in figure 6a, the areas $a = s/\cos\psi$ can be estimated covered by the projections of various fragment cross-sections (s) on the smectic layer plane. For the perpendicularly oriented and cylindrically averaged biphenyl moiety we have $a_B \approx 22$ Å^2 for the smectic A phase of typical nonfluorinated compounds. For the perfluoroalkyl chain tilted by $\psi = 30.5°$ with a typical chain cross section of about 31 Å^2 the projection area is $a_F \approx 35$ Å^2. The alkyl chain deviated by angle 10.6° has a projection area close to that of biphenyl, $a_H \approx 22$ Å^2.

The comparison of a_B and a_F shows that the antiparallel arrangement of two neighbour molecules better satisfies requirements of optimum packing (despite the polyphilic effect) and, of course, such layers are non-polar. The average intermolecular distance for anti-parallel packed molecules is estimated from the average of the projection areas of the biphenyl and the fluorinated chain and is equal to about 5.8 Å. For hexagonal packing, this corresponds to a Bragg reflection at 5.1 Å, in agreement with our data (5.2 Å).

4.2 SMECTIC X′(X). — On transition to the smectic X′ phase, molecules take one of the conformations shown in figures 6d, e. Structure (f) would require too much energy to be fractured ; in addition, one would meet serious problems with a dense packing of fractured molecules. Let us consider the smectic C layers formed by the polyphilic zigzag shaped molecules in the random up and down configurations (Fig. 12a) : this arrangement is not optimum from a purely steric point of view, due to an excess free volume in the region of differently tilted molecular fragments. The rigidity of perfluorinated tails makes impossible compensation of the unfavourable molecular packing as it usually occurs in the smectic C phase formed by molecules with flexible hydrocarbon tails. The most probable structure of a smectic X′ layer, consistent with our measurements of the angles of various fragments and interlayer distances is shown in figure 12b. Now, the projection of the biphenyl cross-section onto the smectic layer plane is $22/\cos 55.7° \approx 39$ Å^2 and that of the fluorinated chain is $31/\cos 26.5° \approx 35$ Å^2. The two estimates are close to one another and the parallel (polar) packing of molecules shown in figure 12b is preferable, due to the polyphilic effect. In addition, a tilted arrangement of fluorocarbon chains results in their shift with respect to each other which optimizes local electrostatic interactions between dipolar CF_2 groups of neighbour molecules [13,20].

If we accept such a picture in general, there are two problems to be solved. The first concerns the packing of flexible hydrocarbon chains. To fill the space available between the biphenyl core and the rigid perfluorinated chain we must assume that the hydrocarbon chains are not in a completely stretched conformation. Then hydrocarbon chains take a more disordered form with a lower absolute value of the « order parameter » S^* for the C-H oscillators. The discrepancy between the assumed and measured values of S^* are in fact within the range of experimental accuracy and perhaps could be eliminated, if a more precise analysis of the dichroism is done with account taken of the symmetric stretching vibrations as well (band at $\nu = 2\,859$ cm^{-1}). With disordered hydrocarbon chains, the total length of the molecule is reduced and, to have the same interlayer distance, we must admit that the molecules are slightly shifted with respect to each other (Fig. 12d). Another way to solve the same steric problem is the formation of a modulated structure in which distortions of opposite

