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Synthesis, characterization and crystal structure of mesogenic compounds with an alkyloxy and a semi-perfluorinated chain. Influence of the alkyloxy chain length on molecular arrangement and molecular interactions

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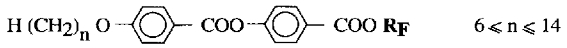
This paper describes the synthesis and study of the mesomorphic properties (by DSC, microscopic observation and X-ray diffraction) of three new series of semi-perfluorinated liquid crystals: 4-(2,2,3,3,4,4,4-heptafluorobutyloxycarbonyl)phenyl, 4-(2,2,3,3,4,4,5,5-octafluoropentyloxycarbonyl)phenyl, and 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octyloxycarbonyl)phenyl 4-(*n*-alkyloxy)benzoates. One compound of the second family crystallizes in the $P\bar{1}$ space group with $Z=2$. The molecule adopts a slightly bent conformation with a fully extended alkyloxy and semi-perfluorinated chain in a smectic C-like structure. The comparison of the present structure is made with that of a similar compound of the first family with a longer alkyloxy chain (this latter crystallizes in the $P1$ space group with two independent molecules in the unit cell). Comparison of the molecular packing shows the importance of the chain lengths in the molecular arrangement and molecular interactions in both structures.

1. Introduction

There are numerous ways to introduce fluorine into the molecules of liquid crystals, but here we limit the brief discussion to materials in which one of the tails is a semi-perfluorinated alkyl chain. Earlier work [1–5] on these materials showed that the smectic mesophases were enhanced, but the effect on the mesomorphic properties of the extent of the fluorination has not been widely explored. This paper describes the synthesis and mesomorphic properties of three series with the following formulae:



$R_F = CH_2\,(CF_2)_3F$ for series **1A**
$R_F = CH_2\,(CF_2)_4H$ for series **1B**
$R_F = (CH_2)_2(CF_2)_6F$ for series **1C**

At the present time there are very few reports dealing with the crystal structures of perfluorinated mesogenic compounds. Let us mention the crystal structures of two cyano compounds, 4-cyanophenyl 4-perfluorohexyl (or heptyl) benzoate [6,7] which give birth to smectic S_{A2} mesophases and for which the molecular arrangement in the crystal perfectly foreshadows that of the mesophase. Moreover, these structures provided us with evidence of the precise geometry of the $(CF_2)_n$ chains with mean C–C and C–F bond lengths close to 1·52 Å and 1·34 Å, respectively, and F–C–F and C–C–C bond angles close to 107° and 119°, respectively. In order to understand the molecular arrangement in the crystal and the relation between this structure and that in the mesophase, we performed the crystal structure study of the two compounds.

2. Synthesis

Three series of mesogenic compounds with a semi-perfluorinated chain and having a dibenzoate core have now been synthesized. The compounds were obtained through the scheme shown overleaf.

3. Mesomorphic properties

All the compounds are mesomorphic. The nature of the phases, the transition temperatures and the enthalpies were determined both by microscopic observation (Leitz microscope equipped with a heating and cooling stage Mettler FP52) and by calorimetric measurements (DSC7 Perkin Elmer). The transition temperatures (°C)

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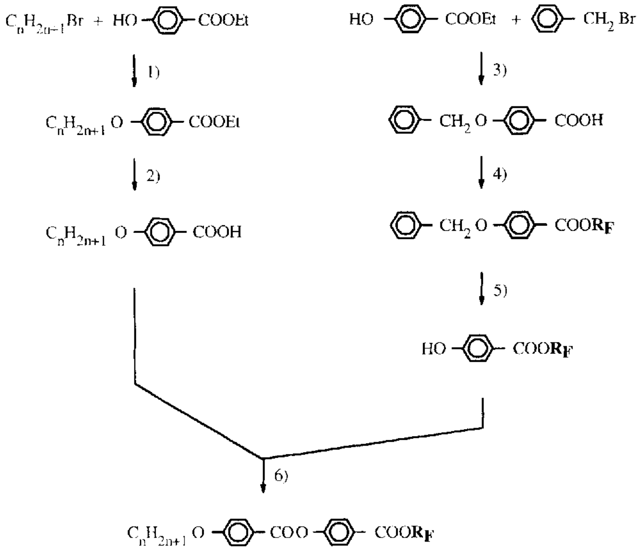


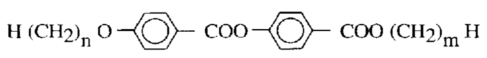
1) KOH, H_2O, EtOH, reflux 2h
2) KOH, HCl
3) 1) KOH, H_2O, EtOH, reflux 4h 2) KOH, H_2O 3) H_3O^+
4) HOR_F, DCC, DMAP, CH_2Cl_2 (A)
5) H_2, Pd/C, EtOAc
6) DCC, DMAP, CH_2Cl_2 (A)

Scheme

and enthalpies (kJ mol^{-1}) of the three synthesized families **1A,B,C** are reported in tables 1 (*a*),(*b*),(*c*). The phase diagrams or plots of transition temperatures against the number of carbon atoms of the alkoxy chains, figures 1 (*a*) and (*b*), correspond, respectively, to families **1A** and **1C**.

