This article was downloaded by: On: *25 January 2011* Access details: *Access Details: Free Access* Publisher *Taylor & Francis* Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713926090

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

H. T. Nguyen; J. C. Rouillon; A. Babeau; J. P. Marcerou; H. Allouchi; G. Sigaud; M. Cotrait

Online publication date: 06 August 2010

To cite this Article Nguyen, H. T., Rouillon, J. C., Babeau, A., Marcerou, J. P., Allouchi, H., Sigaud, G. and Cotrait, M.(1999) 'Synthesis, properties and crystal structure of chiral semiperfluorinated liquid crystals with ferro and anticlinic smectic phases', Liquid Crystals, 26: 7, 1007 — 1019 **To link to this Article: DOI:** 10.1080/026782999204354

URL: http://dx.doi.org/10.1080/026782999204354

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

H. T. NGUYEN*, J. C. ROUILLON, A. BABEAU, J. P. MARCEROU, G. SIGAUD

Centre de Recherche Paul Pascal, Université de Bordeaux I, Avenue A. Schweitzer, 33600 Pessac, France

M. COTRAIT

Laboratoire de Cristallographie, Université de Bordeaux I, 33405 Talence Cedex, France

and H. ALLOUCHI

Laboratoire de Chimie Physique, Faculté de Pharmacie, 31 Avenue Monge, 37200 Tours, France

(Received 30 June 1998; in final form 1 October 1998; accepted 30 October 1998)

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} H₃₅ O₇ F₉, M_x = 750.6 g mol⁻¹, crystallizes in the triclinic system, space group *P*1, 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:

$$F(CF_2)_m$$
-(CH₂)_nO- (I) -COO- (I) -COO- (I) -COO-CH*-C₆H₁₂
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:

Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online ©1999 Taylor & Francis Ltd http://www.tandf.co.uk/JNLS/lct.htm http://www.taylorandfrancis.com/JNLS/lct.htm

*Author for correspondence.



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.

т	п	Cr		SmA		Ι	d	L
4 6 6 7 8 8	5 6 4 5 6 5 5 6	•	49 37 44 47 42 50 66 60	• • • •	46 (39) 45 (37) (59) 66	• • • •	26 35	25.1 26.3 26.5 27.6 28.7 28.8 30.0 31.1





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^{*}_{α} 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 $m \ge 6$, 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

т	п	Cr		SmC^*_A		SmC*		SmA		Ι
2	8	•	97.4	•	106.9	•	133.8	•	142	•
3	6	•	<i>42.2</i> 112.6		0.05	•	0.7 144.6	•	4.8 151	•
4	3	•	<i>42.4</i> 88.2	•	116.6	•	0.8 159	•	<i>4.7</i> 164	•
4	4		30 924	•	<i>0.04</i> 115		<i>1.6</i> 152		<i>4</i> 158	
т 4	-	·	19	·	0.04	·	152 1	·	3.4	·
4	3	•	95 33.5	•	0.03	•	155 1.2	•	160 <i>4.4</i>	•
4	6	•	108 33	•	111.7 0.04	•	151 1	•	159 4.6	•
6	4	•	97.6 27.5			•	166	•	177	•
6	5	•	87.6			•	165.5	•	177	•
6	6	•	32.7 106.8			•	0.7 164	•	3.1 177	•
7	5	•	46 95.1			•	<i>0.63</i> 166.8	•	5.5 189	•
			32.5				0.9		5.4	

Table 2. Transition temperatures (°C) and enthalpies in italics (kJ mol⁻¹) of the compounds of series I.



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 $7.5 \mu\text{m}$. Figure 4 shows the spontaneous polarization under an a.c. field at saturation ($E = \pm 4 \text{ V} \mu\text{m}^{-1}$; $\nu = 100 \text{ Hz}$). 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; $P_s = 80 \text{ nC cm}^{-2}$). Figures 5 and 6 represent the polarization dependence on the a.c. field in the SmC* and SmC* phases. It shows significant differences from one phase to another. The SmC* 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		$\mathrm{Sm}\mathrm{C}^*_{\!\scriptscriptstyle A}$		SmC^*_{FII}		SmC^*_{F12}		SmC*		SmC^*_{α}		SmA		Ι
7	•	82.7 31.6							•	(69.8) 0.002	•	(72.6) 0.015	•	144.1 5.7	•
8	•	89 34.7	•	(60) 0.003 ^a	•	(72)	•	(87.8) 0.004	•	94.8 0.004	•	95.7 0.04	•	141.8 5.6	•
9	•	95.8 38.6	•	(94) 0.006	•	96.6 0.002	•	100.5	•	108	•	110.5 0.1	•	138.1 5.4	•
10	•	90.3 34.5	•	102.8	•	104.6 0.002	•	106.1 0.016	•	116.2 0.2 ^ь	•	117.2	•	138.2 5.3	•
11	•	82.5 34.4	•	91.6 0.006ª	•	94.6	•	98.1 0.013	•	118.7 0.3			•	134.3 5.2	•
12	•	69 37	•	98 ^a 0	•	99.3 ª0	•	101 ^a 0	•	121 0.3			•	134 5.2	•

^a The sum of the transition enthalpies of SmC^{*}_A–SmC^{*}_{F11} and SmC^{*}_{F11}–SmC^{*}_{F12}. ^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 $20\,\mu$ s, 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), $C_{36} H_{35} O_7 F_9$, $M_x = 750.6 \text{ g mol}^{-1}$ crystallizes in the triclinic system, space group P1 (Z = 4).

The unit-cell parameters were obtained by a leastsquares fit of the setting angles of 25 reflections with θ between 12° and 18° and are as follows: a = 11.355(8), b = 15.537(7), c = 22.574(4)Å, $\alpha = 109.31(5)^{\circ}, \beta = 95.55(4)^{\circ}$ and $\gamma = 90.51(4)^\circ$, with a cell volume of 3694Å³. 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 $\mu = 0.122 \text{ mm}^{-1}$ for the $Mo(K_{\alpha})$ radiation.

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



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 ψ 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 $P = (F_o^2 + 2F_o^2)/3$. The relatively high *R* value can



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 Φ 1 (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} (Å²).

