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Synthesis, characterization and crystal structures of two polyphilic mesogenic compounds

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Synthesis, characterization and crystal structures of two polyphilic mesogenic compounds

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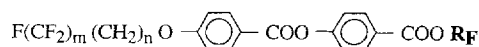
Three homologous series of semi-perfluorinated liquid crystals: 4-(2,2,3,3,4,4,4-heptafluorobutyloxycarbonyl)phenyl, 4-(2,2,3,3,4,4,5,5-octafluoropentyloxycarbonyl)phenyl and 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxycarbonyl)phenyl 4-[(*n*-perfluoroalkyl)alkoxy]benzoates have been synthesized. Their mesomorphic properties were studied by DSC, microscopic observation and X-ray diffraction. Their layer spacings are smaller than the molecular length (*L*). The ratio d_{s_x}/L is about 0.7. The crystal structure of two derivatives of the first family have also been investigated. In both structures the molecules pack in smectic C-like sheets where neighbouring molecules are antiparallel, interacting through dipolar and van der Waals forces. The interactions between contiguous sheets, through the ends of perfluorinated chains are very weak. The X-ray diffraction results on the mesophases and on the crystalline structures of two compounds of the first family are compared. From this, we propose a model of the smectic phases with a zig-zag structure.

1. Introduction

Earlier work [1-5] by different groups on liquid crystals with perfluoroalkyl or perfluoroalkoxy chains showed that smectic mesophases were enhanced, but the effects on mesomorphic properties of fluorination have not been extensively explored. Recent studies [6, 7] on mesomorphic compounds having three parts of a different chemical nature, such as molecules with a biphenyl core and two semi-perfluorinated chains, have shown that these molecules give rise to ferroelectric properties, in spite of the absence of any chiral centre. Such compounds are called polyphilic, because of the segregation domains formed by the different parts. Owing to their interest, we undertook the study of new polyphilic compounds with a dibenzoate core and semi-perfluorinated chains.

This paper describes the synthesis of the series with the formulae shown opposite.

Moreover, to understand the molecular arrangement in the mesophase, we report here the crystal structures of two compounds of this new polyphilic family (series 1A). It is now well established that there is often



for $m = 4$ or 6 and $n = 4, 5$ or 6

$\text{R}_F = \text{CH}_2(\text{CF}_2)_3\text{F}$ for series 1A

$\text{R}_F = \text{CH}_2(\text{CF}_2)_4\text{H}$ for series 1B

$\text{R}_F = (\text{CH}_2)_2(\text{CF}_2)_6\text{F}$ for series 1C

a relationship between the crystal and the mesophase arrangement [8-10]; the compounds studied are 1A ($m = 4, n = 5$) and 1A ($m = 6, n = 4$), named for the sake of clarity as compounds I and II.