All compounds present a smectic A mesophase and, for some, a smectic C mesophase; the latter is in most cases enantiotropic, but in some cases monotropic (**1B** series with $n > 7$). Generally speaking, there is a decrease of the $S_A \to I$ transition temperature when the number of carbon atoms in the alkoxy chain increases, corresponding to the transition from a rigid system (short chains) to a more flexible one (long chains). As far as the **1A** series is concerned, the smectic A domain decreases ($n = 10$, domain $< 3°C$) when the alkoxy chain length increases. It is the same for compounds of the **1C** series with $n \leqslant 10$. In fact, with n greater than 11, the S_A mesophase disappears and the S_C domain increases.

Let us point out that the hydrogenous compounds (containing no fluorine) with the general formula:



display only the smectic A phase, table 1 (*d*).

These results show that the semi-perfluorinated chains favour not only the smectic A phase (for the series

Table 1 (*a*). Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of series **1A**. Cr = crystal; S_C, S_A = smectic phases C and A; I = isotropic liquid; ● = the phase exists; [ ] = ΔH.

n	Cr	S_C	S_A	I
6	● 63·7 [19·49]	● 72·0 [0·31]	● 99·2 [6·18]	●
7	● 59·3 [21·47]	● 83·6 [0·32]	● 95·4 [6·08]	●
8	● 65·5 [26·83]	● 85·2 [0·44]	● 92·0 [6·29]	●
9	● 64·6 [17·72]	● 77·7 [0·45]	● 84·3 [6·28]	●
10	● 59·9 [17·86]	● 80·5 [0·46]	● 83·1 [6·15]	●
11	● 59·7 [25·78]	● 76·8 [0·48]	● 79·2 [6·12]	●
12	● 65·7 [27·00]	● 73·0 [0·36]	● 75·6 [6·02]	●

Table 1 (*b*). Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of series **1B**. Cr = crystal; S_C, S_A = smectic phases C and A; I = isotropic liquid; ● = the phase exists; — = the phase does not exist; ( ) = monotropic phase; [ ] = ΔH.

n	Cr	S_C	S_A	I
6	● 56·8 [37·31]	—	● 71·2 [5·56]	●
7	● 43·1 [17·16]	—	● 51·5 [5·68]	●
8	● 57·3 [21·61]	(● 50·3 [−0·12])	● 63·4 [5·20]	●
9	● 48·6 [16·74]	—	● 53·6 [4·37]	●
10	● 50·8 [21·60]	(● 50·1 [−0·18])	● 58·1 [5·14]	●
11	● 50·9 [15·84]	● 51·9 [0·31]	● 57·2 [5·32]	●
12	● 46·2 [15·87]	● 52·0 [0·27]	● 54·0 [5·30]	●

Table 1 (*c*). Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of series **1C**. Cr = crystal; S_C, S_A = smectic phases C and A; I = isotropic liquid; ● = the phase exists; — = the phase does not exist; [ ] = ΔH.

n	Cr	S_C	S_A	I
6	● 83·4 [30·55]	● 109·4 [0·07]	● 141·2 [9·36]	●
7	● 89·1 [29·83]	● 118·7 [0·07]	● 134·6 [8·92]	●
8	● 86·2 [28·14]	● 122·3 [0·21]	● 130·6 [8·81]	●
9	● 84·3 [29·49]	● 113·5 [0·29]	● 120·0 [8·39]	●
10	● 82·2 [27·45]	● 109·0 [0·30]	● 112·5 [8·41]	●
11	● 89·2 [35·55]	● 113·8 [10·08]	—	●
12	● 85·2 [16·44]	● 108·1 [10·58]	—	●
14	● 92·3 [23·84]	● 101·7 [11·12]	—	●

Table 1 (*d*). Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of the hydrogenous series (containing no fluorine). Cr = crystal; S_A = smectic A phase; I = isotropic liquid; ● = the phase exists.

n	*m*	Cr	S_A	I	Ref
10	4	● 59	● 72	●	
12	4	● 62	● 72·5	●	
10	7	● 64	● 74	●	
12	7	● 71	● 75	●	
8	6	● 51	● 69	●	[4]
8	10	● 54	● 67	●	[4]