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Atom	x/a	y/b	z/c	$U_{ m eq}$	Atom	x/a	y/b	z/c	$U_{\rm eq}$
$ \begin{array}{ccccc} c_1 & c_2 c_2 c_1 (1) & c_2 c_2 c_1 (1) & c_2 c_2 c_2 (1) & c_2 c_2 c_2 (1) & c_2 c_2 c_2 (1) & c_2 c_$	Mole 1	0.2((2(11))	0.0100/0)	0.0050(6)	0.072(4)	C6	1.0197(12)	0.8781(8)	0.5336(5)	0.076(4)
$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c}$	CI	0.3662(11)	0.0189(8)	0.2258(6)	0.073(4)	O/	0.9410(8)	0.6348(5)	0.4540(5)	0.079(3)
$ \begin{array}{c} C4 & 0.5070(16) & 0.1074(2) & 0.2080(0) & 0.0714(1) & C10 & 0.800(0) & 0.4948(7) & 0.4278(5) & 0.0474(5) \\ C5 & 0.4571(13) & 0.0458(8) & 0.2049(6) & 0.0714(1) & C11 & 0.7807(12) & 0.4415(8) & 0.376(6) & 0.094(5) \\ C6 & 0.4771(13) & 0.0458(8) & 0.2631(6) & 0.086(5) & C12 & 0.7899(12) & 0.3472(8) & 0.376(6) & 0.094(5) \\ C7 & 0.497(10) & 0.288(6) & 0.3404(5) & 0.087(3) & C13 & 0.8933(12) & 0.3572(8) & 0.3228(7) & 0.088(5) \\ C9 & 0.269(10) & 0.288(7) & 0.097(5) & 0.087(3) & C15 & 0.0724(12) & 0.4555(9) & 0.368(8) & 0.098(4) \\ C11 & 0.304(12) & 0.4877(10) & 0.4606(6) & 0.087(6) & C17 & 0.4840(13) & 0.1599(9) & 0.3488(8) & 0.098(4) \\ C12 & 0.2380(1) & 0.548(4) & 0.4327(1) & 0.4606(6) & 0.087(6) & C17 & 0.4840(13) & 0.1599(9) & 0.3488(8) & 0.008(4) \\ C13 & 0.4231(11) & 0.6157(8) & 0.4741(6) & 0.071(4) & C20 & 0.3665(1) & 0.0530(7) & 0.2458(6) & 0.088(4) \\ C14 & 0.4933(12) & 0.5644(8) & 0.4327(7) & 0.088(5) & C22 & 0.8261(12) & -0.1073(9) & 0.2458(6) & 0.088(5) \\ C16 & 0.4738(11) & 0.4099(9) & 0.4045(7) & 0.089(5) & C22 & 0.8261(12) & -0.1073(9) & 0.2458(6) & 0.088(5) \\ C16 & 0.4708(10) & 0.721(6) & 0.5064(4) & C24 & 0.967(13) & -0.0598(8) & 0.1387(6) & 0.088(5) \\ C10 & 0.4469(9) & 0.8887(7) & 0.2573(5) & 0.060(3) & C25 & 0.377(113) & -0.0549(8) & 0.1387(6) & 0.088(5) \\ C20 & 0.4169(9) & 0.388(7) & 0.5574(6) & 0.094(4) & C25 & 0.9347(8) & 0.2219(6) & 0.048(5) \\ C20 & 0.4169(9) & 0.8887(7) & 0.5574(6) & 0.096(4) & C24 & 0.957(13) & -0.0549(8) & 0.1373(6) & 0.088(5) \\ C20 & 0.4469(9) & 0.8887(7) & 0.5774(6) & 0.096(4) & C24 & 0.957(7)18 & -0.0549(8) & 0.1387(6) & 0.088(5) \\ C20 & 0.4469(9) & 0.888(7) & 0.5574(6) & 0.097(6) & C29 & 0.857(2) & 1.0773(10) & 0.137(6) & 0.038(4) \\ C20 & 0.339(12) & 0.0248(8) & 0.576(6) & 0.079(5) & C29 & 0.357(11) & 0.0158(6) & 0.0243(1) \\ C20 & 0.339(12) & 0.0248(8) & 0.556(6) & 0.077(4) & C29 & 0.0552(2) & 0.0377(11) & 0.0388(1) & 0.0187(6) \\ C20 & 0.339(12) & 0.0248(8) & 0$	C_2	0.2/6/(12) 0.2006(12)	0.0799(8) 0.1694(9)	0.2275(6) 0.2674(6)	0.081(5) 0.070(4)	$\frac{1}{0}$	0.8529(12) 0.7705(11)	0.5919(8) 0.6325(6)	0.4081(7) 0.3068(5)	0.074(4) 0.096(3)
$ \begin{array}{c} \hline c \\ c$	C_4	0.2900(12) 0.3970(10)	0.1094(7) 0.1974(7)	0.2074(0) 0.3058(6)	0.073(4)	C10	0.7703(11) 0.8690(9)	0.0323(0) 0.4948(7)	0.3784(5)	0.050(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C5	0.4851(11)	0.1365(8)	0.3049(6)	0.071(4)	Cli	0.7807(12)	0.4415(8)	0.3365(6)	0.084(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	O 7	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)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
C10 0.3780(10) 0.4387(7) 0.4491(5) 0.008(4) O1c 0.9100(10) 0.2138(b) 0.2889(c) 0.092(4) C12 0.3280(11) 0.65741(8) 0.4884(7) 0.087(5) O18 0.7842(12) 0.1711(7) 0.3482(c) 0.110(4) 0.0550(7) 0.3482(c) 0.0050(7) 0.3482(c) 0.0050(7) 0.3482(c) 0.0050(7) 0.3482(c) 0.005(3) C14 0.4983(12) 0.5741(8) 0.4332(7) 0.003(5) C21 0.866(5) 0.0053(7) 0.2453(c) 0.008(5) 0.008(5) C15 0.4758(11) 0.4099(9) 0.40457(c) 0.009(5) C2 0.826(12) -0.1073(9) 0.2453(c) 0.008(5) 0.008(5) 0.016 0.4510(10) 0.7121(c) 0.5064(5) 0.004(3) C23 0.9022(12) -0.1274(8) 0.2453(c) 0.008(5) 0.016 0.4510(10) 0.7121(c) 0.5064(5) 0.094(3) C23 0.9023(12) -0.1274(8) 0.2473(c) 0.008(5) 0.023 0.9023(12) -0.0124(8) 0.2187(7) 0.088(5) 0.023 0.917(11) -0.2172(c) 0.1053(4) 0.0383(5) 0.023 0.917(11) -0.2172(c) 0.1053(4) 0.0384(5) 0.223 0.817(7) 0.5376(5) 0.072(4) C27 0.9923(18) -0.3793(11) 0.0156(14) 0.131(9) 0.223 0.817(11) 0.09380(8) 0.5156(5) 0.072(4) C27 0.9923(18) -0.3793(11) 0.0516(14) 0.132(9) 0.2531(11) 