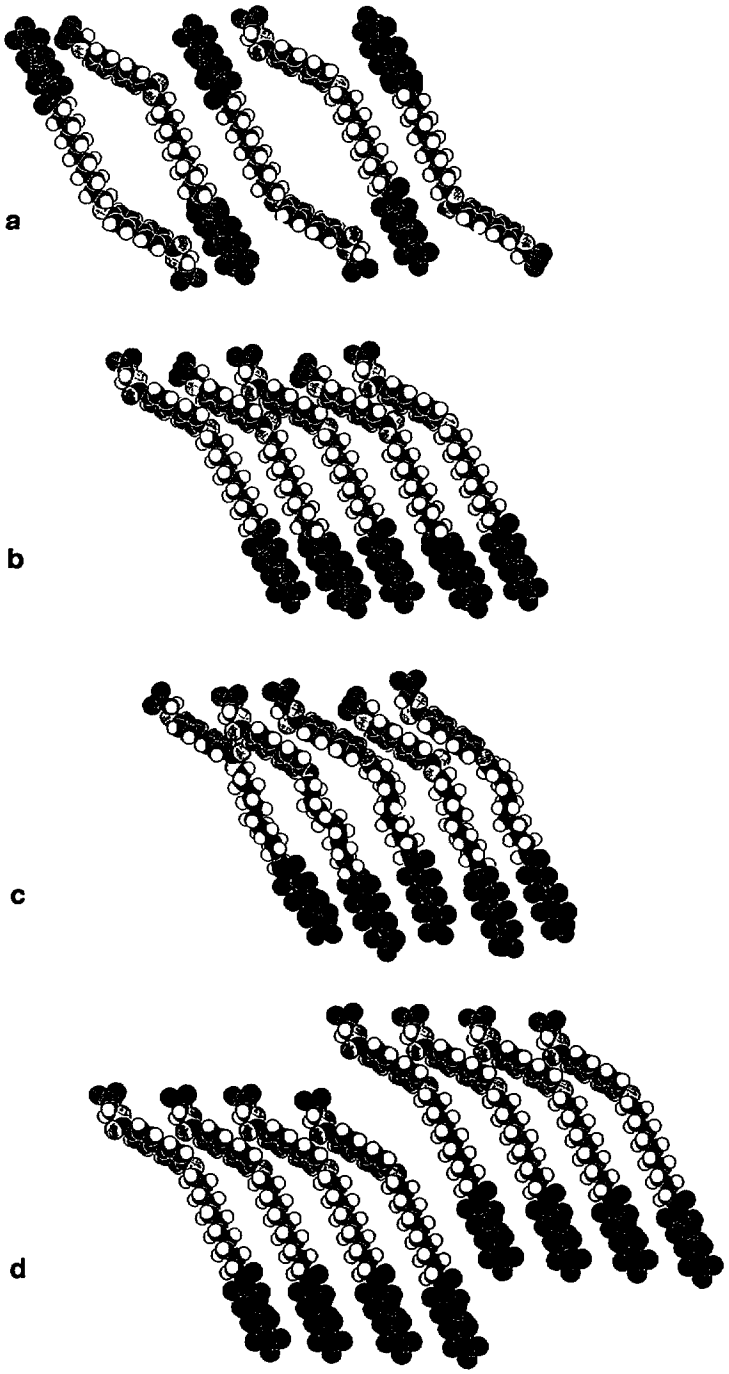

Fig. 12. — Schematic representation of the tilted layer structures with the polyphilic molecules in zigzag conformation. (a) The random up-down configuration ; (b) polar structure with fully elongated alkyl chains ; (c) polar structure with disordered alkyl chains. The mesogens are slightly shifted with respect to each other ; (d) two-dimensional (modulated) polar structure.

signs are compensated (Fig. 12d). Such a phenomenon may be responsible for the occurrence of the modulated structure of compound I. According to our X-ray data, the polar smectic C layer in the X-phase are shifted by the half of a period with respect to each other.

The second problem concerns the two characteristic distances, 4.4 and 4.8 Å, observed in the smectic layer plane. Such a complicated structure factor might be related to a small distortion of the original local-hexagonal lattice due to the tilt of molecules, this corresponds to a centered rectangular lattice with parameters $a = 9.6$ Å, $b = 4.9$ Å for which the area available per molecule is 24 Å^2. The projections of the molecular moiety cross-sections in the X′ (and X) phase cover much more area than available with this model. However, one may relate the two distances under question to two in-plane dimensions characteristic of the structure shown in figure 12 : 4.8 Å is a typical distance corresponding to the tight packing of fluorinated chains (in our model, in the direction perpendicular to the plane of the figure), and period 4.4 Å might be related to the densely packed disordered hydrocarbon chains, perhaps in both directions, parallel and perpendicular to the plane of the figure.

A similar behaviour, when two characteristic lengths are not related to lattice planes, has been described earlier for other media with flexible, almost molten hydrocarbon tails, for example in discotic mesophases [21, 22] where two diffraction peaks were attributed to distances between rigid cores and molten hydrocarbon chains, and in polymer liquid crystals [23, 24] where mesogenic moieties behave almost independently of main chains.

4.3 DEFECTIVE STRUCTURE AND FERROELECTRICITY. — Let us now consider the possible packings of polar monolayers. If the polar direction is conserved in neighbour layers, the macroscopic structure is polar (Fig. 13a). The opposite case of antiferroelectric packing of monolayers is shown in figure 13b. Both structures are generally characterized by the azimuthal degeneration of the direction of the C-director, which leads to the existence of azimuthally disordered microdomains with defect walls between them. However, the antiferroelectric packing of the layers shown in figure 13b must be disregarded because of the absence of the diffraction spots corresponding to the doubling of the fundamental layer spacing $d \approx 35$ Å.