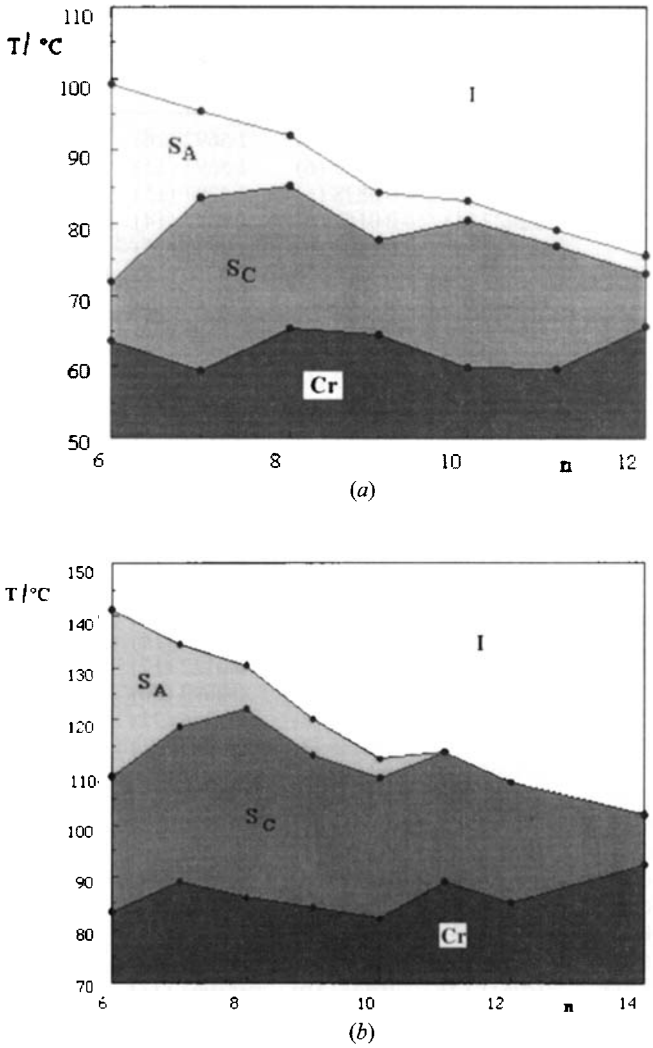


Figure 1. (*a*) Evolution of the polymorphism of series **1A** as a function of the number *n* of carbon atoms of the alkoxy chain. (*b*) Evolution of the polymorphism of series **1C** as a function of the number *n* of carbon atoms of the alkoxy chain.

displaying the nematic phase) but also the smectic C phase; for example with series **1C**, we obtained three derivatives ($n=10$–12) which only exhibit the S_C phase.

Three compounds ($n=6$, 8 and 11) per family were studied by X-ray diffraction (λ $CuK_\alpha=1{\cdot}54178$ Å, Imaging Plate Scanner Marresearch). The results are presented in table 2. The S_C and S_A sheet thickness (d_{S_C} and d_{S_A}), the calculated molecular length L (evaluated from a molecular model) and the d_{S_A}/L ratio are given. With regard to the sheet thickness, the following is to be noted:

(1) The thickness of the S_A and S_C sheets increases within a given family when the number of carbon atoms in the alkoxy chain increases.

Table 2. Characteristics of the S_C and S_A phases for series **1A**, **1B** and **1C**. d_{S_C}, d_{S_A} = layer thickness of the smectic C and A phases; L = calculated molecular length; d/L = layer thickness in the S_A phase/calculated molecular length.

Series	n	d_{S_C}	d_{S_A}	L	d_{S_A}/L
1A	6	26·8	27·3	30·3	0·90
	8	27·2	27·9	32·5	0·86
	11	28·8	29·8	35·8	0·83
1B	6	—	28·7	31·4	0·91
	8	29·2	29·8	33·6	0·89
	11	31·1	31·8	36·9	0·86
1C	6	32·8	33·1	35·0	0·94
	8	32·9	33·3	37·2	0·89
	11	33·7	—	—	—

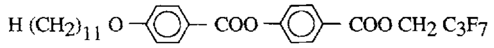
(2) For a fixed *n* value, there is an increase in S_A and S_C sheets along with the number of fluorinated carbon atoms.

(3) The thickness difference between S_A and S_C is small ($<0{\cdot}9$ Å), involving limited reorganization between the two mesomorphic states (confirmed by the transition energies S_C/S_A lower than 0·5 kJ mole^{-1}).

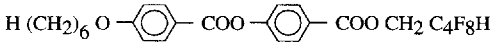
(4) The d_{S_A}/L ratio, close to 1, but always less than 1, for all compounds, shows the existence of monomolecular sheets, called S_{A_m}. This result is different from that obtained by Doi *et al.* [4] for long fluorinated chains (C_2H_4–C_8F_{17} or C_2H_4–$C_{10}F_{21}$). They showed that the layer spacings of the S_A or S_C phases are equal to or greater than the molecular lengths.

4. Crystal structures

Compounds **1A** ($n=11$) and **1B** ($n=6$) have the polymorphism and formulae shown below:



$$\mathbf{1A}\ (n=11)\ \mathrm{Cr} \xrightarrow{59{\cdot}7^\circ C} S_C \xrightarrow{76{\cdot}8^\circ C} S_A \xrightarrow{79{\cdot}2^\circ C} \mathrm{I}$$



$$\mathbf{1B}\ (n=6)\ \mathrm{Cr} \xrightarrow{56{\cdot}7^\circ C} S_A \xrightarrow{71{\cdot}2^\circ C} \mathrm{I}$$

4.1. *Experimental*

Colourless crystals from compound **1B** ($n=6$) were obtained with some difficulty by evaporation from hexane solutions. They were fragile, soft and often twinned. One crystal was lamellar, with dimensions 0·45 mm × 0·25 mm × 0·05 mm. The unit-cell parameters were obtained by a least-squares fit of the setting angles of 25 reflections, with θ between 10 and 17°. The crystal data are given in table 3. Intensity data were collected on a CAD-4 Enraf Nonius diffractometer for the monochromatized MoK$_\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) with $\theta_{\max} = 25^\circ$, $(-19 \leqslant h \leqslant 19)$, $(-15 \leqslant k \leqslant 15)$ and $(0 \leqslant l \leqslant 6)$ using the ω–2θ scan mode. The scan range was $(1{\cdot}5 + 0{\cdot}35 \tan \theta)^\circ$ and the detector width $(2{\cdot}0 + 2{\cdot}9 \tan \theta)$ mm; 6129 reflections were measured of which 2936 were unique ($R_{\text{int}} = 0{\cdot}016$) and 1521 observed ($I > 2{\cdot}5\sigma\ (I)$). Experimental absorption was performed; minimum and maximum transmission factors were 0·97 and 0·99, respectively.