0.109(9) 0.5517(6) 0.008(5) C23 0.8479(20) -0.4488(13) 0.0187(10) 0.213(20) 0.223 0.5124(12) 0.9807(7) 0.6101(6) 0.081(5) C29 0.8552(18) -0.3793(11) 0.0516(14) 0.142(11) 0.22 0.5124(12) 0.9807(7) 0.6101(6) 0.081(5) C29 0.8552(18) -0.3793(11) 0.0516(14) 0.1213(20) 0.223 0.5124(12) 0.9807(7) 0.6101(6) 0.081(5) C30 0.8479(20) -0.4233(13) 0.0056(14) 0.213(20) 0.223 0.5124(12) 0.9807(7) 0.6101(6) 0.016(6) C31 0.7189(24) -0.5164(19) -0.0096(13) 0.207(9) 0.171 0.226 0.5424(12) 0.9807(7) 0.6101(6) 0.016(6) C31 0.7189(24) -0.5164(19) -0.0096(13) 0.207(9) 0.171 0.226 0.5524(12) 0.9807(7) 0.6101(6) 0.019(6) C32 0.708(52) -0.0496(13) 0.0256(24) 0.035(16) 0.274 F132 0.5066(22) -0.4936(13) 0.0356(14) 0.221 0.200 0.755(15) 0.519 0.329 0.773 0.530(14) -0.556(24) 0.0356(14) 0.220 0.773 0.1326(16) 0.274 F132 0.706(521) -0.039(14) 0.256(12) 0.036(15) 0.239 0.773 0.530(14) -0.556(24) 0.055(24) 0.055(24) 0.055(24) 0.055(24) 0.055(24) 0.055(24) 0.055(24) 0.055(24) 0.055(24) 0.0556(24) 0.0556(24) 0.0556(24) 0.0557(2) 0.0330 0.530 0.530(13) -0.0023(9) 0.0038(5) 0.220 0.773 0.1330(14) 0.	O9	0.2669(10)	0.2889(6)	0.3990(5)	0.087(3)	Cl5	0.9724(12)	0.4525(9)	0.3924(7)	0.083(4)
C11 0.3441(12) 0.4400(10) 0.4400(1) 0.067(6) C17 0.4401(1) 0.179(9) 0.3088(1) 0.050(1) C12 0.3280(11) 0.5774(18) 0.4480(1) 0.071(4) C20 0.8665(10) 0.0530(7) 0.2678(5) 0.068(3) C15 0.4231(11) 0.4699(9) 0.4045(7) 0.080(5) C22 0.8276(12) -0.0168(8) 0.2801(7) 0.2678(5) C15 0.4758(11) 0.4699(9) 0.4045(7) 0.080(5) C22 0.8276(12) -0.0158(8) 0.2801(7) 0.088(5) C16 0.4510(10) 0.712(16) 0.5064(5) 0.084(3) C23 0.9028(12) -0.0154(8) 0.1873(7) 0.088(5) C17 0.3836(12) 0.7746(8) 0.4875(6) 0.069(4) C24 0.9627(13) -0.0549(8) 0.1873(7) 0.088(5) C18 0.3045(9) 0.744(8) 0.4875(6) 0.069(4) C24 0.9627(13) -0.0549(8) 0.1873(7) 0.088(5) C20 0.4169(9) 0.8687(7) 0.5273(5) 0.060(3) 026 0.9117(11) -0.2172(6) 0.1625(6) 0.1034(5) C21 0.3519(10) 0.9380(8) 0.515(5) 0.072(4) C27 0.9923(18) -0.3479(11) 0.0137(8) 0.2219(6) 0.084(5) C22 0.3817(11) 1.0290(9) 0.5517(6) 0.085(5) C28 0.9787(18) -0.3479(11) 0.0137(10) 0.213(2) C23 0.4733(11) 1.0496(7) 0.5978(6) 0.079(5) C29 0.8552(18) -0.3793(11) 0.0517(10) 0.213(2) C24 0.539(11) 0.178(10) 0.6808(9) 0.102(6) C31 0.7189(24) -0.5164(19) -0.0059(11) 0.213(2) C25 0.5124(12) 0.8887(8) 0.5748(6) 0.077(6) F130 0.9319(16) -0.506(13) 0.027(9) 0.213(2) C26 0.4949(11) 1.1470(7) 0.6512(5) 0.086(6) 2.74 F132 0.8846(20) -0.5253(17) 0.0596(11) 0.213(2) C26 0.5492(17) 1.2768(10) 0.7148(11) 0.124(13) F131 0.616(122) -0.4958(13) 0.0453(12) 0.220 C4762(16) 1.2995(12) 0.7428(8) 0.109(6) F231 0.6612(22) -0.495(18) 0.0453(12) 0.223 C30 0.468(12) 1.398(19) 0.7962(20) 0.337 C33 0.7119(33) -0.6835(26) -0.0515(16) 0.265 C30 0.468(12) 1.398(19) 0.7965(15) 0.519 C32 0.7005(24) -0.0532(11) -0.0515(16) 0.265 C30 0.468(12) 1.1498(25) 0.8365(16) 0.274 F132 0.584(427) -0.6332(13) -0.0458(12) 0.2095(13) 0.223 C31 0.3369(25) 1.4520(20) 0.367(73) 0.337 C33 0.7119(33) -0.6835(26) -0.0137(16) 0.558 C31 0.4363(12) 1.548(21) 0.8167(30) 0.337 C33 0.7119(33) -0.6835(26) -0.0137(16) 0.558 C31 0.3369(16) 1.5255(7) 0.083(5) 0.532 C37 1.0322(16) 1.1491(19) 0.6694(17) 0.1076(10) 0.559(12) -0.0758(13) -0.0552(10) 0.057(11) 0.55	CIU	0.3786(10)	0.4308(7)	0.4191(5)	0.068(4)	Ol6	0.9100(10)	0.2138(6)	0.2889(6)	0.092(4)
$ \begin{array}{c} C13 & 0.423(11) & 0.01718 \\ C13 & 0.423(11) & 0.01718 \\ C14 & 0.4983(12) & 0.5044(8) & 0.4332(7) & 0.003(5) \\ C14 & 0.4983(12) & 0.5044(8) & 0.4332(7) & 0.003(5) \\ C15 & 0.4758(11) & 0.0499(9) & 0.0448(7) & 0.008(5) \\ C15 & 0.4758(11) & 0.0499(9) & 0.0448(7) & 0.008(5) \\ C16 & 0.4510(10) & 0.7121(6) & 0.5064(5) & 0.0084(3) \\ C17 & 0.356(12) & 0.774(8) & 0.4875(6) & 0.009(4) & C24 & 0.9027(13) & -0.0549(8) & 0.1873(7) & 0.008(5) \\ C18 & 0.3045(9) & 0.7481(7) & 0.4475(6) & 0.091(4) & C25 & 0.9436(12) & 0.0374(8) & 0.2219(6) & 0.084(5) \\ C18 & 0.3045(9) & 0.7481(7) & 0.4475(6) & 0.091(4) & C25 & 0.9436(12) & 0.0374(8) & 0.2219(6) & 0.084(5) \\ C21 & 0.3519(10) & 0.9380(8) & 0.5156(5) & 0.072(4) & C27 & 0.9923(18) & -0.0459(8) & 0.013(4) & 0.131(9) \\ C22 & 0.317(11) & 1.0296(7) & 0.5978(6) & 0.079(5) & C29 & 0.8552(18) & -0.379(11) & 0.0513(11) & 0.131(9) \\ C23 & 0.4733(11) & 1.0496(7) & 0.5978(6) & 0.079(5) & C29 & 0.8552(18) & -0.379(11) & 0.0518(14) & 0.142(11) \\ C24 & 0.539(12) & 0.9887(8) & 0.5748(6) & 0.077(6) & F130 & 0.939(9)(1) & -0.0596(11) & 0.0187(10) & 0.213(20) \\ C25 & 0.5928(15) & 1.1716(10) & 0.6808(9) & 0.02(6) & F130 & 0.9849(20) & -0.5253(17) & 0.0095(11) & 0.213 \\ C25 & 0.5928(17) & 1.2768(10) & 0.7448(11) & 0.124(13) & F131 & 0.703(30) & -0.4488(13) & -0.0515(16) & 0.265 \\ C29 & 0.4762(16) & 1.2993(12) & 0.7428(8) & 0.106(6) & F231 & 0.703(30) & -0.4548(63) & -0.0055(12) & 0.230 \\ C30 & 0.468(121) & 1.3908(19) & 0.7956(15) & 0.517 & C33 & 0.7019(33) & -0.6315(23) & -0.00515(16) & 0.265 \\ C29 & 0.4762(16) & 1.2498(2) & 0.057(12) & C32 & 0.7005(24) & -0.6152(21) & 0.04945(12) & 0.200 \\ C31 & 0.3899(25) & 1.4520(20) & 0.762(21) & 0.337 & F133 & 0.616(53) & -0.741(23) & -0.00556(24) & 0.055(24) & 0.037(24) & 0.0556(24) & 0.037(24) & 0.0556(24) & 0.0571(21) & -0.0390(44) & 0.256(27) & 0.033 \\ C32 & 0.3790(69) & 1.5456(20) & 0.357 & F133 & 0.6194(20) & -0.6791(21) & -0.0390(14) & 0.248(13) & 0.237(17) & 0.338(14) & 0.876(52) & 0.337 & F133 & 0.8194(26) & -0.6791(21) & -0.039(14) & 0.248(13) & $	C12	0.3041(12) 0.3280(11)	0.4607(10) 0.5741(8)	0.4000(0) 0.4884(7)	0.087(0)	O18	0.8480(15) 0.7842(12)	0.1309(9) 0.1711(7)	0.3088(8) 0.3482(6)	0.080(4) 0.110(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C12	0.3230(11) 0.4231(11)	0.5741(8) 0.6157(8)	0.4334(7)	0.037(3)	C_{20}	0.7642(12) 0.8665(10)	0.0530(7)	0.3482(0) 0.2678(5)	0.065(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$ \begin{array}{ccccc} 221 & 0.519(10) & 0.868/(1) & 0.5156(5) & 0.072(4) & C27 & 0.9923(18) & -0.2472(6) & 0.1625(6) & 0.103(4) \\ 222 & 0.3817(11) & 1.0290(9) & 0.5157(6) & 0.085(5) & C28 & 0.9787(18) & -0.3479(11) & 0.0833(11) & 0.135(9) \\ 223 & 0.4733(11) & 1.0496(7) & 0.6101(6) & 0.081(5) & C29 & 0.8552(18) & -0.3799(11) & 0.0516(14) & 0.142(11) \\ 224 & 0.5391(12) & 0.9807(7) & 0.6101(6) & 0.081(5) & C30 & 0.8479(20) & -0.4688(13) & 0.0187(10) & 0.213(20) \\ 225 & 0.5124(12) & 0.8887(8) & 0.5748(6) & 0.077(6) & F130 & 0.9319(16) & -0.506(13) & -0.0057(9) & 0.171 \\ 226 & 0.4949(11) & 1.1407(7) & 0.6312(5) & 0.096(4) & F230 & 0.8966(20) & -0.5253(17) & 0.0551(16) & 0.216 \\ 226 & 0.4792(16) & 1.2993(12) & 0.748(8) & 0.102(6) & C31 & 0.7188(24) & -0.5164(19) & -0.0059(13) & 0.509 \\ 228 & 0.5892(17) & 1.2768(10) & 0.7148(11) & 0.124(13) & F131 & 0.7003(30) & -0.4818(23) & -0.0551(16) & 0.265 \\ 230 & 0.468(121) & 1.3908(19) & 0.7148(11) & 0.124(13) & F131 & 0.7003(30) & -0.4818(23) & -0.0551(16) & 0.265 \\ F130 & 0.3800(27) & 1.4038(25) & 0.8365(16) & 0.274 & F132 & 0.5814(27) & -0.6330(34) & -0.055(24) & 0.365 \\ F130 & 0.3809(27) & 1.4038(25) & 0.8365(16) & 0.274 & F132 & 0.5814(27) & -0.6330(34) & -0.055(24) & 0.365 \\ F131 & 0.2772(18) & 1.4202(14) & 0.7622(10) & 0.137 & F133 & 0.599(63) & -0.0447(122) & -0.0965(13) & 0.253 \\ C31 & 0.3899(25) & 1.5456(20) & 0.8167(30) & 0.537 & F333 & 0.8194(26) & -0.6791(21) & -0.0302(14) & 0.244 \\ C32 & 0.3790(69) & 1.5458(21) & 0.161 & C34 & 0.9239(13) & 1.0003(10) & 0.0655(27) & 0.403 \\ F232 & 0.4230(41) & 1.6179(32) & 0.8076(23) & 0.330 & C33 & 0.519(51) & -0.058(57) & 0.032(39) & 0.6578(53) & -0.002(239) & 0.464 \\ C32 & 0.3790(69) & 1.5456(20) & 0.8167(30) & 0.537 & F333 & 0.8194(26) & -0.6791(21) & -0.0392(14) & 0.244 \\ C32 & 0.3790(69) & 1.5456(20) & 0.8167(20) & 0.537 & F333 & 0.8194(26) & -0.6791(21) & -0.0392(14) & 0.256(13) & 0.0375(17) & 0.038(14) & 0.632(51) & 0.038(14) & 0.632(51) & 0.038(14) & 0.632(51) & 0.0337(11) & 0.0397(11) & 0.0399(14) & 0.0297(13) & 0.2092(13) & 0.039$	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)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C20	0.4169(9)	0.868/(7)	0.52/3(5)	0.060(3)	O26	0.911/(11)	-0.2172(6)	0.1625(6)	0.103(4)