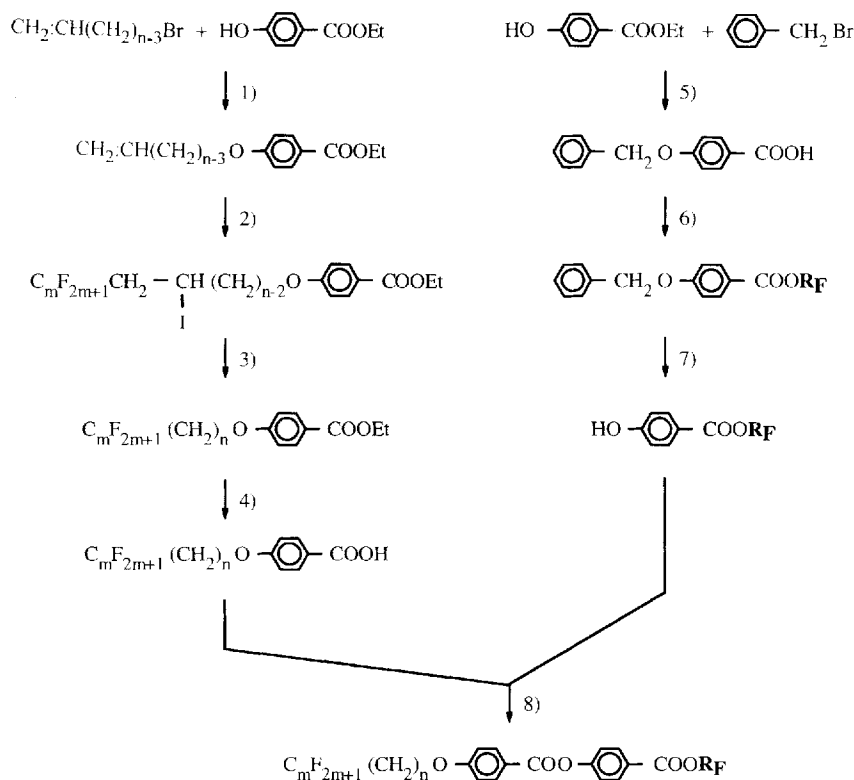
2. Synthesis

Three series of polyphilic compounds (1A, 1B and 1C) with a dibenzoate core which favours lamellar structures were synthesized. Such compounds were obtained through the scheme shown overleaf.

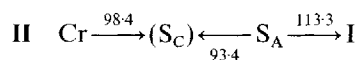
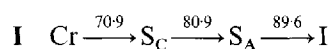
3. Crystal structures

Compounds I and II present the following polymorphism:

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- 1) KOH, EtOH, reflux 4h
- 2) AIBN, $\text{F}(\text{CF}_2)_m\text{I}$
- 3) HCl gas Zn, 95°C
- 4) 1) KOH 2) HCl
- 5) 1) KOH, H_2O , EtOH, reflux 4h 2) KOH, H_2O 3) H_3O^+
- 6) HOR_F , DCC, DMAP, CH_2Cl_2 (A)
- 7) H_2 , Pd/C, EtOAc
- 8) DCC, DMAP, CH_2Cl_2 (A)



3.1. Experimental

Suitable crystals were grown by evaporation of ethanol/chloroform solutions for both **I** and **II**. The crystal setting, the cell parameters and the data collection were performed with an Enraf-Nonius CAD-4 diffractometer, equipped with a graphite monochromator for the CuK_α radiation ($\lambda = 1.54178 \text{ \AA}$). Twenty-five reflections with $18 < \theta < 35^\circ$ for **I** and $19 < \theta < 43^\circ$ for **II** were used for the crystal setting and least squares refinement of the cell parameters. Data collection was performed with an ω - 2θ scan, up to 50° for **I** and 60° for **II**. For both compounds there was no significant decrease of reference

reflections. The absorption corrections were performed using the ψ scan technique [11] thanks to the SDP package [12]. Respectively, 4907 and 5432 reflections were collected for **I** and **II**, of which 2805 for **I** and 2118 for **II** were considered as observed ($I > 3\sigma(I)$). The crystal data, data collection conditions and refinement characteristics are given in table 1.

Both structures were solved by direct methods, using the Mithril package [13], which led to the positions of almost all non-hydrogen atoms; the missing atoms appeared after successive Fourier syntheses. The atomic parameters were refined using the full squares matrix of Shelx76 [14] using constraints [15, 16] on several bond lengths and angles. Hydrogen atoms were placed in their theoretical positions [17] and allowed to ride on the carbon atoms to which they are attached [14]. The atomic scattering factors were from International Tables and X-ray Crystallography [18]. The final reliability

Table 1. Crystal data, data collection conditions and refinement characteristics for compounds **I** and **II**.

	Compound I	Compound II
Crystal data		
Chemical formula	C ₂₇ H ₂₀ O ₅ F ₁₆	C ₂₈ H ₁₈ O ₅ F ₂₀
Molecular weight/g mol ⁻¹	728.4	814.4
<i>a</i> (Å)	5.867(1)	58.158(9)
<i>b</i> (Å)	11.317(3)	5.536(2)
<i>c</i> (Å)	23.548(6)	20.381(2)
α (°)	96.96(2)	90
β (°)	93.85(2)	103.15(1)
γ (°)	103.78(2)	90
Volume of cell/Å ³	1499	6389
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>Z</i>	2	8
Density/g cm ⁻³	1.613	1.692
Absorption coefficient μ /mm ⁻¹	1.64	1.81
Data collection conditions		
θ range for data collection	1–50°	1–60°
$h_{\min}; k_{\min}; l_{\min}$	0; –12; –26	0; 0; –23
$h_{\max}; k_{\max}; l_{\max}$	6; 12; 26	68; 6; 23
Number of reflections collected	4838	5432
Number of independent reflections	3782	3658
Number of observed reflections	2805	2127
Criterion for observed data	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$
Structure refinement		
Refinement program	Shelx76 with constraints	
Weighting scheme	11.1067/ $(\sigma(F)^2 + 0.000109F^2)$	16.3843/ $(\sigma(F)^2 + 0.000083F^2)$
<i>R</i> factor	0.088	0.083
<i>R</i> _w factor	0.095	0.089