The structure was solved using the MITHRIL package [8] which allowed us to locate most non-hydrogen atoms. The remaining atoms were positioned by a single Fourier refinement performed using the local Crisaf program. The hydrogen atoms were then introduced at their theoretical positions [9] and allowed to ride with the carbon atoms to which they are attached. The refinement was concluded with final reliability factors $R = 0{\cdot}066$ and $R = 0{\cdot}067$ with $S = 1{\cdot}17$.

4.2. *Molecular conformation*

Atomic parameters (x, y, z, Beq) are given in table 4. The atom labelling along with the molecular conformation are presented in a SNOOPI drawing [10] in figure 2. The thermal motion equivalent Beq factors of the dibenzoate central core (atoms C_1 to O_{18}), of the beginning of both the alkoxy chain (atoms O_{30} to C_{34}) and of the perfluorinated chain (atoms C_{19}, C_{20}) are moderate. The Beq factors are much higher at the end of both chains, especially those of the perfluorinated terminal chain (atoms C_{21}, C_{22}, C_{23}) and the fluorine atoms attached to them.

Bond lengths and bond angles are given in tables 5 (*a*) and 5 (*b*). The molecule can be split into three parts: the central dibenzoate core, the hexyloxy chain and the semi-perfluorinated chain. Bond lengths and angles of the central core are close to those found in compound **1A** ($n = 11$) [11]. C–C bond lengths and C–C–C bond angles in the alkoxy chain are in agreement with those observed in other structures [12,13]. Average values of the C–C and C–F bond lengths are equal to 1·54 and 1·34 Å, respectively. The C–C–C and the F–C–F angles, close to 115° and 107°, respectively, are in agreement with those found in the precisely determined 4-cyanophenyl 4-perfluoroheptylbenzoate structure [7].

Table 3. Crystal data for the compound **1B** ($n = 6$).

$C_{25}H_{24}O_5F_8$	$M_x = 556{\cdot}5\ \text{g mol}^{-1}$
Triclinic	$P\bar{1}$ space group ($Z = 2$)
$a = 16{\cdot}620\ (7)$ Å	$\alpha = 98{\cdot}64(4)^\circ$
$b = 13{\cdot}355(4)$ Å	$\beta = 87{\cdot}00(4)^\circ$
$c = 5{\cdot}843(3)$ Å	$\gamma = 95{\cdot}73(3)^\circ$
$v = 1275$ Å^3	$d_c = 1{\cdot}47\ \text{g cm}^{-3}$
	$\mu(\text{MoK}\alpha) = 0{\cdot}15\ \text{mm}^{-1}$

Table 4. Atomic coordinates x, y, z and Beq factors for the compound **1B** ($n = 6$) ($\text{Beq} = 4/3 \Sigma_i \Sigma_j \beta_{ij} a_i a_j$ Å^2).

	x/a	y/b	z/c	Beq
C1	0·3561 (4)	−0·0661 (6)	1·5692 (16)	6·7 (5)
C2	0·2788 (4)	−0·1137 (6)	1·5693 (15)	6·6 (4)
C3	0·2233 (4)	−0·0878 (6)	1·4297 (15)	6·3 (4)
C4	0·2427 (4)	−0·0157 (6)	1·2847 (14)	5·7 (4)
C5	0·3212 (5)	0·0304 (6)	1·2837 (15)	7·0 (5)
C6	0·3763 (4)	0·0061 (6)	1·4250 (17)	7·8 (5)
C7	0·1814 (4)	0·0060 (6)	1·1319 (14)	5·9 (4)
O8	0·1149 (3)	−0·0353 (4)	1·1164 (11)	8·2 (3)
O9	0·2100 (3)	0·0819 (4)	1·0131 (10)	7·0 (3)
C10	0·1686 (4)	0·1197 (6)	0·8487 (15)	6·3 (4)
C11	0·0903 (4)	0·0884 (6)	0·7800 (15)	6·6 (4)
C12	0·0598 (4)	0·1351 (6)	0·6146 (15)	6·6 (4)
C13	0·1042 (5)	0·2114 (6)	0·5205 (14)	5·9 (4)
C14	0·1822 (5)	0·2405 (6)	0·5905 (16)	7·2 (5)
C15	0·2134 (4)	0·1951 (6)	0·7521 (16)	7·1 (5)
C16	0·0733 (5)	0·2632 (6)	0·3404 (15)	6·9 (5)
O17	0·1113 (4)	0·3275 (5)	0·2463 (11)	9·2 (4)
O18	−0·0041 (3)	0·2292 (4)	0·2914 (10)	7·6 (3)
C19	−0·0374 (5)	0·2693 (6)	0·1083 (15)	7·7 (5)
C20	−0·0940 (5)	0·3450 (6)	0·2056 (14)	6·7 (5)
C21	−0·1389 (5)	0·3842 (7)	0·0122 (17)	8·8 (6)
C22	−0·2059 (6)	0·4464 (8)	0·0699 (20)	10·3 (7)
C23	−0·2329 (5)	0·4917 (8)	−0·1366 (21)	10·2 (7)
O30	0·4161 (3)	−0·0871 (4)	1·7005 (11)	8·1 (3)
C31	0·3995 (5)	−0·1669 (6)	1·8375 (16)	7·1 (5)
C32	0·4748 (5)	−0·1800 (7)	1·9548 (17)	8·1 (5)
C33	0·4644 (5)	−0·2657 (7)	2·0959 (16)	8·1 (5)
C34	0·5379 (5)	−0·2818 (7)	2·2212 (17)	8·2 (5)
C35	0·5286 (6)	−0·3673 (8)	2·3557 (19)	10·4 (7)
C36	0·5990 (7)	−0·3803 (9)	2·4863 (21)	12·2 (8)
F201	−0·0571 (3)	0·4222 (4)	0·3391 (9)	9·3 (3)
F202	−0·1520 (3)	0·3035 (4)	0·3423 (10)	10·0 (3)
F211	−0·0821 (3)	0·4327 (6)	−0·1087 (12)	13·7 (4)
F212	−0·1728 (4)	0·2997 (4)	−0·1304 (11)	12·9 (4)
F221	−0·1756 (5)	0·5217 (5)	0·2337 (13)	16·0 (5)
F222	−0·2674 (4)	0·3928 (6)	0·1613 (12)	13·8 (5)
F231	−0·2755 (4)	0·4185 (5)	−0·2734 (12)	13·5 (4)
F232	−0·2881 (4)	0·5527 (5)	−0·0461 (12)	14·5 (5)