$\begin{array}{ccccc} 223 & 0.4733(11) & 1.0296(7) & 0.5978(6) & 0.09(5) & C29 & 0.575(18) & -0.5793(11) & 0.0505(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) & -0.5506(13) & -0.0207(9) & 0.171 \\ C26 & 0.4949(11) & 1.1407(7) & 0.6312(5) & 0.096(4) & F230 & 0.8966(20) & -0.5253(17) & 0.0596(11) & 0.213(20) \\ C28 & 0.589(15) & 1.1716(10) & 0.6808(9) & 0.102(6) & C31 & 0.7189(24) & -0.5164(19) & -0.0059(13) & 0.509 \\ C28 & 0.589(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) & 0.748(8) & 0.109(6) & F231 & 0.6612(22) & -0.4936(18) & 0.0435(12) & 0.220 \\ F130 & 0.3800(27) & 1.4038(25) & 0.8365(16) & 0.274 & F132 & 0.5814(27) & -0.6330(34) & -0.0556(24) & 0.336 \\ F130 & 0.3809(27) & 1.4038(25) & 0.8365(16) & 0.274 & F132 & 0.5814(27) & -0.6330(34) & -0.0556(24) & 0.336 \\ F131 & 0.3790(69) & 1.5450(20) & 0.7662(20) & 0.187 & F133 & 0.6516(53) & -0.0447(22) & -0.0965(13) & 0.223 \\ C23 & 0.3790(69) & 1.5456(20) & 0.7867(30) & 0.537 & F133 & 0.6516(53) & -0.0653(52) & -0.043(55) \\ F131 & 0.2772(18) & 1.4202(14) & 0.7254(19) & 0.169 & F233 & 0.599(59) & -0.6788(53) & -0.0052(27) & 0.464 \\ C32 & 0.3790(69) & 1.5456(20) & 0.8167(30) & 0.537 & F133 & 0.6516(53) & -0.0022(9) & 0.464 \\ F132 & 0.306(76) & 1.5950(60) & 0.7903(44) & 0.546 & C34 & 0.0239(13) & 1.0013(10) & 0.6179(18) & 0.023(51) \\ F133 & 0.299(115) & 1.6235(51) & 0.896(159) & 0.632 & C37 & 1.0322(16) & 1.1491(9) & 0.6604(7) & 0.101(6) \\ F133 & 0.2446(4)9) & 1.5576(57) & 0.0876(21) & 0.516 & O36 & 0.8514(11) & 1.0257(8) & 0.6592(4) & 0.092(3) \\ C33 & 0.3367(37) & 1.5383(48) & 0.8765(21) & 0.516 & O36 & 0.8514(11) & 1.0265(8) & 0.6592(6) & 0.097(3) \\ C33 & 0.3458(9) & -0.1311(6) & 0.1801(7) & 0.075(4) & C38 & 0.8555(11) & 1.250(10) & 0.6434(8) & 0.106(7) \\ F333 & 0.24464(39) & 1.5576(57) & 0.0957(52) & 0.360 & C33 & 0.05557(16) & 0.579(17) &$	C_{21}	0.3319(10) 0.3817(11)	1.9380(8) 1.0290(9)	0.5150(5) 0.5517(6)	0.072(4) 0.085(5)	C_{28}	0.9923(18) 0.9787(18)	-0.2431(11) 0.3470(11)	0.11/3(10) 0.0833(11)	0.131(9) 0.135(9)
$ \begin{array}{ccccc} 224 & 0.5391(12) & 0.9807(7) & 0.6101(6) & 0.081(5) & C30 & 0.8470(20) & -0.4868(13) & 0.0187(10) & 0.213(20) \\ 0.225 & 0.5124(12) & 0.8887(8) & 0.5748(6) & 0.077(6) & F130 & 0.9310(16) & -0.5060(13) & -0.0297(9) & 0.171 \\ 0.26 & 0.494(11) & 1.1407(7) & 0.6312(5) & 0.096(4) & F230 & 0.8966(20) & -0.5253(17) & 0.0596(11) & 0.211(20) \\ 0.26 & 0.494(11) & 1.1407(7) & 0.6312(5) & 0.096(4) & F130 & 0.8966(20) & -0.5253(17) & 0.0596(11) & 0.205(20) \\ 0.28 & 0.5892(17) & 1.2768(10) & 0.7148(11) & 0.124(13) & F131 & 0.7003(30) & -0.4818(23) & -0.0515(16) & 0.265 \\ 0.29 & 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 & 0.7885(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 & 0.596(53) & -0.0716(21) & -0.0399(14) & 0.244 \\ F132 & 0.309(67) & 1.5950(60) & 0.7903(44) & 0.546 & C34 & 0.9239(13) & 1.0013(10) & 0.6157(8) & 0.083(5) \\ F232 & 0.4230(41) & 1.6179(32) & 0.8076(22) & 0.330 & O35 & 1.0165(11) & 1.0567(6) & 0.6135(5) & 0.092(3) \\ F233 & 0.446(439) & 1.5256(37) & 0.905(12) & 0.362 & C37 & 1.0322(16) & 1.1491(9) & 0.6640(7) & 0.101(6) \\ F333 & 0.249(41) & 1.5414(31) & 0.8768(2) & 0.325 & C39 & 0.9626(22) & 1.3038(14) & 0.6597(12) & 0.092(12) \\ C34 & 0.332(12) & 0.0767(8) & 0.1801(7) & 0.075(4) & C40 & 0.8803(22) & 1.3768(10) & 0.6797(13) & 0.220(27) \\ C35 & 0.338(10) & -0.1234(7) & 0.1480(6) & 0.097(4) & C44 & 0.8194(32) & 1.5238(17) & 0.7376(17) & 0.028(27) \\ C37 & 0.433(16) & -0.2235(8) & 0.1370(8) & 0.097(4) & C44 & 0.8194(32) & 1.5238(17) & 0.7376(17) & 0.026(12) \\ C37 & 0.331(16) & -0.1234(7) & 0.1480(6) & 0.097(4) & C44 & 0.8194(32) & 1.5238(17) & 0.7376(17) & 0.0256(5) \\ C38 & 0.3690(17) & -0.2235(8) & 0.1370(8) & 0.097($	C22	0.3317(11) 0.4733(11)	1.0290(9) 1.0496(7)	0.5978(6)	0.033(5)	C20	0.9787(18) 0.8552(18)	= 0.3793(11)	0.0000(11)	0.133(9) 0.142(11)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C24	0.5391(12)	0.9807(7)	0.6101(6)	0.081(5)	C30	0.8332(10) 0.8479(20)	-0.4868(13)	0.0187(10)	0.213(20)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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
