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# Synthesis, properties and crystal structure of chiral semiperfluorinated liquid crystals with ferro and anticlinic smectic phases

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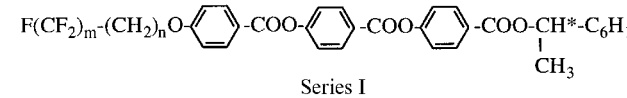
A new chiral and semiperfluorinated series with ferro and anticlinic properties has been synthesized and characterized. The mesomorphic behaviour has been established on the grounds of both microscopic observations and DSC measurements. The non-chiral intermediate ethyl 4-semiperfluorinated alkyloxybenzoates exhibit SmA phases, unusual for compounds with a single phenyl ring. The final derivatives display SmA, SmC* and in several cases $SmC^*_A$ phases. The longer fluorinated chains favour the SmA and SmC* phases at the expense of the $SmC^*_A$ phase. Electro-optical measurements were carried out with the classical SSFLC geometry. The spontaneous polarization and tilt angle at saturation are higher than those of the hydrogenous homologues, around 140 nC cm$^{-2}$ at 40°C. One compound of the series, the 4,4,5,5,6,6,7,7,8,8,8-nonafluoroheptyloxy derivative, $C_{36}H_{35}O_7F_9$, $M_x = 750.6$ g mol$^{-1}$, crystallizes in the triclinic system, space group $P1$, with four independent molecules in the asymmetric unit ($Z = 4$). The molecules are arranged in a head-to-tail fashion with two molecules oriented in the same direction and the two others in the opposite direction. They give rise to sheets with a smectic C-like arrangement. The final reliability factors were $R = 0.117$ and $w_R = 0.134$; the goodness of fit was $S = 1.366$.

## 1. Introduction

Chiral liquid crystals have been paid much attention since the conjecture of antiferroelectric character (rather anticlinic) associated with the $SmC^*_A$ phase [1] and with the twist grain boundary smectic A phase (TGB phase) [2], and the search for novel chiral materials with new structures has been accelerated. Several recent studies by different groups show that fluorination of the hydrocarbon chain strongly favours smectic phases [3–9]. Other benefits from fluorination of the hydrocarbon are lower viscosity, lower birefringence and enhanced chemical stability. These properties are all desirable for ferroelectric liquid crystals (FLC) applications and various studies in this domain have been reported [10–13].

Interest in the influence on ferro- and antiferro electric smectic phases has led us to synthesize a series of chiral and fluorinated compounds having the general formula:




Series I

where $m = 2$, 3–7 and $n = 3$–6, 8.

## 2. Synthesis

The chiral semiperfluorinated series **I** was prepared following the scheme shown below:

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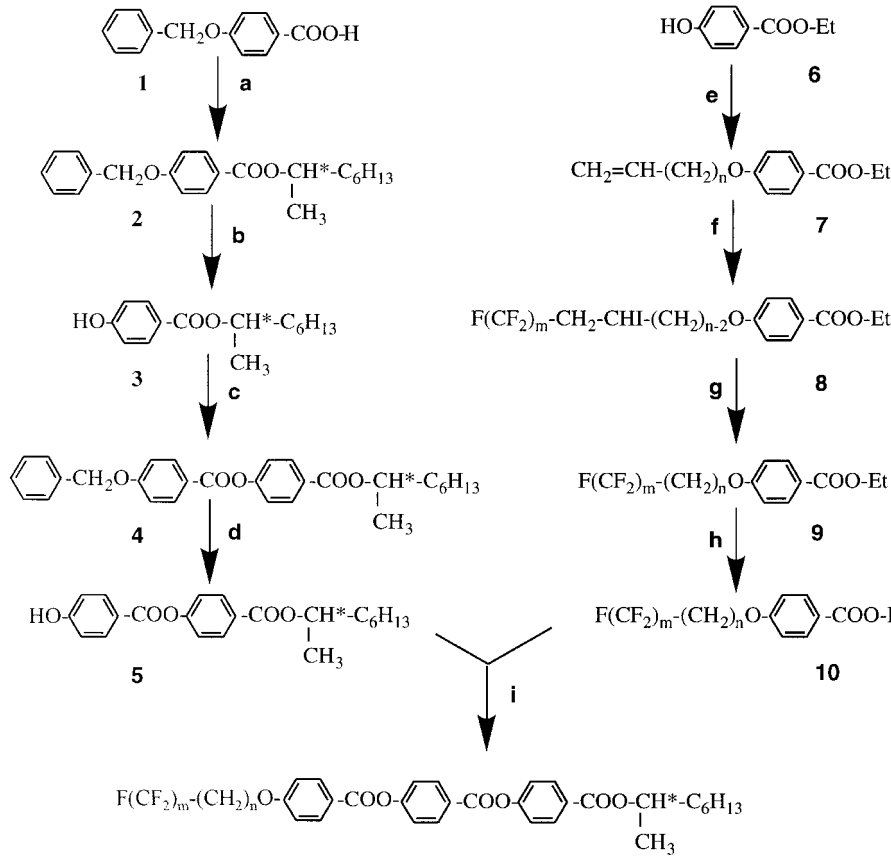


Scheme

(a) (*R*) or (*S*) 2-octanol, DCC, DMAP, $CH_2Cl_2$ (b) $H_2$, Pd/C, EtOH 95%
(c) Ph–$CH_2$O–Ph–COOH, DCC, DMAP, $CH_2Cl_2$ (d) $H_2$, Pd/C, EtOH 95%
(e) $CH_2$=CH–$(CH_2)_n$–Br, KOH, EtOH (f) $F(CF_2)I_m$, AIBN
(g) HCl(g), Zn, EtOH (h) KOH, EtOH; HCl, $H_2O$
(i) DCC, DMAP, $CH_2Cl_2$.

Scheme.



The chiral phenol **5** [14] was obtained by esterification of 4-benzyloxybenzoic acid with chiral phenol **3** followed by catalytic hydrogenation. The chiral phenol **3** was prepared by similar reactions. The semiperfluorinated benzoic acids **10** were synthesized following the classical method [4]. The esterification of the acid **10** and the chiral phenol **5** in dichloromethane as solvent with DCC and DMAP as catalysts affords the desired compounds **I**.

All the final compounds **I** was chromatographed on silica gel with dichloromethane as eluent and recrystallized from absolute ethanol. Owing to their mesogenic properties the intermediate compounds **9** were also purified to allow a reliable characterization.

## 3. Mesomorphic characterization

### 3.1. *Fluorinated esters* ***9***

These compounds, based on a single phenyl ring in the core, nevertheless display a simple but rather unexpected mesomorphism. Provided that the fluorinated chain is long enough a smectic A phase is observed. Its stability depends on a clear-cut even–odd effect (table 1, figure 1). The I–SmA transition is enantiotropic for an even number of carbons in the hydrogenous ($n$) and in the fluorinated ($m$) chains, i.e. ($n$, $m$) = (6, 6); (8, 6), etc. With odd numbers, the transition is monotropic. From a structural point of view measurements of the layer spacing ($d$) compared with molecular length ($L$) show

Table 1. Transition temperatures (°C) and layer spacing (Å) of intermediate compounds **9**.

| $m$ | $n$ | Cr | | SmA | | I | $d$ | $L$ |
|---|---|---|---|---|---|---|---|---|
| 4 | 5 | • | 49 | | | • | | 25.1 |
| 4 | 6 | • | 37 | | | • | | 26.3 |
| 6 | 4 | • | 44 | • | 46 | • | 26 | 26.5 |
| 6 | 5 | • | 47 | • | (39) | • | | 27.6 |
| 6 | 6 | • | 42 | • | 45 | • | | 28.7 |
| 7 | 5 | • | 50 | • | (37) | • | | 28.8 |
| 8 | 5 | • | 66 | • | (59) | • | | 30.0 |
| 8 | 6 | • | 60 | • | 66 | • | 35 | 31.1 |

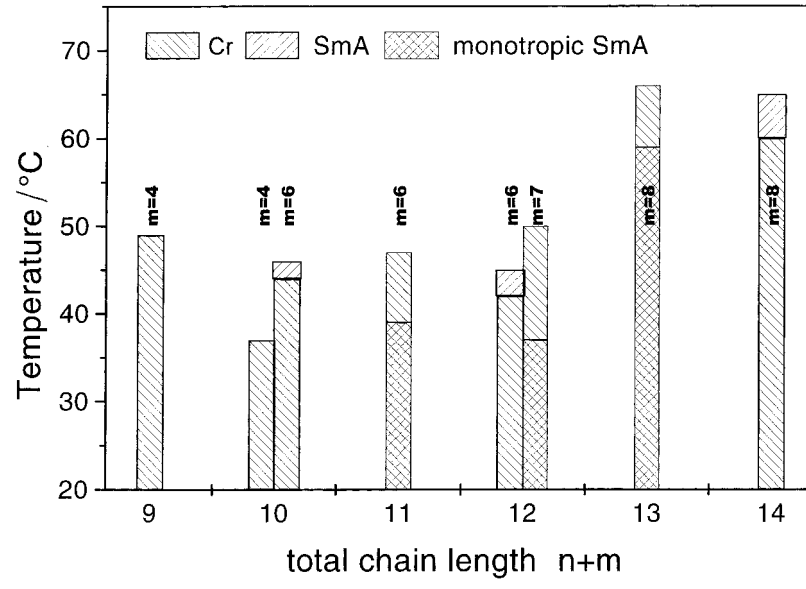


Figure 1. Plot of transition temperatures (°C) versus total chain length $(n+m)$ of intermediate fluorinated esters **9**.



that the ratio $d/L$ is slightly below 1 for the first compound quoted (table 1). However the difference becomes more significant and the ratio exceeds 1 as the length of the fluorinated part increases and exceeds the length of the aliphatic part. This supports the models proposed so far for the molecular arrangement of mesogens with one fluorinated end chain: a packing of alternating up and down molecules with no overlapping of the bulky fluorinated parts of adjacent molecules. This example of a liquid crystalline phase obtained with a one ring molecular architecture is thus different from the mesomorphism obtained by intermolecular hydrogen bonding [4, 15, 16] or dimerization by partial overlapping of two neighbouring molecules [17] and deserves to be noted.