The molecular conformation of compound **1B** ($n = 6$) can be described by considering successively the three parts previously defined. The dibenzoate central core is quasi-planar with the C4–C7–C9–C10 torsion angle equal to 178·3(7)° which is quite unusual; in structures with a dibenzoate core [14–16], this torsion angle is generally greater than 40°. The total length of the core is equal to 11·20(1) Å ($C_1 \dots O_{18}$). The alkyloxy chain is fully extended with torsion angles differing by less than 5° from the *trans*-conformation (180°) and has a length of 7·41(1) Å ($O_{30} \dots C_{36}$); the semi-perfluorinated chain also has an extended conformation with torsion angles differing by less than 10° from the *trans*-conformation (180°) [13,17] and has a length of 6·09(1) Å ($C_{19} \dots$

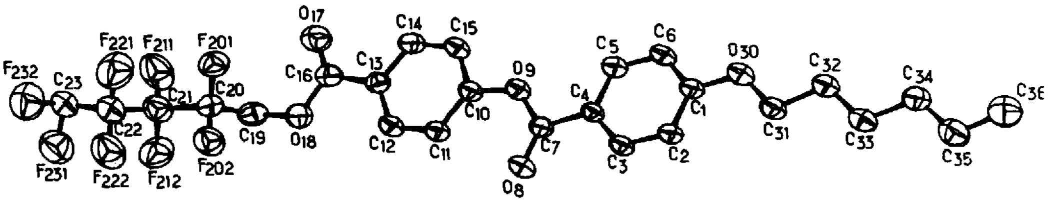


Figure 2. SNOOPI drawing and atom labelling of one of the molecules studied. Displacement ellipsoids are shown at 50% probability level.

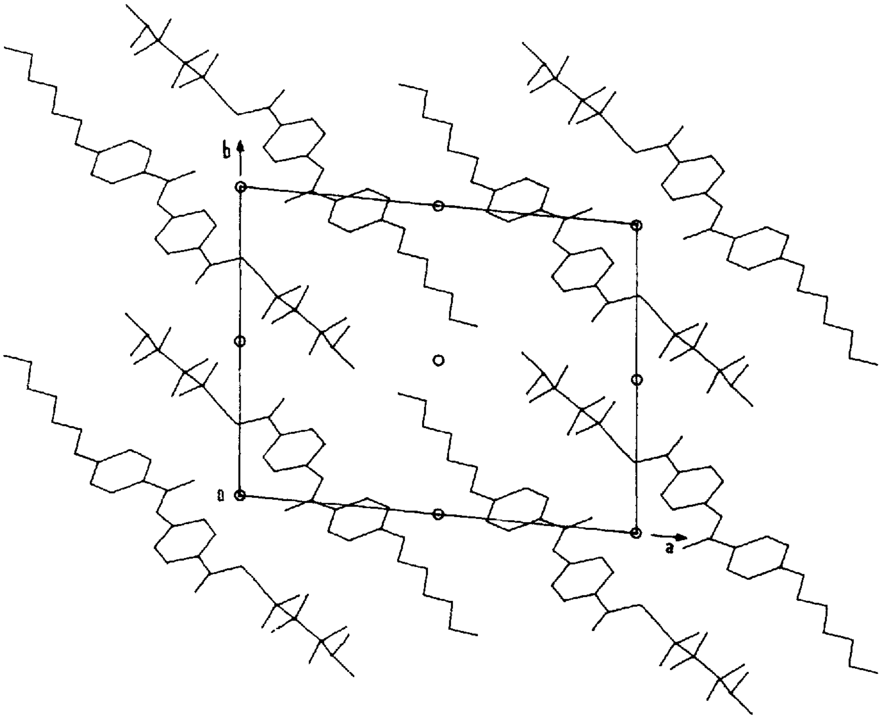


Figure 3. Projection of structure **1B** ($n=6$) onto the ($x0y$) plane.