$\begin{array}{cccccc} 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 \\ 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 & 0.899(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 & C35 & 1.0165(11) & 1.0567(6) & 0.6135(5) & 0.092(3) \\ C33 & 0.3367(37) & 1.5383(48) & 0.876(21) & 0.516 & C36 & 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 & 0.332(12) & 0.0767(8) & 0.180(7) & 0.075(4) & C40 & 0.8803(22) & 1.3768(10) & 0.6797(13) & 0.220(27) \\ C35 & 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) \\ C36 & 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 & 0.4318(16) & -0.2235(8) & 0.1370(8) & 0.097(7) & C44 & 1.1625(29) & 1.1677(15) & 0.6654(14) & 0.162(12) \\ 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) & 0.0158(13) & 0.2356(51) & 1.59$	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
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C30 E120	0.4681(21)	1.3908(19)	0.7956(15)	0.519	C32 E122	0.7005(24)	-0.6152(21)	-0.0499(14)	0.596
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	F130 F230	0.5800(27) 0.5738(14)	1.4038(23) 1.4382(11)	0.8303(10) 0.8109(7)	0.274	F132 F232	0.3814(27) 0.7685(26)	-0.0550(34) 0.6447(22)	-0.0330(24) 0.0965(13)	0.350
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C31	0.3899(25)	1.4520(20)	0.7662(20)	0.337	C33	0.7119(33)	-0.6835(26)	-0.0137(26)	0.588
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	F131	0.2772(18)	1.4202(14)	0.7625(10)	0.187	F133	0.6516(53)	-0.7416(38)	-0.0655(27)	0.403
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	F231	0.4742(16)	1.4484(13)	0.7254(9)	0.169	F233	0.5996(39)	- 0.6788(53)	– 0.0022(39)	0.464
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C32	0.3790(69)	1.5456(20)	0.8167(30)	0.537	F333	0.8194(26)	-0.6791(21)	-0.0309(14)	0.244
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	F232	0.4230(41)	1.6179(32)	0.80/6(23)	0.330	035	1.0165(11)	1.056/(6)	0.6135(5)	0.092(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C33 E122	0.330/(37)	1.3383(48) 1.6225(51)	0.8/03(21) 0.8061(50)	0.510	C27	0.8314(11) 1.0222(16)	1.0203(8) 1.1401(0)	0.0302(0)	0.097(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	F233	0.2939(113) 0.4464(39)	1.0235(31) 1.5576(37)	0.8901(39) 0.9057(25)	0.052	C38	0.9559(18)	1.1491(9) 1.2150(10)	0.0004(7) 0.6346(8)	0.101(0) 0.106(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	F333	0.2194(34)	1.5414(31)	0.9037(23)	0.325	C39	0.9626(25)	1.3038(14)	0.6897(12)	0.208(20)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C38	0.3690(17)	-0.2938(9)	0.158/(8) 0.1062(10)	0.103(7)	C44	1.1625(29)	1.16//(15)	0.6654(14)	0.162(12)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C39 C40	0.3414(25) 0.2677(21)	-0.5647(12) 0.4499(13)	0.1005(10) 0.1301(10)	0.135(9) 0.146(21)	Mala 3				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C40 C41	0.2677(21) 0.2615(40)	= 0.4499(13) = 0.5473(15)	0.1301(10) 0.0820(13)	0.140(21) 0.230(23)	C1	0.0691(10)	-0.5159(8)	0.2442(5)	0.071(4)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C42	0.2189(56)	-0.5470(26)	0.0020(13)	0.504	C2	0.1596(12)	-0.4706(9)	0.2904(6)	0.088(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	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)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$. ,		C5	-0.0314(14)	-0.3765(9)	0.2567(7)	0.101(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mole 2	0.0001/11)	0.0072(0)	0.5705(())	0.075(4)	C6	-0.0269(12)	-0.4714(7)	0.2265(7)	0.095(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C	0.9281(11)	0.90/3(8)	0.5/05(6)	0.070(4)	0/	0.0433(9) 0.1112(12)	-0.2366(5)	0.3326(5)	0.081(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C_2	0.0309(11) 0.8383(11)	0.6428(8) 0.7524(10)	0.303/(0)	0.079(4) 0.083(5)	0	0.1112(12) 0.1847(13)	-0.1/34(8) 0.1000(7)	0.31/3(7) 0.2760(6)	0.078(4) 0.111(5)
(1)	C4	0.0303(11) 0.9333(11)	0.727(8)	0.3239(7) 0.4898(6)	0.003(3) 0.077(4)	C10	0.1047(13) 0.0931(10)	-0.1799(7) -0.0791(8)	0.2709(0) 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)	Č5	1.0243(11)	0.7895(8)	0.4931(6)	0.075(4)	ČĨĨ	0.1637(10)	-0.0110(8)	0.3480(6)	0.084(5)