The structure of figure 13a is in agreement with our experimental data. However in this case a slight difference in projection area for the biphenyl and the fluorinated chain results in a stress accumulated on proceeding along a smectic layer. To compensate for the stress, the direction of the molecular tilt must alternate with a flip-flop of the polar structure of the layer. Thus, a number of defects (walls) must be created in the smectic layer plane which separate domains of opposite polarity. In principle, the defects may form a regular superlattice. The situation reminds us of the helical smectic A* phase [25], however, in our case the dimension of domains is much smaller than the pitch of the A* phase. The latter is not surprising as the effect of polyphilicity on the structure is much stronger than the influence of molecular chirality. The period of the superstructure (or the modulated smectic-like antiphase) of about 50 Å provides a natural estimate of the in-plane domain dimensions.

Once the polar structure of a smectic X′(X) monolayer is established (at least, in a single domain area), the magnitude of the spontaneous polarization (P_S) can be calculated. Molecules I and II have the component of their dipole moment parallel to the p-axis of the biphenyl moiety $\mu_\parallel = -1.3\,D$ directed from the ester to the ether group. The perpendicular component is assumed to be averaged out, at least in the simplest approach, due to the presence of various conformers like those shown in figure 7. With the biphenyl angle $\psi = 55.7°$ for both I and II molecules in mixture M70 and the molecular volume $V = 1\,047$ Å^3, one can calculate the virtual values for longitudinal and transverse (with respect to the smectic normal) polarization of each of the molecules separately to be of $P_S^{\parallel} = -250$ nC/cm^2 and $P_S^{\perp} = -375$ nC/cm^2, respectively. Both components lie in the tilt

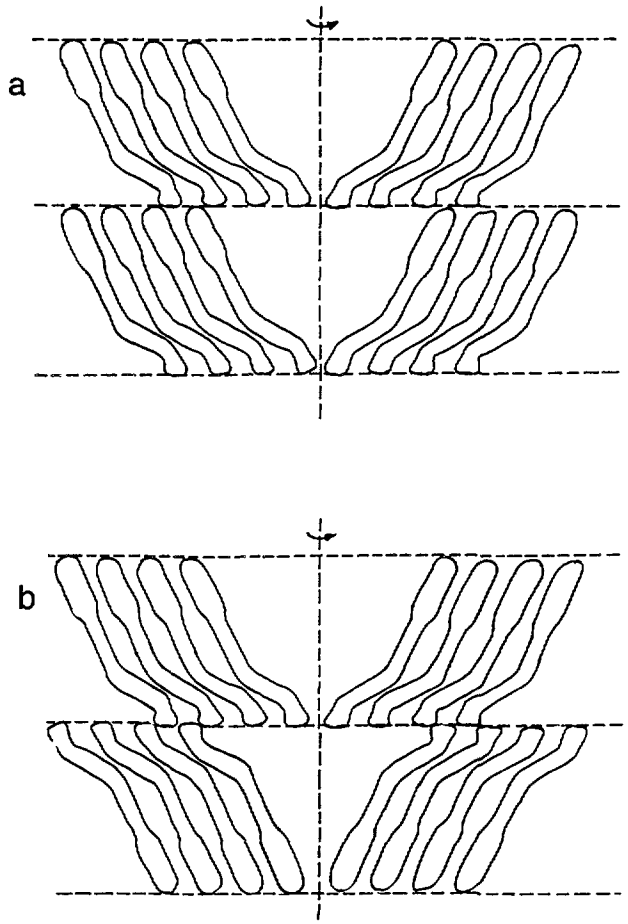

Fig. 13. — Possible packings of polar monolayers : (a) polar structure with azimuthal disorder ; (b) antiferroelectric structure with azimuthal disorder.

(mirror) plane (Fig. 12b). Due to the opposite direction of μ in I and II and partial compensation of both values, mixture M70 should have $P_S^{\perp}$ and $P_S^{\parallel}$ values reduced to $-100\ nC/cm^2$ and $-150\ nC/cm^2$, respectively. Thus, both the longitudinal and transverse polarization components are allowed in a smectic monolayer and the polarizations might be two orders of magnitude higher than those observed in experiments [6]. Probably, contributions from domains of different polarity compensate for each other.

It is still unclear why and how polar monolayers of polyphilic compounds are stacking together in a macroscopically polar multilayered structure and new studies, both theoretical and experimental, are necessary to solve this problem.

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