### 3.2. *Series* ***I***

The compounds in this series are all mesomorphic and display SmA and SmC* phases. In addition to these phases, some of them exhibit an antiferroelectric (anticlinic) smectic C* phase ($SmC^*_A$). Their thermal behaviour was investigated by differential scanning calorimetry (Perkin Elmer DSC7) and the phase identification was made by thermal microscopy using a Zeiss Ortholux polarizing microscope equipped with a Mettler FP5 hot stage. The transition temperatures and enthalpies for the series are given in table 2 and figure 2.

The SmA and SmC* phases have classical optical textures with fan-shaped or homeotropic domains for the SmA phase and broken fan-shaped or coloured schlieren textures for the SmC* phase. In the case where $SmC^*_A$ exists, the transition between the SmC* and $SmC^*_A$ phases occurs via a $SmC^*_{FI}$ phase, but its temperature range is too short to be detected by DSC measurements.

The mesomorphic properties of liquid crystals are well known to depend on the nature, the polarity and the length of the terminal group. For this reason, the replacement of hydrogen atoms of the alkyloxy chain by fluorine atoms modifies the molecular interactions and causes the changes in the mesomorphic properties. In comparison with the hydrogenous compounds, series **II** [14] (table 3, figure 3), we can observe the following important modifications of the liquid crystal sequences:

(1) The $SmC^*_\alpha$ phase is not obtained with fluorinated materials.
(2) There are two different $SmC^*_{FI}$ phases in series **II**, but they could not be detected by DSC in series **I**. Their existence could be seen by microscopy at the transition between the SmC* and $SmC^*_A$ phases, but their temperature ranges are too short, and for this reason we do not mention them in table 2.
(3) The stability domain of the SmC* phase and the clearing temperature increase with the fluorine atom number. This behaviour is general for different benzoate series [3, 4].
(4) The heptyloxy derivative of series **II** does not display the $SmC^*_A$ phase, but its existence is observed virtually when we make mixtures between the heptyloxy and octyloxy compounds. The member of series **I** with $n = 4$ and $m = 3$ $(n + m = 7)$ exhibits SmC* and $SmC^*_A$ phases. For short chains, the semifluorinated compounds could favour the $SmC^*_A$ phase, but with long chains and with $m \geqslant 6$, the phase totally disappears.
(5) The SmA–I transition enthalpies are in general lower in fluorinated compounds than in hydrogenous compounds (except for C12). On the other

Table 2. Transition temperatures (°C) and enthalpies in italics (kJ mol$^{-1}$) of the compounds of series **I**.

| *m* | *n* | Cr | | $SmC^*_A$ | | SmC* | | SmA | | I |
|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 8 | • | 97.4 | • | 106.9 | • | 133.8 | • | 142 | • |
| | | | *42.2* | | *0.05* | | *0.7* | | *4.8* | |
| 3 | 6 | • | 112.6 | | | • | 144.6 | • | 151 | • |
| | | | *42.4* | | | | *0.8* | | *4.7* | |
| 4 | 3 | • | 88.2 | • | 116.6 | • | 159 | • | 164 | • |
| | | | *30* | | *0.04* | | *1.6* | | *4* | |
| 4 | 4 | • | 92.4 | • | 115 | • | 152 | • | 158 | • |
| | | | *19* | | *0.04* | | *1* | | *3.4* | |
| 4 | 5 | • | 95 | • | 113 | • | 153 | • | 160 | • |
| | | | *33.5* | | *0.03* | | *1.2* | | *4.4* | |
| 4 | 6 | • | 108 | • | 111.7 | • | 151 | • | 159 | • |
| | | | *33* | | *0.04* | | *1* | | *4.6* | |
| 6 | 4 | • | 97.6 | | | • | 166 | • | 177 | • |
| | | | *27.5* | | | | *1.1* | | *4.9* | |
| 6 | 5 | • | 87.6 | | | • | 165.5 | • | 177 | • |
| | | | *32.7* | | | | *0.7* | | *5.1* | |
| 6 | 6 | • | 106.8 | | | • | 164 | • | 177 | • |
| | | | *46* | | | | *0.63* | | *5.5* | |
| 7 | 5 | • | 95.1 | | | • | 166.8 | • | 189 | • |
| | | | *32.5* | | | | *0.9* | | *5.4* | |



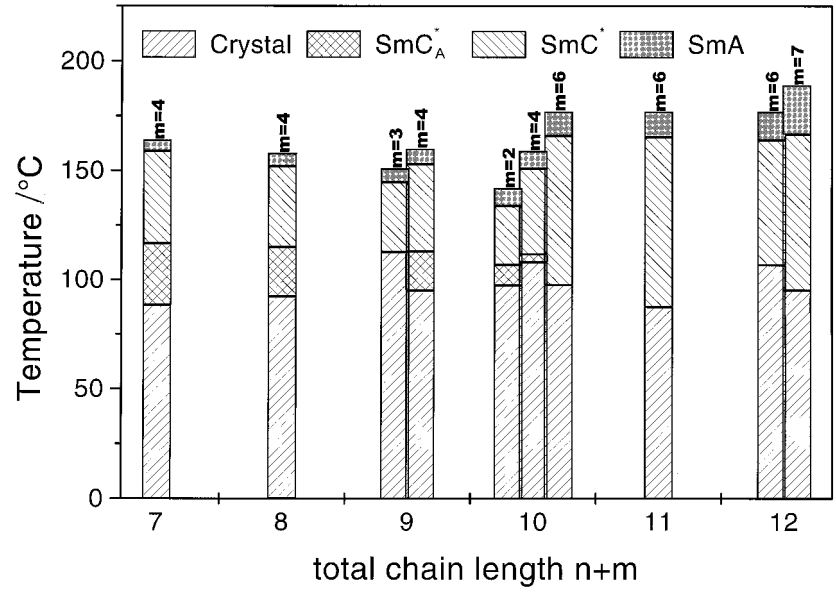


Figure 2. Plot of transition temperatures (°C) versus total chain length ($n+m$) of fluorinated series **I**.

hand, the SmA–SmC* transition enthalpies are higher for the fluorinated compounds with respect to the hydrogenous derivatives. Following from tables 2 and 3, we may note that the semifluorinated chains favour the SmC* phase more than the $SmC^*_A$ phase.

## 4. Electro-optic properties

A classical electro-optical set-up was used for the measurements of polarization, response time and tilt angle for the series **I** derivative ($m=4$, $n=6$). The thickness of commercial cells (from Linkam), coated with ITO over a 0.25 cm$^2$ active area, was 7.5 μm. Figure 4 shows the spontaneous polarization under an a.c. field at saturation ($E=\pm 4$ V μm$^{-1}$; $\nu=100$ Hz). The polarization increases when the temperature decreases with a saturation at about 140 nC cm$^{-2}$, higher than that of hydrogenous compound **II** ($n=10$; $\mathbf{P}_s=80$ nC cm$^{-2}$). Figures 5 and 6 represent the polarization dependence on the a.c. field in the SmC* and $SmC^*_A$ phases. It shows significant differences from one phase to another. The $SmC^*_A$ phase requires a relatively high field to accomplish transition to the ferroelectric phase; this threshold field decreases while the temperature increases. The response

Table 3. Transition temperatures (°C) and enthalpies in italics (kJ mol$^{-1}$) of the hydrogenous compounds of series **II**.

| $n$ | Cr | $SmC^*_A$ | $SmC^*_{FI1}$ | $SmC^*_{FI2}$ | SmC* | $SmC^*_\alpha$ | SmA | I |
|---|---|---|---|---|---|---|---|---|
| 7 | • 82.7 | | | | • (69.8) | • (72.6) | • 144.1 | • |
| | *31.6* | | | | *0.002* | *0.015* | *5.7* | |
| 8 | • 89 | • (60) | • (72) | • (87.8) | • 94.8 | • 95.7 | • 141.8 | • |
| | *34.7* | *0.003*[a] | | *0.004* | *0.004* | *0.04* | *5.6* | |
| 9 | • 95.8 | • (94) | • 96.6 | • 100.5 | • 108 | • 110.5 | • 138.1 | • |
| | *38.6* | *0.006* | *0.002* | *0.009* | *0.01* | *0.1* | *5.4* | |
| 10 | • 90.3 | • 102.8 | • 104.6 | • 106.1 | • 116.2 | • 117.2 | • 138.2 | • |
| | *34.5* | *0.009* | *0.002* | *0.016* | *0.2*[b] | | *5.3* | |
| 11 | • 82.5 | • 91.6 | • 94.6 | • 98.1 | • 118.7 | | • 134.3 | • |
| | *34.4* | *0.006*[a] | | *0.013* | *0.3* | | *5.2* | |
| 12 | • 69 | • 98 | • 99.3 | • 101 | • 121 | | • 134 | • |
| | *37* | [a]*0* | [a]*0* | [a]*0* | *0.3* | | *5.2* | |

[a] The sum of the transition enthalpies of $SmC^*_A$–$SmC^*_{FI1}$ and $SmC^*_{FI1}$–$SmC^*_{FI2}$.
[b] The sum of the transition enthalpies of SmC*–$SmC^*_\alpha$ and $SmC^*_\alpha$–SmA.