Atom	x/a	y/b	z/c	$U_{ m eq}$	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)	O 7	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	0.1332(10) 0.2192(11)	0.3807(8)	0.5901(6)	0.086(4)	C14	0.2821(10) 0.4832(12)	0.8822(7)	0.3595(6)	0.072(4)
C22	0.2122(11) 0.2127(11)	0.239(8)	0.6241(7)	0.083(4)	C15	0.5100(10)	0.0022(7)	0.3973(5)	0.064(4)
C23	0.2127(11) 0.1175(11)	0.1799(0) 0.5189(7)	0.6269(6)	0.003(1) 0.073(4)	016	0.5353(9)	0.723(5)	0.3373(4)	0.074(3)
C^{24}	0.0327(14)	0.3105(7)	0.0000(0)	0.079(4)	C17	0.5555(7)	0.7233(3)	0.3323(4) 0.2873(6)	0.073(3)
C_{25}	0.0327(14) 0.0412(11)	0.3798(8)	0.5246(6)	0.070(3)	018	0.6872(11)	0.7265(7)	0.2776(6)	0.075(5) 0.100(4)
C_{27}	0.0412(11)	0.5750(8)	0.5240(0) 0.6287(9)	0.077(4)	C_{20}	0.0072(11) 0.5784(9)	0.7203(7)	0.2770(0)	0.100(4)
C^{28}	0.0200(10)	0.0072(0)	0.0207(9)	0.161(0)	C_{20}	0.5764(7)	0.5002(7)	0.2309(5)	0.000(3)
C_{20}	0.0345(17)	0.7387(14) 0.8088(10)	0.0779(14)	0.100(13) 0.122(8)	C^{21}	0.0470(11) 0.6253(12)	0.3400(8)	0.2075(0) 0.1735(6)	0.086(7)
C_{20}	0.1320(10) 0.1406(21)	0.8086(10)	0.0949(11) 0.7504(11)	0.122(8) 0.285(35)	C^{22}	0.0233(12) 0.5344(11)	0.4474(0)	0.1733(0) 0.1884(6)	0.000(5)
E130	0.1490(21) 0.1378(28)	0.8990(12) 0.8824(21)	0.7304(11) 0.8032(13)	0.285(33)	C_{23}	0.3344(11) 0.4652(11)	0.4003(7)	0.100+(0)	0.078(3)
E220	0.1378(20)	0.0024(21)	0.8052(15) 0.7250(8)	0.250	C24	0.4032(11) 0.4003(11)	0.4442(7) 0.5275(8)	0.2300(0)	0.073(3)
C21	0.0922(10) 0.2722(20)	0.9372(12)	0.7239(8) 0.7672(15)	0.108	O_{23}	0.4903(11) 0.5222(11)	0.3373(8)	0.2090(0) 0.1527(6)	0.073(4) 0.100(4)
C31 E121	0.2752(20) 0.2170(26)	0.9404(14)	0.7072(13)	0.309	C20	0.3222(11) 0.4214(19)	0.3090(0)	0.1327(0) 0.1608(0)	0.100(4)
F131 F221	0.5170(50) 0.2514(20)	0.9342(29)	0.7127(17) 0.7825(11)	0.502	C_{2}	0.4314(10) 0.4120(10)	0.2347(10) 0.1605(12)	0.1008(9) 0.1005(10)	0.107(7) 0.125(11)
C22	0.5514(20)	0.0003(10) 1.0290(17)	0.7823(11)	0.198	C20	0.4120(10)	0.1003(12) 0.1007(11)	0.1093(10) 0.1017(12)	0.155(11) 0.145(11)
C32 E122	0.2092(33)	1.0389(17)	0.8219(14)	0.377	C29	0.5284(20)	0.1097(11)	0.1017(12)	0.143(11)
F132	0.2034(28)	1.0990(21) 1.0220(21)	0.8032(13)	0.239	C30 E120	0.3184(21) 0.4285(26)	0.0242(12)	0.0437(12)	0.182(18)
F232	0.2730(27)	1.0230(21)	0.8709(14)	0.248	F130	0.4383(20)	-0.0287(21)	0.0393(13)	0.259
C33	0.398/(36)	1.0801(27)	0.838/(24)	0.358	F230	0.446/(28)	0.0225(22)	-0.0054(14)	0.254
F133	0.3/82(50)	1.158/(33)	0.8819(24)	0.388	C31	0.63/9(34)	-0.0198(25)	0.0324(18)	0.3/1
F233	0.4233(49)	1.0830(39)	0.7836(27)	0.384	F131	0.6/41(43)	0.03/6(33)	0.0048(23)	0.342
F333	0.4860(42)	1.032/(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	0.62/9(56)	-0.0939(34)	-0.0363(17)	0.506
035	-0.0189(9)	-0.6573(6)	0.1728(5)	0.089(3)	F132	0.540/(48)	-0.1432(38)	-0.086/(23)	0.379
O36	0.1550(10)	-0.662/(6)	0.2298(6)	0.098(4)	F232	0.7393(58)	-0.1354(54)	-0.0555(35)	0.447
C37	-0.02/2(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 $\Phi 2$ 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 1.34Å 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
C1C6	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)
C4O7	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)
C3/-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 $\Phi 1$ ring (figure 9). They are fully defined by the values of the torsion angles given in table 6. The polyaromatic central cores have three quasiplanar 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 $\Phi 1$ –COO (C1 to C6, C34, O35, O36), $\Phi 2$ –COO (O7, C8, O9 and C10 to C15) and $\Phi 3$ –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	Mole4
Ф2-СОО/Ф1-СОО	59°	57°	75°	76°
Ф3-СОО/Ф2-СОО	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 CH₃ [$r(CH_3) = 2.0$ Å] and CF₃ [$r(CF_3) = 2.80$ Å] groups, these latter distances lie between 39.4 and 40.8Å.