F_{232}). The molecular conformation can be described with only the C_{16}–O_{18}–C_{19}–C_{20} torsion angle equal to $-104{\cdot}9(7)^\circ$. (The other torsion angles are close to 180°.) Finally the moiety including the central core (C_1 to C_{18}) and the alkoxy chain (O_{30} to C_{38}) is nearly planar and together with the semi-perfluorinated chain (C_{19} to C_{23}) makes an angle close to 75°. The molecule is bent at the C19 atom level with a $C_{36} \ldots C_{19} \ldots C_{23}$ angle close to $156{\cdot}1(2)^\circ$. The total length of the molecule is 26·58(2) Å ($C_{36} \ldots F_{232}$).

4.3. *Molecular arrangement*

The projection of the structure onto the ($x0y$) plane is displayed in figure 3. It shows the existence of sheets parallel to the ($y0z$) plane with a thickness close to the b parameter, i.e. 13·35 Å, while the thickness of the sheets in the S_A mesophase is close to 28·67 Å. The tilt angle† in these sheets is very high and close to 63°. Molecules are antiparallel through the centres of symmetry. The molecular arrangement in the crystal is S_C-like. The crystal cohesion results from dipolar interactions between antiparallel carbonyl groups and from van der Waals interactions between neighbouring molecules. The interactions between sheets are of van der Waals type and presumably very weak.

The molecular arrangement of compound **1B** ($n=6$) can be represented by scheme 1 in figure 4.

This arrangement can be compared to that observed in the crystal structure of compound **1A** ($n=11$). The

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†The tilt angle is the angle between the direction of the core (atoms C_1 to C_{18}) and the normal to the sheet.

Table 5(*a*). Bond lengths (Å) and their standard deviations for compound **1B** ($n=6$).

C1-C2	1·38 (1)	**O18-C19**	1·42 (1)
C1-C6	1·38 (1)	**C19-C20**	1·48 (1)
C1-O30	1·37 (1)	**C20-C21**	1·57 (1)
C2-C3	1·36 (1)	**C20-F201**	1·31 (1)
C3-C4	1·38 (1)	**C20-F202**	1·35 (1)
C4-C5	1·39 (1)	**C21-C22**	1·45 (2)
C4-C7	1·47 (1)	**C21-F211**	1·33 (1)
C5-C6	1·36 (1)	**C21-F212**	1·39 (1)
C7-C8	1·19 (1)	**C22-C23**	1·54 (2)
C7-O9	1·35 (1)	**C22-F221**	1·36 (1)
O9-C10	1·39 (1)	**C22-F222**	1·32 (1)
C10-C11	1·39 (1)	**C23-F231**	1·33 (1)
C10-C15	1·37 (1)	**C23-F232**	1·33 (1)
C11-C12	1·37 (1)	**O30-C31**	1·42 (1)
C12-C13	1·37 (1)	**C31-C32**	1·50 (1)
C13-C14	1·38 (1)	**C32-C33**	1·50 (1)
C13-C16	1·48 (1)	**C33-C34**	1·50 (1)
C14-C15	1·35 (1)	**C34-C35**	1·47 (2)
C16-O17	1·20 (1)	**C35-C36**	1·47 (2)
C16-O18	1·35 (1)		

Table 5(*b*) Bond angles (°) and their standard deviations for compound **1B** ($n=6$).

C2-C1-C6	119·1 (8)	**O18-C19-C20**	109·6 (7)
C2-C1-O30	124·1 (8)	**C19-C20-C21**	111·9 (8)
C6-C1-O30	116·8 (8)	**C19-C20-F201**	111·7 (8)
C1-C2-C3	119·7 (8)	**C19-C20-F202**	110·7 (7)
C2-C3-C4	121·8 (8)	**C21-C20-F201**	110·1 (7)
C3-C4-C5	117·9 (8)	**C21-C20-F202**	106·3 (7)
C3-C4-C7	119·4 (7)	**F201-C20-F202**	105·9 (7)
C5-C4-C7	122·7 (8)	**C20-C21-C22**	120·9 (9)
C4-C5-C6	120·5 (8)	**C20-C21-F211**	106·0 (8)
C1-C6-C5	121·0 (9)	**C20-C21-F212**	107·5 (8)
C4-C7-O8	125·5 (8)	**C22-C21-F211**	109·6 (9)
C4-C7-O9	110·8 (7)	**C22-C21-F212**	103·5 (9)
O8-C7-O9	123·7 (8)	**F211-C21-F212**	108·8 (8)
C7-O9-C10	125·8 (7)	**C21-C22-C23**	113 (1)
O9-C10-C11	126·9 (8)	**C21-C22-F221**	103·3 (9)
O9-C10-C15	113·0 (7)	**C21-C22-F222**	110 (1)
C11-C10-C15	120·1 (8)	**C23-C22-F221**	110·2 (9)
C10-C11-C12	118·3 (8)	**C23-C22-F222**	110·6 (9)
C11-C12-C13	121·6 (8)	**F221-C22-F222**	109·5 (9)
C12-C13-C14	118·9 (8)	**C22-C23-F231**	108·3 (9)
C12-C13-C16	123·0 (8)	**C22-C23-F232**	104·2 (9)
C14-C13-C16	118·0 (8)	**F231-C23-F232**	103·3 (9)
C13-C14-C15	120·3 (8)	**C1-O30-C31**	118·4 (7)
C10-C15-C14	120·7 (8)	**O30-C31-C32**	109·0 (7)
C13-C16-O17	125·1 (8)	**C31-C32-C33**	113·1 (8)
C13-C16-O18	112·0 (7)	**C32-C33-C34**	115·5 (8)
O17-C16-O18	122·9 (8)	**C33-C34-C35**	115·8 (9)
C16-O18-C19	116·2 (7)	**C34-C35-C36**	116 (1)