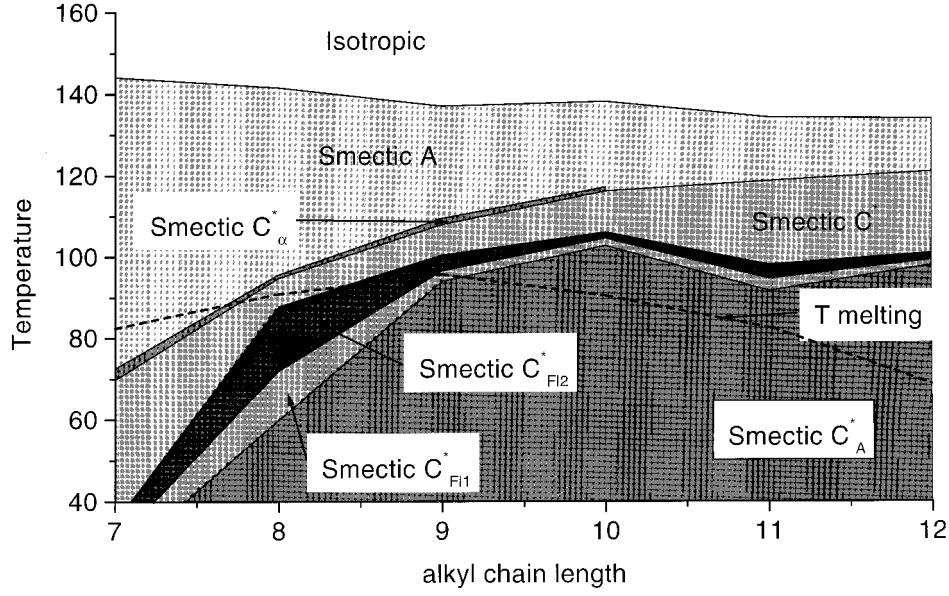


Figure 3. Plot of transition temperatures (°C) versus total chain length ($n+m$) of hydrogenous series **II**.

time, measured by the half width of the polarization peak versus temperature, given in figure 4, is about 20 μs, lower than that of the hydrogenous compound. The angle from the normal to the layers in the smectic phases is measured in the classical way at very low frequency (0.1 Hz). It increases quickly from the SmA–SmC* transition and reaches a value of about 40° (figure 7).

## 5. Crystal structure

Colourless prismatic crystals were grown by slow evaporation of ethanol/chloroform solutions. The compound studied, the member of series **I** with $n=3$ and $m=4$ ($n+m=7$), $C_{36}H_{35}O_7F_9$, $M_x=750.6$ g mol$^{-1}$ crystallizes in the triclinic system, space group $P1$ ($Z=4$). The unit-cell parameters were obtained by a least-squares fit of the setting angles of 25 reflections with $\theta$ between 12° and 18° and are as follows: $a=11.355(8)$, $b=15.537(7)$, $c=22.574(4)$ Å, $\alpha=109.31(5)°$, $\beta=95.55(4)°$ and $\gamma=90.51(4)°$, with a cell volume of 3694 Å$^3$. The calculated density of 1.350 g cm$^{-3}$ is much lower than that observed for other mesogenic perfluorinated crystal structures [18, 19], but only slightly less than that observed for some semiperfluorinated structures [3, 4]. The linear absorption coefficient is $\mu=0.122$ mm$^{-1}$ for the Mo($K_\alpha$) radiation.

The diffracted intensities were collected with a CAD-4 Enraf-Nonius diffractometer equipped with a graphite monochromator for $\theta_{max}=23.5°$: $0\leqslant h\leqslant 11$, $-17\leqslant k\leqslant 17$, $-25\leqslant l\leqslant 25$. Three standard reflections were used to

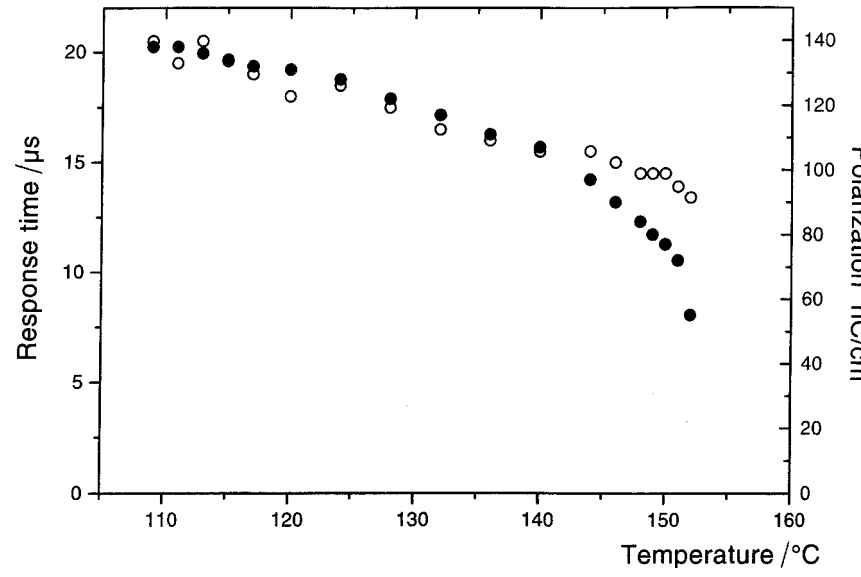


Figure 4. Saturated polarization (nC cm$^{-2}$, solid circles) and response time (μs, open circles) as functions of temperature.

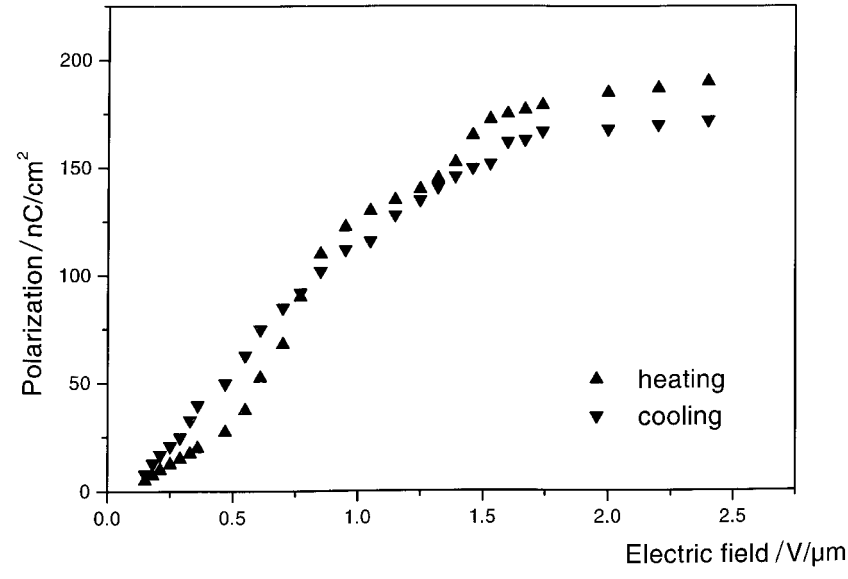


Figure 5. Polarization (nC cm$^{-2}$) in the SmC* phase versus field.



monitor the data collection and detect any decrease of intensity; the transmission factor $T(h\,k\,l)$ lies between 0.97 and 1.0. Nevertheless the crystal absorption correction was performed using the $\psi$ scan technique [20]. There were 10 371 independent reflections of which 9973 were unique ($R_{int} = 0.023$) and 6196 were considered as observed ($I > 3\sigma(I)$).