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°.

C34-O35-C37-C38 - 86 O35-C37-C38-C39 167 C37-C38-C39-C40 <i>trans</i> C38-C39-C40 C41 169	– 89 trans trans – 169 – 142	– 85 trans trans 153	– 89 trans trans trans
$\begin{array}{rcrcrc} C39-C40-C41 & -109\\ C39-C40-C41-C42 & -52\\ C40-C41-C42-C43 & trans\\ C3-C4-O7-C8 & 63\\ C12-C13-O16-C17 & -78\\ C22-C23-O26-C27 & trans\\ C23-O26-C27-C28 & trans\\ O26-C27-C28-C29 & 59\\ C27-C28-C29-C30 & 160\\ C28-C29-C30-C31 & 108\\ C29-C30-C31-C32 & trans\\ C30-C31-C32 & trans\\ C30-C31-C32 & -53\\ \end{array}$	160 61 - 80 <i>trans</i> 57 <i>trans</i> 57 <i>trans</i> 68 76	64 143 77 - 75 trans trans 52 trans trans trans trans	trans trans 86 - 70 trans trans 53 trans trans - 165 - 112

groups. Let us recall that the fluorinated and semiperfluorinated 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



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

spectra were recorded on a Perkin Elmer 783 spectrophotometer and NMR spectra on a Bruker HV200 MHz spectrometer.

(R)-4-(1-Methylheptyloxycarbonyl) 4-[4-(4,4,5,5,6,6,7,7,7nonafluoroheptyloxy)benzoyloxy] benzoate I: To a solution of (R)-1-methylheptyl 4-(4-hydroxybenzoyloxy)benzoate 5 [14] (0.37 g, 1 mmol) in CH₂ Cl₂ was added DCC (0.22 g, 1.1 mmol), DMAP (10 mg) and 4-(4,4,5,5,6,6,7,7,7nonafluoroheptyloxy)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%). ¹H NMR (CDCl₃): δ (ppm): 0.88 (t, 3H, CH₃), 1.24 (m, 10H, 5CH₂), 1.35 (d, 3H, CH₃-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: v_{max} (nujol), 2594, 2850, 1730, 1610, 1285, 1218, $850 \,\mathrm{cm}^{-1}$.

The authors would like to thank Miss N. Q. Q. Nguyen for her technical assistance.

References

- [1] CHANDANI, A. D. L., OUCHI, Y., TAKEZOE, H., FUKUDA, A., FURUKAWA, K., and KICHI, A., 1989, Jpn J. appl. Phys., 28, 1261.
- [2] GOODBY, J. W., WAUGH, M. A., STEIN, S. M., CHIN, E., PINDAK, R., and PATEL, J., 1989, *Nature*, 337, 449.
- [3] KROMM, P., COTRAIT, M., and NGUYEN, H. T., 1996. *Liq. Cryst.*, **21**, 95.
- [4] KROMM, P., COTRAIT, M., ROUILLON, J. C., BAROIS, P., and NGUYEN, H. T., 1996, *Liq. Cryst.*, 21, 121.
- [5] IVASHENKO, A. V., KOSHEV, E. I., LAZAREVA, V. T., PRUNIKOVA, E. K., TITOV, V. V., ZVERKOVA, T. I., BARNIK, H. I., and YAGUPOLSKI, L. M., 1981, *Mol. Cryst. liq. Cryst.*, 67, 235.
- [6] DOI, T., SAKURAI, Y., TAMATANI, A., TAKANEKA, S., KUSABAYASHI, S., NISHIHATA, Y., and TERAUSHI, H., 1991, *J. mater. Chem.*, 1, 169.
- [7] TOURNILHAC, F., and SIMON, J., 1991, *Ferroelectrics*, **114**, 283.
- [8] NGUYEN, H. T., SIGAUD, G., ACHARD, M. F., HARDOUIN, F., TWIEG, R. J., and BETTERTON, K., 1991, *Liq. Cryst.*, **10**, 389.
- [9] LOSE, D., DIELE, S., PELZL, G., DIETZMANN, E., and WEISSFLOG, W., 1998, *Liq. Cryst.*, 24, 707.
- [10] JANULIS, E. P., NORACK, J. C., PAPAPOLYMEROU, G. A., TRISTANI-KENDRA, M., and HUFFMAN, W. A., 1988, *Ferroelectrics*, 85, 375.
- [11] TWIEG, R. J., BETTERTON, K., DIE PIETRO, R., GRAVERT, D., NGUYEN, C., NGUYEN, H. T., BABEAU, A., and DESTRADE, C., 1991, SPIE, 1455, 86.
- [12] LIU, H., and NOHIRA, H., 1996, Liq. Cryst., 20, 581.
- [13] LIU, H., and NOHIRA, H., 1997, *Liq. Cryst.*, 22, 217.
- [14] FAYE, V., ROUILLON, J. C., DESTRADE, C., and NGUYEN, H. T., 1995, *Liq. Cryst.*, 19, 47.

- [15] BENNETT, G. M., and JONES, B., 1939, J. chem. Soc., 420.
- [16] (a) MATSUNAGA, Y., and TERADA, M., 1986, Mol. Cryst. liq. Cryst., 141, 321; (b) PUCCI, D., VEBER, M., and MALTHÊTE, J., 1996, Liq. Cryst., 21, 153.
- [17] TAKENAKA, S., 1992, J. chem. Soc. chem. Commun., 1748.
- [18] KROMM, P., ALLOUCHI, H., BIDEAU, J. P., and COTRAIT, M., 1994, *Mol. Cryst. liq. Cryst.*, 257, 9.
- [19] KROMM, P., ALLOUCHI, H., BIDEAU, J. P., COTRAIT, M., and NGUYEN, H. T., 1995, *Acta Cryst.*, **C51**, 1229.
- [20] NORTH, A. C. T., PHILLIPS, D. C., and MATTHEWS, F. S., 1968, Acta Cryst., A24, 351.

- [21] SHELDRICK, G. M., 1986, Shelxs86, Program for the Solution of Crystal Structures, University of Gottingen, Germany.
- [22] SHELDRICK, G. M., 1993, Shelxs93, Program for the Refinement of Crystal Structures, University of Gottingen, Germany.
- [23] International Tables for X-Ray Crystallography, 1974, Vol. IV (Birmingham: Kynoch Press).
- [24] DRZEWINSKI, W., DABROWSKI, R., CZUPRYNSKI, K., PRZEDMOJSKI, J., and NEUBERT, M., 1997, in Proceedings of the 6th International Conference on FLCs, Brest, 20–24 July, 1997, p. 156.