latter crystallizes in the $P1(Z=2)$, space group, i.e. with two independent molecules (mol I and mol II) in the asymmetric unit as shown in figure 5. These molecules have very similar conformations and are quasi-parallel. The molecular arrangement in the structure of **1A** ($n=11$) can be seen in figure 6, which shows the projection of the structure onto the ($x0z$) plane, with sheets parallel to the ($y0z$) plane, and whose thickness is close to the *a* parameter (30·91 Å). Because there are no

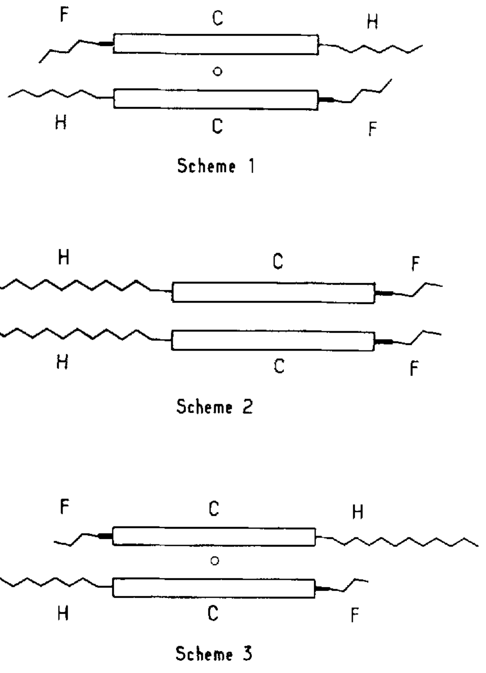

Figure 4. Scheme 1: schematic molecular arrangement in the crystal of compound **1B** ($n=6$). **C**, **F** and **H** show the core, the semi-perfluorinated chain and the alkyloxy chain, respectively. Scheme 2: schematic molecular arrangement in the crystal of compound **1A** ($n=11$). Scheme 3: hypothetical centrosymmetrical molecular arrangement of compound **1A** ($n=11$) if the molecules are related by centres of symmetry.

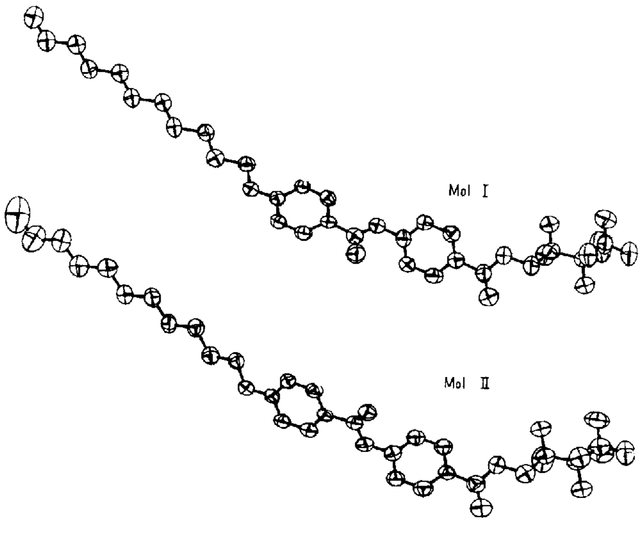

Figure 5. SNOOPI drawing of the two independent molecules I and II in the asymmetric unit of **1A** ($n=11$). Displacement ellipsoids are shown at 50% probability levels.

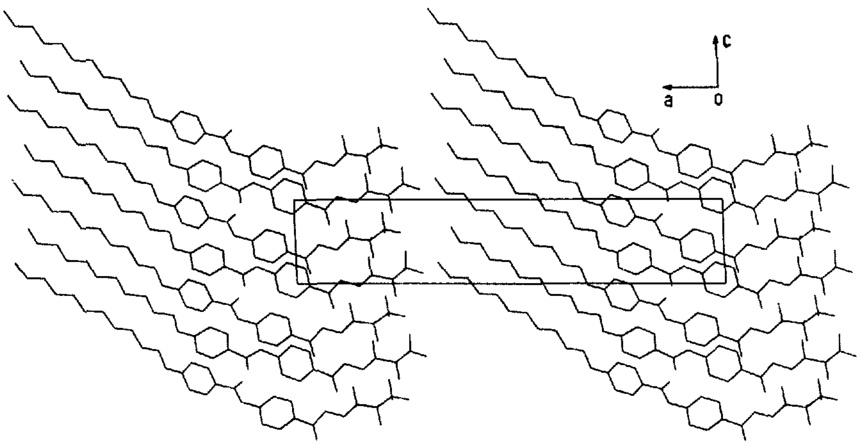

Figure 6. Projection of the structure of compound **1A** ($n=11$) onto the ($x0z$) plane.

centres of symmetry, all molecules in a sheet are parallel. The molecular arrangement in **1A** ($n=11$) can be represented by scheme 2 in figure 4.