The crystal structure was solved with some difficulties using the SHELXS86 program [21] (several successive Fourier syntheses were necessary to generate the whole molecule) and refined using the SHELXL93 package [22] with restraints on a few C–C and C–F bond lengths of the perfluorinated moieties in which the carbon and fluorine atoms could only be refined isotropically (there are limits within which a distance or an angle is allowed to vary: 1.54 ± 0.03 Å and 1.32 ± 0.03 Å, respectively for the C–C and C–F bonds; 2.80 ± 0.05 Å between non contiguous $C_i$ and $C_{i+2}$ carbon atoms). Moreover, all phenyl rings were considered as rigid bodies. This notably increases the (number of observations/number of parameters) ratio and thence the viability of the structure. Scattering factors were taken from the International Tables for Crystallography [23]. The hydrogen atoms were introduced in their theoretical positions and allowed to ride with the atoms to which they are attached; the refinement was then resumed.

The final reliability factors were $R = 0.117$ and $w_R = 0.134$; the goodness of fit was $S = 1.366$ and the weighting factor $w$ was taken as: $w = 1/[\sigma^2(F_o^2) + (0.3413P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. The relatively high $R$ value can

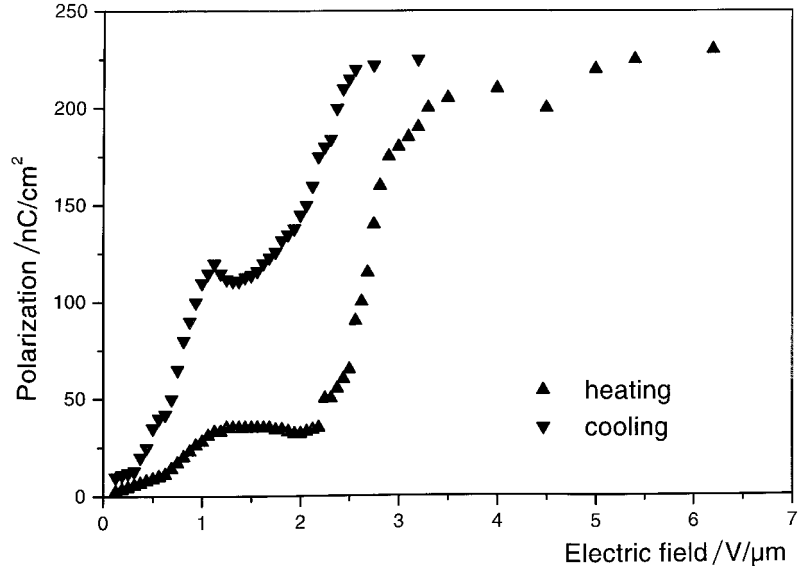


Figure 6. Polarization (nC cm$^{-2}$) in the $SmC^*_A$ phase versus field.

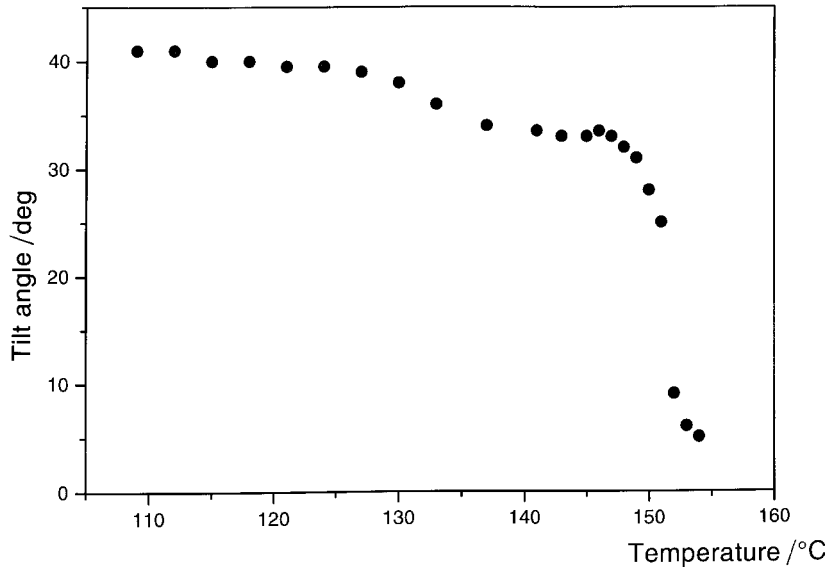


Figure 7. Tilt angle (°) versus temperature (°C).



be related to some disorder and quite high atomic motion factors. The developed molecular formula and the atom labelling are presented in figure 8. The fractional atomic coordinates for the four independent molecules with their $U_{eq}$ (equivalent thermal motion factors), except for the fluorine atoms for which there are only the isotropic Debye–Waller $B$ factors, are given in table 4. The molecular projections of the four molecules on their Φ1 (C10 to C15) mean planes are presented in figure 9. The thermal motion of the atoms is shown in figure 10 for one of the four independent molecules. The atoms of the central core and of the chiral chain could be

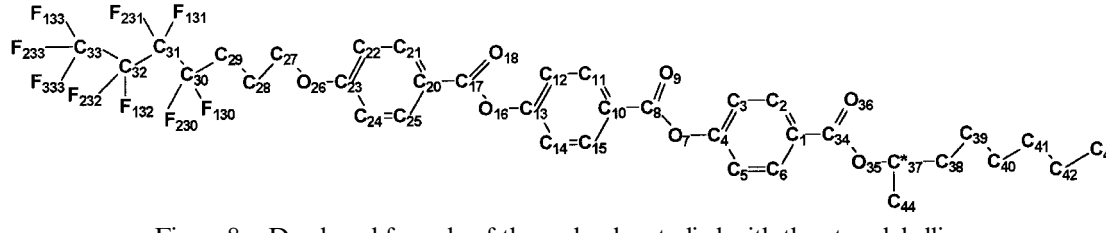


Figure 8. Developed formula of the molecules studied with the atom labelling.

Table 4. Fractional atomic coordinates and their equivalent thermal motion factors, $U_{eq}$ (Å$^2$).