factors were $R = 0.088$ and $R_w = 0.095$ for **I**, $R = 0.083$ and $R_w = 0.089$ for **II**. These rather high reliability factors can be related to some disorder located at the end of the perfluorinated terminal chains; this is a common feature with mesogenic compounds with long alkyl or perfluorinated alkyl chains [10]. This is illustrated in tables 2(a) and 2(b) by the high values of atomic U_{eq} (Å²) factors.

3.2. Description of the structures

The fractional coordinates x/a , y/b , z/c and U_{eq} (Å²) factors are listed in tables 2(a) and 2(b). Note the very high U_{eq} values of C and F atoms of the terminal part of the perfluorinated chains in both compounds, as illustrated by the SNOOPI [19] drawing of molecules **I** and **II** in figures 1(a) and 1(b). For both compounds the U_{eq} value increases from the beginning to the end of the perfluorinated chains. The C–C and C–F bond lengths in the perfluorinated chains of both compounds have an average value close to 1.51 and 1.33 Å, respectively, in agreement with those found in the crystal structure of the 4-cyanophenyl 4-perfluoroheptylbenzoate [16]. The C–C–C and F–C–F bond angles in the perfluorinated chains of compounds **I** and **II** have

average values around 117° and 111°, respectively; the C–C–C mean value is significantly greater than that usually observed in alkyl chains (close to 109°). This is probably due to the numerous contacts between F atoms in contiguous CF₂ groups, separated generally below the sum of the van der Waals radii (1.47 Å) according to Nyburg and Faerman [20]. Bond lengths and angles with their standard-deviations in brackets are presented respectively in tables 3(a), 3(b) and 4(a), 4(b).

For both molecules **I** and **II**, the molecular conformations can easily be described by dividing the molecules into three parts: (1) the central part of the molecule (the dibenzoate core) which corresponds to atoms C1 and O18; (2) the semi-perfluorinated chain CH₂C₃F₇ (atoms C19 to F223); (3) the semi-perfluorinated chains, OC₃H₁₀C₄F₉ (atoms O30 to F393) for **I** and OC₄H₈C₆F₁₃ (atoms O30 to F403) for **II**.

- (1) The central core of molecules **I** and **II** is composed of two successive benzoate groups (atoms C1 to O9 and C10 to O18). In molecule **I**, the second benzoate group is planar, but the first is not; the C5–C4–C7–O9 torsion angle is equal to –168.5(7)°. The torsion angle C7–O9–C10–C11

Table 2(a),(b). Fractional coordinates x/a , y/b , z/c ($\times 10^4$) and isotropic equivalent thermal parameters U_{eq} (\AA^2) ($\times 10^3$) for molecules **I** and **II**, respectively. $U_{\text{eq}} = 1/3 \sum_i \sum_j u_{ij} a_i^* a_j^* a_i a_j$.