Such a molecular arrangement is characterized by a permanent dipole moment and should give rise to ferroelectric properties which will be studied later. If we suppose that the molecules are related through centres of symmetry, the hypothetical molecular arrangement can be represented by scheme 3 in figure 4. Such a hypothetical molecular arrangement cannot give rise to sheets, because of the very different lengths of the alkoxy chain on one side and the semi-perfluorinated heptafluorobutyloxy chain on the other side. Therefore, we can predict that in such perfluorinated compounds, the molecular arrangement can be related to the relative lengths of chains on both sides of the polyaromatic central core. This can give useful suggestions for the synthesis of similar compounds with chains of very different lengths, e.g. compounds with the same alkyloxy chain and with very different semi-perfluorinated chain lengths.

5. Conclusion

We have synthesized three different dibenzoate series with semi-perfluorinated chains. The compounds exhibit S_A and/or S_C phases, and favour the formation of the S_C phase when compared with the hydrogenated derivatives which only display the S_A phase. The layer spacing of the S_A phase is slightly lower than the molecular length. This result is concordant with the crystal structure which shows the dibenzoate core tilted to the layer. One of the interesting results is the ferroelectric symmetry of the crystal structure observed for the compounds **1A** ($n=11$), and a model for obtaining this structure is proposed.

6. Experimental

The chemical structures of all compounds were checked by nuclear magnetic resonance (Bruker ARX 300) and by Fourier Transform Infrared Spectroscopy (Nicolet MX-1). The purity of intermediates and final products was checked by thin layer chromatography and by normal-phase HPLC.

6.1. *4-Benzyloxybenzoic acid*

20 g of potassium hydroxide were dissolved in 30 ml of water and 400 ml of ethanol. 52·5 g of ethyl 4-hydroxybenzoate were added and then 51·3 g of benzyl bromide (0·3 mol). The mixture was boiled for 4 h with stirring. A solution of potassium hydroxyde (20 g in 30 ml of water) was added slowly and then boiled for 2 h. The mixture was cooled to room temperature and hydrolysed with 40 ml of concentrated HCl, 200 g of crushed ice and 400 ml of water. The solid was filtered off and washed with water. The product was recrystallized from ethanol (95%). Yield: 58 per cent.

6.2. *2,2,3,3,4,4,4-Heptafluorobutyl 4-benzyloxybenzoate*

To a solution of 4 g of 2,2,3,3,4,4,4-heptafluoro-1-butanol (0·02 mol), 4·13 g (0·022 mol) of dicyclohexylcarbodiimide (DCC), and 0·2 g of 4-dimethylaminopyridine (DMAP) in 100 ml of dichloromethane, under argon, was added 4·74 g (0·02 mol) of 4-benzyloxybenzoic acid. The mixture was stirred at room temperature overnight. It was then filtered, the solvent was evaporated and the residue was chromatographed on silica gel with toluene as solvent. Yield: 82 per cent.

6.3. *2,2,3,3,4,4,4-Heptafluorobutyl 4-hydroxybenzoate*

Hydrogenolysis of a solution of 6·5 g (0·016 mol) of 2,2,3,3,4,4,4-heptafluorobutyl 4-benzyloxybenzoate in 100 ml of ethyl acetate, 10 ml of 95% ethanol and 300 mg of palladium on active carbon afforded quantitatively the corresponding phenol. Yield: 87 per cent, m.p. 77°C. IR (KBr): 3620, 1694, 1609, 1590, 1350, 1235, 1160, 1019 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS): 4·8 (m, 3H, OH, CF_2CH_2), 6·9 (d, 2H, aromatic), 8·0 (d, 2H, aromatic)

6.4. *2,2,3,3,4,4,4-Heptafluorobutyloxycarbonylphenyl 4-hexyloxybenzoate*

To a mixture of 0·32 g (1·0 mmol) of 2,2,3,3,4,4,4-heptafluorobutyl 4-hydroxybenzoate, 0·22 g (1·0 mmol) of DCC, and 10 mg of DMAP in 10 ml of dichloromethane, was added 0·54 g (1·0 mmol) of 4-hexyloxybenzoic acid. The solution was stirred at room temperature overnight. The precipitate was filtered off, the solvent evaporated, and chromatography on silica gel with toluene as solvent afforded the desired product. Yield: 76 per cent. IR (KBr): 2962, 1732, 1630, 1274–1145 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS): 1·1 (t, 3H, CH_3), 1·9 (m, 8H, CH_2), 2·2 (m, 2H, CH_2 β), 4·1 (t, 2H, CH_2 α), 4·9 (t, 2H, CO_2CH_2), 6·9 (d, 2H, aromatic), 7·4 (d, 2H, aromatic), 8·1 (m, 4H, aromatic)

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