| Atom | *x/a* | *y/b* | *z/c* | $U_{eq}$ | Atom | *x/a* | *y/b* | *z/c* | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| *Mole 1* | | | | | C6 | 1.0197(12) | 0.8781(8) | 0.5336(5) | 0.076(4) |
| C1 | 0.3662(11) | 0.0189(8) | 0.2258(6) | 0.073(4) | O7 | 0.9410(8) | 0.6348(5) | 0.4540(5) | 0.079(3) |
| C2 | 0.2767(12) | 0.0799(8) | 0.2275(6) | 0.081(5) | C8 | 0.8529(12) | 0.5919(8) | 0.4081(7) | 0.074(4) |
| C3 | 0.2906(12) | 0.1694(9) | 0.2674(6) | 0.079(4) | O9 | 0.7705(11) | 0.6325(6) | 0.3968(5) | 0.096(3) |
| C4 | 0.3970(10) | 0.1974(7) | 0.3058(6) | 0.073(4) | C10 | 0.8690(9) | 0.4948(7) | 0.3784(5) | 0.064(3) |
| C5 | 0.4851(11) | 0.1365(8) | 0.3049(6) | 0.071(4) | C11 | 0.7807(12) | 0.4415(8) | 0.3365(6) | 0.084(5) |
| C6 | 0.4712(13) | 0.0455(8) | 0.2631(6) | 0.086(5) | C12 | 0.7899(12) | 0.3473(8) | 0.3075(6) | 0.091(5) |
| O7 | 0.4197(9) | 0.2896(6) | 0.3424(5) | 0.087(3) | C13 | 0.8922(12) | 0.3072(8) | 0.3226(7) | 0.090(5) |
| C8 | 0.3491(11) | 0.3310(7) | 0.3887(6) | 0.067(4) | C14 | 0.9833(13) | 0.3581(9) | 0.3638(7) | 0.085(5) |
| O9 | 0.2669(10) | 0.2889(6) | 0.3990(5) | 0.087(3) | C15 | 0.9724(12) | 0.4525(9) | 0.3924(7) | 0.083(4) |
| C10 | 0.3786(10) | 0.4308(7) | 0.4191(5) | 0.068(4) | O16 | 0.9100(10) | 0.2138(6) | 0.2889(6) | 0.092(4) |
| C11 | 0.3041(12) | 0.4807(10) | 0.4606(6) | 0.087(6) | C17 | 0.8480(13) | 0.1509(9) | 0.3088(8) | 0.080(4) |
| C12 | 0.3280(11) | 0.5741(8) | 0.4884(7) | 0.087(5) | O18 | 0.7842(12) | 0.1711(7) | 0.3482(6) | 0.110(4) |
| C13 | 0.4231(11) | 0.6157(8) | 0.4741(6) | 0.071(4) | C20 | 0.8665(10) | 0.0530(7) | 0.2678(5) | 0.065(3) |
| C14 | 0.4983(12) | 0.5644(8) | 0.4332(7) | 0.083(5) | C21 | 0.8076(12) | – 0.0168(8) | 0.2801(7) | 0.088(5) |
| C15 | 0.4758(11) | 0.4699(9) | 0.4045(7) | 0.080(5) | C22 | 0.8261(12) | – 0.1073(9) | 0.2453(6) | 0.086(5) |
| O16 | 0.4510(10) | 0.7121(6) | 0.5064(5) | 0.084(3) | C23 | 0.9028(12) | – 0.1264(8) | 0.1988(6) | 0.083(5) |
| C17 | 0.3836(12) | 0.7746(8) | 0.4875(6) | 0.069(4) | C24 | 0.9627(13) | – 0.0549(8) | 0.1873(7) | 0.089(5) |
| O18 | 0.3045(9) | 0.7481(7) | 0.4475(6) | 0.091(4) | C25 | 0.9436(12) | 0.0347(8) | 0.2219(6) | 0.084(5) |
| C20 | 0.4169(9) | 0.8687(7) | 0.5273(5) | 0.060(3) | O26 | 0.9117(11) | – 0.2172(6) | 0.1625(6) | 0.103(4) |
| C21 | 0.3519(10) | 0.9380(8) | 0.5156(5) | 0.072(4) | C27 | 0.9923(18) | – 0.2451(11) | 0.1173(10) | 0.131(9) |
| C22 | 0.3817(11) | 1.0290(9) | 0.5517(6) | 0.085(5) | C28 | 0.9787(18) | – 0.3479(11) | 0.0833(11) | 0.135(9) |
| C23 | 0.4733(11) | 1.0496(7) | 0.5978(6) | 0.079(5) | C29 | 0.8552(18) | – 0.3793(11) | 0.0516(14) | 0.142(11) |
| C24 | 0.5391(12) | 0.9807(7) | 0.6101(6) | 0.081(5) | C30 | 0.8479(20) | – 0.4868(13) | 0.0187(10) | 0.213(20) |
| C25 | 0.5124(12) | 0.8887(8) | 0.5748(6) | 0.077(6) | F130 | 0.9319(16) | – 0.5060(13) | – 0.0207(9) | 0.171 |
| O26 | 0.4949(11) | 1.1407(7) | 0.6312(5) | 0.096(4) | F230 | 0.8966(20) | – 0.5253(17) | 0.0596(11) | 0.211 |
| C27 | 0.5958(15) | 1.1716(10) | 0.6808(9) | 0.102(6) | C31 | 0.7189(24) | – 0.5164(19) | – 0.0059(13) | 0.509 |
| C28 | 0.5892(17) | 1.2768(10) | 0.7148(11) | 0.124(13) | F131 | 0.7003(30) | – 0.4818(23) | – 0.0515(16) | 0.265 |
| C29 | 0.4762(16) | 1.2993(12) | 0.7428(8) | 0.109(6) | F231 | 0.6612(22) | – 0.4936(18) | 0.0435(12) | 0.220 |
| C30 | 0.4681(21) | 1.3908(19) | 0.7956(15) | 0.519 | C32 | 0.7005(24) | – 0.6152(21) | – 0.0499(14) | 0.596 |
| F130 | 0.3800(27) | 1.4038(25) | 0.8365(16) | 0.274 | F132 | 0.5814(27) | – 0.6330(34) | – 0.0556(24) | 0.336 |
| F230 | 0.5738(14) | 1.4382(11) | 0.8109(7) | 0.151 | F232 | 0.7685(26) | – 0.6447(22) | – 0.0965(13) | 0.253 |
| C31 | 0.3899(25) | 1.4520(20) | 0.7662(20) | 0.337 | C33 | 0.7119(33) | – 0.6835(26) | – 0.0137(26) | 0.588 |
| F131 | 0.2772(18) | 1.4202(14) | 0.7625(10) | 0.187 | F133 | 0.6516(53) | – 0.7416(38) | – 0.0655(27) | 0.403 |
| F231 | 0.4742(16) | 1.4484(13) | 0.7254(9) | 0.169 | F233 | 0.5996(39) | – 0.6788(53) | – 0.0022(39) | 0.464 |
| C32 | 0.3790(69) | 1.5456(20) | 0.8167(30) | 0.537 | F333 | 0.8194(26) | – 0.6791(21) | – 0.0309(14) | 0.244 |
| F132 | 0.3096(76) | 1.5950(60) | 0.7903(44) | 0.546 | C34 | 0.9239(13) | 1.0013(10) | 0.6179(8) | 0.083(5) |
| F232 | 0.4230(41) | 1.6179(32) | 0.8076(23) | 0.330 | O35 | 1.0165(11) | 1.0567(6) | 0.6135(5) | 0.092(3) |
| C33 | 0.3367(37) | 1.5383(48) | 0.8765(21) | 0.516 | O36 | 0.8514(11) | 1.0265(8) | 0.6502(6) | 0.097(3) |
| F133 | 0.2959(115) | 1.6235(51) | 0.8961(59) | 0.632 | C37 | 1.0322(16) | 1.1491(9) | 0.6604(7) | 0.101(6) |
| F233 | 0.4464(39) | 1.5576(37) | 0.9057(25) | 0.360 | C38 | 0.9559(18) | 1.2150(10) | 0.6346(8) | 0.106(7) |
| F333 | 0.2194(34) | 1.5414(31) | 0.8768(2) | 0.325 | C39 | 0.9626(25) | 1.3038(14) | 0.6897(12) | 0.208(20) |
| C34 | 0.3432(12) | 0.0767(8) | 0.1801(7) | 0.075(4) | C40 | 0.8803(22) | 1.3768(10) | 0.6797(13) | 0.220(27) |
| O35 | 0.4358(9) | – 0.1311(6) | 0.1819(4) | 0.083(3) | C41 | 0.9166(27) | 1.4671(17) | 0.7346(18) | 0.472(66) |
| O36 | 0.2583(10) | – 0.1024(7) | 0.1440(6) | 0.094(4) | C42 | 0.8149(32) | 1.5238(27) | 0.7597(17) | 1.007(242) |
| C37 | 0.4313(16) | – 0.2235(8) | 0.1370(8) | 0.097(7) | C43 | 0.8556(51) | 1.5910(37) | 0.8274(22) | 0.458(83) |
| C38 | 0.3690(17) | – 0.2938(9) | 0.1587(8) | 0.103(7) | C44 | 1.1625(29) | 1.1677(15) | 0.6654(14) | 0.162(12) |
| C39 | 0.3414(23) | – 0.3847(12) | 0.1063(10) | 0.133(9) | | | | | |
| C40 | 0.2677(21) | – 0.4499(13) | 0.1301(10) | 0.146(21) | *Mole 3* | | | | |
| C41 | 0.2615(40) | – 0.5473(15) | 0.0820(13) | 0.230(23) | C1 | 0.0691(10) | – 0.5159(8) | 0.2442(5) | 0.071(4) |
| C42 | 0.2189(56) | – 0.5470(26) | 0.0159(13) | 0.504 | C2 | 0.1596(12) | – 0.4706(9) | 0.2904(6) | 0.088(5) |
| C43 | 0.2012(60) | – 0.6501(33) | – 0.0280(22) | 0.543(131) | C3 | 0.1506(13) | – 0.3755(10) | 0.3194(7) | 0.095(5) |
| C44 | 0.5578(22) | – 0.2492(16) | 0.1274(13) | 0.137(11) | C4 | 0.0574(10) | – 0.3308(6) | 0.3029(5) | 0.063(3) |
| | | | | | C5 | – 0.0314(14) | – 0.3765(9) | 0.2567(7) | 0.101(6) |
| *Mole 2* | | | | | C6 | – 0.0269(12) | – 0.4714(7) | 0.2265(7) | 0.095(6) |
| C1 | 0.9281(11) | 0.9073(8) | 0.5705(6) | 0.075(4) | O7 | 0.0433(9) | – 0.2366(5) | 0.3326(5) | 0.081(3) |
| C2 | 0.8389(11) | 0.8428(8) | 0.5657(6) | 0.079(4) | C8 | 0.1112(12) | – 0.1734(8) | 0.3173(7) | 0.078(4) |
| C3 | 0.8383(11) | 0.7524(10) | 0.5259(7) | 0.083(5) | O9 | 0.1847(13) | – 0.1999(7) | 0.2769(6) | 0.111(5) |
| C4 | 0.9333(11) | 0.7277(8) | 0.4898(6) | 0.077(4) | C10 | 0.0931(10) | – 0.0791(8) | 0.3556(6) | 0.069(4) |
| C5 | 1.0243(11) | 0.7895(8) | 0.4931(6) | 0.075(4) | C11 | 0.1637(10) | – 0.0110(8) | 0.3480(6) | 0.084(5) |

Table 4. (*continued*).

| Atom | *x/a* | *y/b* | *z/c* | $U_{eq}$ | Atom | *x/a* | *y/b* | *z/c* | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| C12 | 0.1558(12) | 0.0810(8) | 0.3833(6) | 0.089(5) | C6 | 0.5402(12) | 1.3911(8) | 0.5666(7) | 0.093(8) |
| C13 | 0.0731(11) | 0.1025(8) | 0.4278(6) | 0.071(4) | O7 | 0.5721(8) | 1.1548(5) | 0.4604(5) | 0.080(3) |
| C14 | 0.0011(12) | 0.0366(8) | 0.4356(7) | 0.080(4) | C8 | 0.6407(13) | 1.0949(8) | 0.4799(7) | 0.076(4) |
| C15 | 0.0136(12) | − 0.0550(8) | 0.3994(6) | 0.085(5) | O9 | 0.7212(13) | 1.1176(7) | 0.5199(6) | 0.112(5) |
| O16 | 0.0604(9) | 0.1967(6) | 0.4622(5) | 0.080(3) | C10 | 0.6097(10) | 0.9983(8) | 0.4412(5) | 0.069(3) |
| C17 | 0.1499(11) | 0.2362(7) | 0.5090(6) | 0.067(4) | C11 | 0.6831(12) | 0.9309(9) | 0.4483(7) | 0.085(4) |
| O18 | 0.2347(11) | 0.1942(7) | 0.5178(6) | 0.100(4) | C12 | 0.6596(12) | 0.8406(8) | 0.4126(6) | 0.093(6) |
| C20 | 0.1352(10) | 0.3338(8) | 0.5408(5) | 0.068(3) | C13 | 0.5624(10) | 0.8164(8) | 0.3689(6) | 0.070(4) |
| C21 | 0.2192(11) | 0.3807(8) | 0.5901(6) | 0.086(4) | C14 | 0.4832(12) | 0.8822(7) | 0.3595(6) | 0.072(4) |
| C22 | 0.2127(11) | 0.4739(8) | 0.6241(7) | 0.083(4) | C15 | 0.5100(10) | 0.9727(7) | 0.3973(5) | 0.064(4) |
| C23 | 0.1175(11) | 0.5189(7) | 0.6069(6) | 0.073(4) | O16 | 0.5353(9) | 0.7233(5) | 0.3323(4) | 0.074(3) |
| C24 | 0.0327(14) | 0.4747(8) | 0.5577(6) | 0.090(5) | C17 | 0.6109(12) | 0.6837(9) | 0.2873(6) | 0.073(3) |
| C25 | 0.0412(11) | 0.3798(8) | 0.5246(6) | 0.077(4) | O18 | 0.6872(11) | 0.7265(7) | 0.2776(6) | 0.100(4) |
| C27 | 0.0296(15) | 0.6672(8) | 0.6287(9) | 0.101(6) | C20 | 0.5784(9) | 0.5862(7) | 0.2569(5) | 0.060(3) |
| C28 | 0.0345(19) | 0.7587(14) | 0.6779(14) | 0.166(15) | C21 | 0.6476(11) | 0.5406(8) | 0.2079(6) | 0.088(7) |
| C29 | 0.1526(16) | 0.8088(10) | 0.6949(11) | 0.122(8) | C22 | 0.6253(12) | 0.4474(8) | 0.1735(6) | 0.086(5) |
| C30 | 0.1496(21) | 0.8996(12) | 0.7504(11) | 0.285(35) | C23 | 0.5344(11) | 0.4005(7) | 0.1884(6) | 0.078(5) |
| F130 | 0.1378(28) | 0.8824(21) | 0.8032(13) | 0.256 | C24 | 0.4652(11) | 0.4442(7) | 0.2368(6) | 0.075(5) |
| F230 | 0.0922(16) | 0.9572(12) | 0.7259(8) | 0.168 | C25 | 0.4903(11) | 0.5375(8) | 0.2690(6) | 0.073(4) |
| C31 | 0.2732(20) | 0.9464(14) | 0.7672(15) | 0.309 | O26 | 0.5222(11) | 0.3090(6) | 0.1527(6) | 0.100(4) |
| F131 | 0.3170(36) | 0.9342(29) | 0.7127(17) | 0.302 | C27 | 0.4314(18) | 0.2547(10) | 0.1608(9) | 0.107(7) |
| F231 | 0.3514(20) | 0.8885(16) | 0.7825(11) | 0.198 | C28 | 0.4120(18) | 0.1605(12) | 0.1095(10) | 0.135(11) |
| C32 | 0.2692(33) | 1.0389(17) | 0.8219(14) | 0.377 | C29 | 0.5284(20) | 0.1097(11) | 0.1017(12) | 0.145(11) |
| F132 | 0.2034(28) | 1.0990(21) | 0.8032(15) | 0.259 | C30 | 0.5184(21) | 0.0242(12) | 0.0457(12) | 0.182(18) |
| F232 | 0.2756(27) | 1.0230(21) | 0.8769(14) | 0.248 | F130 | 0.4385(26) | − 0.0287(21) | 0.0593(15) | 0.259 |
| C33 | 0.3987(36) | 1.0801(27) | 0.8387(24) | 0.358 | F230 | 0.4467(28) | 0.0225(22) | − 0.0054(14) | 0.254 |
| F133 | 0.3782(50) | 1.1587(33) | 0.8819(24) | 0.388 | C31 | 0.6379(34) | − 0.0198(25) | 0.0324(18) | 0.371 |
| F233 | 0.4233(49) | 1.0830(39) | 0.7836(27) | 0.384 | F131 | 0.6741(43) | 0.0376(33) | 0.0048(23) | 0.342 |
| F333 | 0.4860(42) | 1.0327(30) | 0.8531(21) | 0.325 | F231 | 0.6593(43) | − 0.0294(33) | 0.0877(21) | 0.344 |
| C34 | 0.0786(11) | − 0.6198(8) | 0.2139(6) | 0.069(4) | C32 | 0.6279(56) | − 0.0939(34) | − 0.0363(17) | 0.506 |
| O35 | − 0.0189(9) | − 0.6573(6) | 0.1728(5) | 0.089(3) | F132 | 0.5407(48) | − 0.1432(38) | − 0.0867(23) | 0.379 |
| O36 | 0.1550(10) | − 0.6627(6) | 0.2298(6) | 0.098(4) | F232 | 0.7393(58) | − 0.1354(54) | − 0.0555(35) | 0.447 |
| C37 | − 0.0272(14) | − 0.7555(8) | 0.1461(8) | 0.086(5) | C33 | 0.6411(34) | − 0.1911(27) | − 0.0265(33) | 0.366 |
| C38 | 0.0397(18) | − 0.7914(11) | 0.0873(8) | 0.112(6) | F133 | 0.7476(38) | − 0.1756(40) | 0.0168(27) | 0.392 |
| C39 | 0.0293(29) | − 0.8980(14) | 0.0626(15) | 0.184(15) | F233 | 0.6437(76) | − 0.2593(57) | − 0.0884(33) | 0.500 |
| C40 | 0.1029(36) | − 0.9335(17) | 0.0067(15) | 0.489(150) | F333 | 0.5231(28) | − 0.1855(22) | − 0.0117(15) | 0.254 |
| C41 | 0.1407(28) | − 1.0304(19) | 0.0041(21) | 0.516(102) | C34 | 0.6509(11) | 1.5377(8) | 0.5766(6) | 0.072(4) |
| C42 | 0.0275(33) | − 1.0939(20) | − 0.0100(20) | 0.257(48) | O35 | 0.5768(9) | 1.5756(5) | 0.6225(5) | 0.084(3) |
| C43 | 0.0618(65) | − 1.1898(28) | − 0.0546(37) | 0.528(69) | O36 | 0.7228(10) | 1.5840(7) | 0.5640(5) | 0.093(3) |
| C44 | − 0.1565(17) | − 0.7762(14) | 0.1301(16) | 0.159(15) | C37 | 0.5762(13) | 1.6747(7) | 0.6451(8) | 0.088(4) |
| | | | | | C38 | 0.6734(17) | 1.7172(8) | 0.7015(8) | 0.103(7) |
| *Mole 4* | | | | | C39 | 0.6798(16) | 1.8206(10) | 0.7192(9) | 0.107(8) |
| C1 | 0.6301(10) | 1.4384(7) | 0.5500(5) | 0.063(3) | C40 | 0.7713(23) | 1.8680(12) | 0.7743(11) | 0.191(5) |
| C2 | 0.6984(12) | 1.3863(10) | 0.5045(6) | 0.086(5) | C41 | 0.7765(22) | 1.9728(11) | 0.7875(11) | 0.149(10) |
| C3 | 0.6823(12) | 1.2934(9) | 0.4767(6) | 0.095(6) | C42 | 0.8550(33) | 2.0224(17) | 0.8484(15) | 0.578(136) |
| C4 | 0.5950(10) | 1.2480(7) | 0.4940(5) | 0.066(3) | C43 | 0.8666(42) | 2.1266(16) | 0.8550(27) | 0.351(66) |
| C5 | 0.5256(13) | 1.2952(8) | 0.5381(7) | 0.088(5) | C44 | 0.4576(18) | 1.6979(12) | 0.6639(11) | 0.124(7) |



refined anisotropically and are represented by ellipsoids; the atoms of the perfluorinated C4F9 chain present a very high thermal motion and were refined isotropically (circles).

## 6. Discussion

It is well known that large transverse permanent electric dipole moments on the chiral end chains and steric effects are responsible for anticlinic ordering; for example if we replace the ramified $CH_3$ group of chiral 2-octanol by $CF_3$, the anticlinic $SmC^*_A$ phase is largely favoured and in some cases the only tilted smectic phase observed is $SmC^*_A$ (the SmC* phase totally disappears). In the series **I** compounds, all the phase transitions are first order and the subphases between SmA and SmC* or between SmC* and $SmC^*_A$ phases are not clearly detected. The same behaviour has also been observed by Drzewinski *et al.* [24]. They also mentioned that the

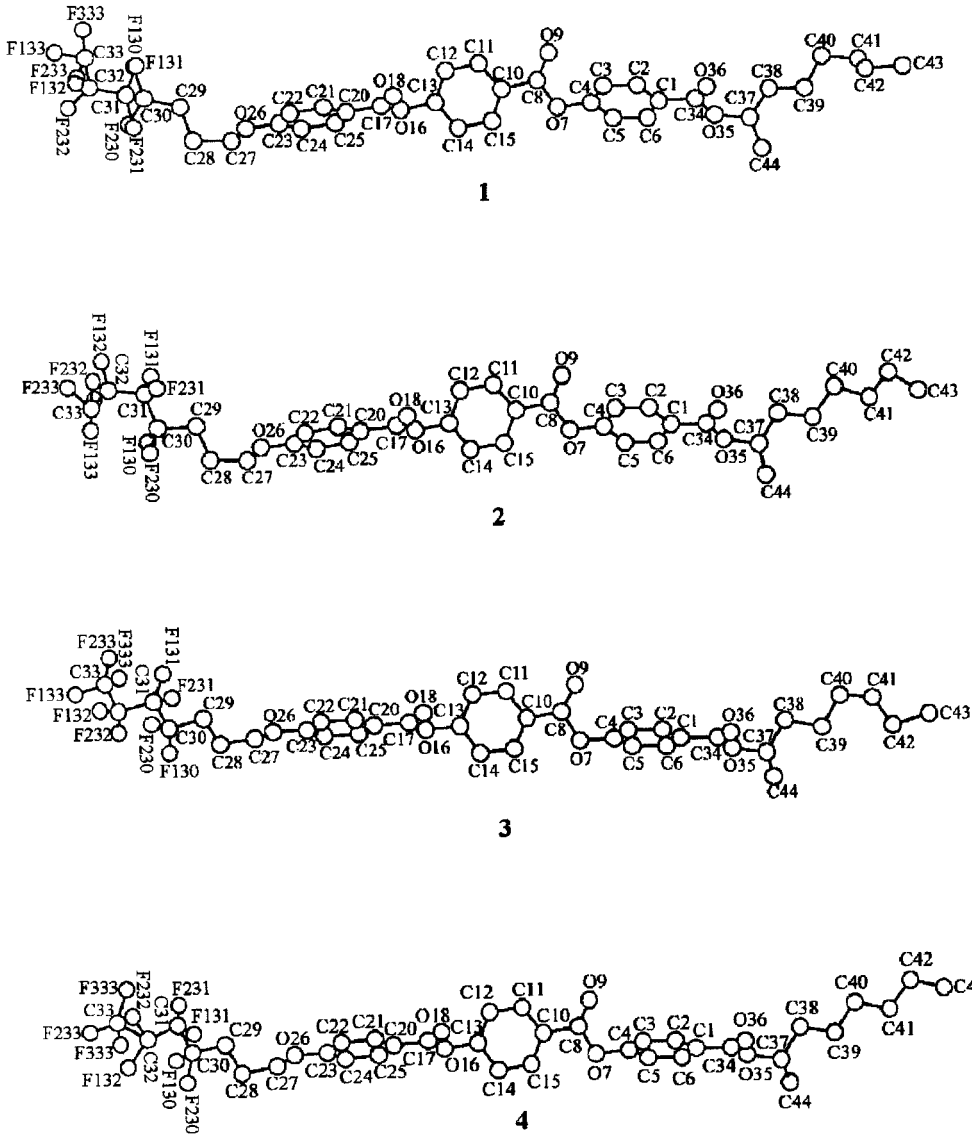


Figure 9. Molecular conformations of the four independent molecules projected on the Φ2 ring.

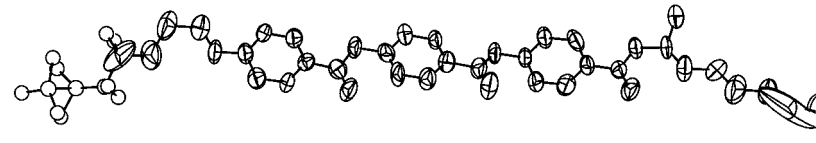

Figure 10. Ellipsoid representation (50% of probability) of one of the four independent molecules.

semifluorinated chains favour the SmC* phase more than the $SmC^*_A$ phase. The remarkable properties of these semiperfluorinated series **I** compounds are their high spontaneous polarization and low response time. They will be used for preparing $SmC^*_A$ mixtures at room temperature.

Until now, all crystal structures of compounds exhibiting the anticlinic $SmC^*_A$ phase show that the chiral end chain is orthogonal to the elongated molecule. We will see now what crystal structure is obtained with the semi-perfluorinated and anticlinic compound.

The bond lengths are given in table 5; they agree quite well with those found in several perfluorinated and semiperfluorinated mesogenic structures [11–14], with C–C and C–F average bond lengths of 1.52 and 1.34 Å and average C–C–C and F–C–F angles close to 118.5° and 106.3°, respectively, instead of a C–C–C angle close to 111° in alkanes [19, 20]. The increase of the C–C–C

Table 5. Bond lengths (Å) and standard deviations in brackets for the four independent molecules.

| Bond | Mole 1 | Mole 2 | Mole 3 | Mole 4 |
|---|---|---|---|---|
| C1–C6 | 1.37(1) | 1.38(1) | 1.39(1) | 1.38(1) |
| C1–C2 | 1.38(1) | 1.38(1) | 1.39(1) | 1.40(1) |
| C1–C34 | 1.49(1) | 1.49(1) | 1.52(1) | 1.47(1) |
| C2–C3 | 1.37(1) | 1.38(1) | 1.40(1) | 1.36(1) |
| C3–C4 | 1.39(1) | 1.39(1) | 1.37(1) | 1.37(1) |
| C4–C5 | 1.37(1) | 1.38(1) | 1.38(1) | 1.36(1) |
| C4–O7 | 1.39(1) | 1.40(1) | 1.40(1) | 1.39(1) |
| C5–C6 | 1.40(1) | 1.37(1) | 1.39(1) | 1.40(1) |
| O7–C8 | 1.37(1) | 1.36(1) | 1.39(1) | 1.37(1) |
| C8–O9 | 1.21(1) | 1.18(1) | 1.23(1) | 1.18(1) |
| C8–C10 | 1.48(1) | 1.44(1) | 1.45(1) | 1.47(1) |
| C10–C15 | 1.37(1) | 1.41(1) | 1.37(1) | 1.39(1) |
| C10–C11 | 1.37(1) | 1.36(1) | 1.38(1) | 1.38(1) |
| C11–C12 | 1.37(1) | 1.39(1) | 1.38(1) | 1.36(1) |
| C12–C13 | 1.37(1) | 1.38(1) | 1.40(1) | 1.37(1) |
| C13–C14 | 1.37(1) | 1.37(1) | 1.36(1) | 1.41(1) |
| C13–O16 | 1.43(1) | 1.41(1) | 1.41(1) | 1.41(1) |
| C14–C15 | 1.39(1) | 1.39(1) | 1.39(1) | 1.38(1) |
| O16–C17 | 1.38(1) | 1.40(1) | 1.37(1) | 1.38(1) |
| C17–O18 | 1.18(1) | 1.16(1) | 1.20(1) | 1.16(1) |
| C17–C20 | 1.46(1) | 1.51(1) | 1.47(1) | 1.45(1) |
| C20–C21 | 1.38(1) | 1.38(1) | 1.38(1) | .41(1) |
| C20–C25 | 1.40(1) | 1.38(1) | 1.37(1) | 1.36(1) |
| C21–C22 | 1.38(1) | 1.38(1) | 1.39(1) | 1.39(1) |
| C22–C23 | 1.35(1) | 1.39(1) | 1.38(1) | 1.38(1) |
| C23–O26 | 1.36(1) | 1.37(1) | 1.38(1) | 1.37(1) |
| C23–C24 | 1.39(1) | 1.39(1) | 1.38(1) | 1.40(1) |
| C24–C25 | 1.39(1) | 1.37(1) | 1.41(1) | 1.39(1) |
| O26–C27 | 1.44(1) | 1.40(1) | 1.43(1) | 1.38(1) |
| C27–C28 | 1.53(1) | 1.51(1) | 1.49(1) | 1.52(1) |
| C28–C29 | 1.50(1) | 1.51(1) | 1.49(1) | 1.54(1) |
| C29–C30 | 1.52(1) | 1.55(1) | 1.54(1) | 1.50(1) |
| C30–F230 | 1.35(1) | 1.33(1) | 1.33(1) | 1.34(1) |
| C30–F130 | 1.37(1) | 1.33(1) | 1.32(1) | 1.34(1) |
| C30–C31 | 1.55(1) | 1.52(1) | 1.53(1) | 1.53(1) |
| C31–F131 | 1.35(2) | 1.31(2) | 1.33(2) | 1.32(2) |
| C31–F231 | 1.35(2) | 1.30(2) | 1.36(2) | 1.31(2) |
| C31–C32 | 1.53(2) | 1.52(2) | 1.55(2) | 1.57(2) |
| C32–F232 | 1.30(2) | 1.33(2) | 1.34(2) | 1.36(2) |
| C32–F132 | 1.33(2) | 1.35(2) | 1.34(2) | 1.37(2) |
| C32–C33 | 1.51(2) | 1.53(2) | 1.56(1) | 1.57(2) |
| C33–F233 | 1.33(3) | 1.32(3) | 1.32(3) | 1.36(3) |
| C33–F333 | 1.33(3) | 1.32(3) | 1.32(3) | 1.37(3) |
| C33–F133 | 1.34(3) | 1.33(3) | 1.32(3) | 1.37(3) |
| C34–O36 | 1.17(1) | 1.16(1) | 1.19(1) | 1.19(1) |
| C34–O35 | 1.35(1) | 1.38(1) | 1.36(1) | 1.38(1) |
| O35–C37 | 1.44(1) | 1.46(1) | 1.43(1) | 1.44(1) |
| C37–C44 | 1.51(2) | 1.50(1) | 1.49(1) | 1.50(1) |
| C37–C38 | 1.52(1) | 1.55(1) | 1.54(1) | 1.56(1) |
| C38–C39 | 1.51(1) | 1.51(1) | 1.54(1) | 1.50(1) |
| C39–C40 | 1.56(1) | 1.53(1) | 1.53(1) | 1.51(1) |
| C40–C41 | 1.53(2) | 1.54(2) | 1.54(2) | 1.54(2) |
| C41–C42 | 1.53(3) | 1.51(3) | 1.55(3) | 1.53(3) |
| C42–C43 | 1.56(3) | 1.55(3) | 1.56(3) | 1.56(3) |

angle is attributed to the radius of the fluorine atom (1.49 Å), greater than the radius of the hydrogen atom (1.17 Å).

The conformations of the four independent molecules can be seen in the projections of their molecular structures on the mean plane of the Φ1 ring (figure 9). They are fully defined by the values of the torsion angles given in table 6. The polyaromatic central cores have three quasi-planar consecutive benzoate groups related to each other through the following torsion angles: C34–O35–C37–C38, C3–C4–O7–C8 and C12–C13–O16–C17 whose values are about the same for the four molecules, which therefore have a similar core conformation. The three benzoate groups Φ1–COO (C1 to C6, C34, O35, O36), Φ2–COO (O7, C8, O9 and C10 to C15) and Φ3–COO (O16, C17, O18 and C20 to C25) in the four independent molecules are related by the following dihedral angles:

| | Mole 1 | Mole 2 | Mole 3 | Mole 4 |
|---|---|---|---|---|
| Φ2–COO/Φ1–COO | 59° | 57° | 75° | 76° |
| Φ3–COO/Φ2–COO | 75° | 75° | 76° | 75° |

These results show the quasi-similarity of the polyaromatic cores in the four independent molecules. The lengths of the polyaromatic central cores LC (distance O26 to C34) and the whole molecule LT (distance C43 … F133, F233 or F333) are, respectively, equal to 18.25(2), 18.31(2), 18.34(2) and 18.28(2) Å for LC and 34.55(2), 35.05(2), 35.59(2) and 36.07(2) Å for LT. Taking into account the bulkiness of the terminal $CH_3$ [$r(CH_3) = 2.0$ Å] and $CF_3$ [$r(CF_3) = 2.80$ Å] groups, these latter distances lie between 39.4 and 40.8 Å.

The chiral alkyl chains (C38 to C43 and C44) are not fully extended except for molecule 4. The semiperfluorinated chains (O26 to C33) are not fully stretched; they depart from this state through the O26–C27–C28–C29 angle of about 60° for all molecules; they also slightly differ through their terminal ethyl

Table 6. Significative torsion angles (°); *trans* relates to angles differing by less than 10° from 180°.

| Torsion angle | Mole 1 | Mole 2 | Mole 3 | Mole 4 |
|---|---|---|---|---|
| C34–O35–C37–C38 | – 86 | – 89 | – 85 | – 89 |
| O35–C37–C38–C39 | 167 | *trans* | *trans* | *trans* |
| C37–C38–C39–C40 | *trans* | *trans* | *trans* | *trans* |
| C38–C39–C40–C41 | – 169 | – 169 | 153 | *trans* |
| C39–C40–C41–C42 | – 52 | – 142 | 64 | *trans* |
| C40–C41–C42–C43 | *trans* | 160 | 143 | *trans* |
| C3–C4–O7–C8 | 63 | 61 | 77 | 86 |
| C12–C13–O16–C17 | – 78 | – 80 | – 75 | – 70 |
| C22–C23–O26–C27 | *trans* | *trans* | *trans* | *trans* |
| C23–O26–C27–C28 | *trans* | *trans* | *trans* | *trans* |
| O26–C27–C28–C29 | 59 | 57 | 52 | 53 |
| C27–C28–C29–C30 | 160 | *trans* | *trans* | *trans* |
| C28–C29–C30–C31 | 108 | *trans* | *trans* | *trans* |
| C29–C30–C31–C32 | *trans* | 68 | *trans* | – 165 |
| C30–C31–C32–C33 | – 53 | 76 | *trans* | – 112 |

groups. Let us recall that the fluorinated and semi-perfluorinated chains were fully extended in several other molecules studied [3, 4, 18, 19].

The main axes of the four independent molecules in the unit cell are arranged in a head-to-tail fashion as observed in all crystal structures of mesogenic compounds. Two molecules are oriented in the same direction and the two others in the opposite direction. The projection of the structure on the ($yOz$) plane is shown in figure 11. The molecular axes are mutually parallel ($P_1$ space group) and approximately parallel to the ($xOz$) plane. They are arranged in a smectic C-like manner as is the case of other structures of semiperfluorinated compounds [11, 14]. The thickness of the sheets is close to 21.6 Å and the tilt angle is about 60°. The molecular interactions within a sheet involve both dipolar forces between transverse polar groups of the cores and van der Waals forces, whereas the interactions between sheets involve only very weak van der Waals forces.

## 7. Experimental

The compounds of series **I** were prepared according to the scheme. The following example is typical of the method used for the final esterification. Infrared spectra were recorded on a Perkin Elmer 783 spectrophotometer and NMR spectra on a Bruker HV200 MHz spectrometer.

(*R*)-4-(1-Methylheptyloxycarbonyl) 4-[4-(4,4,5,5,6,6,7,7,7-nonafluoroheptyloxy)benzoyloxy] benzoate **I**: To a solution of (*R*)-1-methylheptyl 4-(4-hydroxybenzoyloxy)benzoate **5** [14] (0.37 g, 1 mmol) in $CH_2Cl_2$ was added DCC (0.22 g, 1.1 mmol), DMAP (10 mg) and 4-(4,4,5,5,6,6,7,7,7-nonafluoroheptyloxy)benzoic acid **10** [15] (0.44 g, 1.1 mmol). The mixture was stirred at room temperature overnight, and filtered. The solvent was evaporated and the residue chromatographed on silica gel with dichloromethane as eluent. The desired product was recrystallized from absolute ethanol, yielding 0.51 g (64%). $^1$H NMR ($CDCl_3$): $\delta$ (ppm): 0.88 (t, 3H, $CH_3$), 1.24 (m, 10H, $5CH_2$), 1.35 (d, 3H, $CH_3$–CH*), 1.6–1.8 (m, 4H, $2CH_2$), 4.1 (t, 2H, $OCH_2$), 5.2 (m, 1H, CH–$CH_3$), 6.9 (d, 2H arom.), 7.2–7.4 (m, 4H arom.), 8 (m, 6H arom.). IR: $\nu_{max}$ (nujol), 2594, 2850, 1730, 1610, 1285, 1218, 850 cm$^{-1}$.

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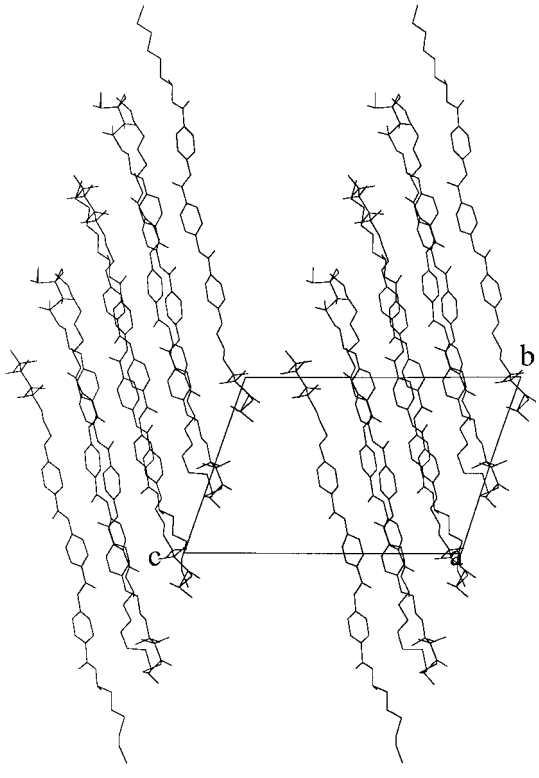


Figure 11. Projection of the structure on the ($yOz$) plane.

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