Compound I	x/a	y/b	z/c	U_{eq}
C1	-2021 (11)	9302 (5)	5610 (3)	63 (6)
C2	-2639 (11)	8791 (6)	5049 (3)	72 (7)
C3	-1607 (12)	7926 (6)	4800 (3)	68 (6)
C4	147 (11)	7550 (5)	5134 (3)	60 (6)
C5	745 (11)	8072 (6)	5699 (3)	65 (6)
C6	-345 (12)	8953 (6)	5940 (3)	67 (6)
C7	1261 (11)	6582 (6)	4893 (3)	69 (7)
O8	2358 (9)	6062 (4)	5185 (2)	85 (5)
O9	834 (7)	6322 (4)	4311 (2)	70 (5)
C10	1536 (11)	5389 (6)	3997 (3)	65 (6)
C11	121 (11)	4867 (6)	3489 (3)	73 (7)
C12	636 (12)	3953 (7)	3125 (3)	74 (7)
C13	2586 (12)	3541 (6)	3264 (3)	64 (6)
C14	4022 (11)	4047 (6)	3773 (3)	65 (6)
C15	3500 (11)	4956 (6)	4133 (3)	69 (7)
C16	3291 (15)	2540 (7)	2900 (3)	81 (8)
O17	4874 (12)	2097 (5)	2984 (2)	111 (6)
O18	1775 (10)	2169 (6)	2411 (3)	116 (6)
C19	2288 (20)	1253 (9)	2012 (5)	134 (10)
C20	-186 (27)	422 (9)	1758 (5)	157 (10)
F201	-1631 (17)	1050 (7)	1609 (4)	262 (9)
F202	-929 (20)	-138 (8)	2229 (5)	270 (10)
C21	437 (23)	-461 (11)	1225 (5)	242 (12)
F211	2049 (21)	95 (9)	886 (4)	283 (10)
F212	1263 (16)	-1235 (7)	1524 (4)	228 (9)
C22	-1767 (35)	-1067 (15)	828 (8)	267 (13)
F221	-2457 (22)	-212 (9)	566 (4)	268 (11)
F222	-3153 (20)	-1447 (9)	1222 (6)	290 (11)
F223	-663 (21)	-1781 (10)	514 (4)	287 (11)
O30	-3206 (8)	10141 (4)	5807 (2)	77 (4)
C31	-2640 (12)	10735 (6)	6400 (3)	78 (7)
C32	-4238 (11)	11559 (6)	6521 (3)	67 (6)
C33	-3729 (12)	12235 (6)	7110 (3)	81 (7)
C34	-5313 (12)	13091 (6)	7266 (3)	73 (6)
C35	-4702 (12)	13749 (7)	7875 (3)	83 (7)
C36	-6331 (12)	14494 (6)	8057 (3)	75 (7)
F361	-6455 (10)	15339 (5)	7706 (2)	142 (6)
F362	-8545 (8)	13793 (5)	8000 (2)	133 (6)
C37	-5909 (13)	15154 (7)	8671 (3)	80 (7)
F371	-3858 (9)	16051 (5)	8692 (2)	140 (6)
F372	-5214 (12)	14455 (5)	9017 (2)	168 (7)
C38	-7709 (17)	15751 (8)	8916 (4)	126 (9)
F381	-8626 (11)	16289 (6)	8545 (2)	182 (7)
F382	-9499 (12)	14805 (7)	9011 (3)	198 (8)
C39	-7154 (18)	16548 (10)	9461 (4)	147 (10)
F391	-5637 (19)	17603 (7)	9403 (4)	248 (10)
F392	-6001 (16)	16174 (7)	9869 (3)	228 (8)
F393	-8790 (17)	16942 (8)	9680 (3)	257 (9)

Table 2(b).

Compound II	x/a	y/b	z/c	U_{eq}
C1	2812 (1)	-795 (12)	7192 (3)	47 (7)
C2	2652 (1)	-2660 (12)	7147 (3)	50 (7)
C3	2457 (1)	-2742 (12)	6609 (4)	54 (8)
C4	2422 (1)	-941 (12)	6120 (3)	48 (7)
C5	2581 (1)	968 (12)	6177 (4)	53 (8)
C6	2772 (1)	1030 (12)	6707 (3)	54 (8)
C7	2208 (1)	-1196 (14)	5567 (3)	55 (9)
O8	2063 (1)	-2747 (9)	5504 (2)	70 (6)
O9	2185 (1)	715 (8)	5123 (2)	63 (5)
C10	1986 (1)	728 (13)	4574 (3)	56 (8)
C11	1845 (1)	2771 (13)	4526 (4)	61 (8)
C12	1659 (1)	2929 (13)	3965 (4)	56 (8)
C13	1626 (1)	1203 (14)	3462 (4)	59 (8)
C14	1772 (1)	-774 (13)	3535 (3)	61 (8)
C15	1956 (1)	-1034 (13)	4083 (4)	57 (8)
C16	1439 (2)	1425 (18)	2842 (4)	76 (11)
O17	1402 (1)	-27 (11)	2379 (3)	100 (8)
O18	1311 (1)	3428 (14)	2821 (3)	113 (9)
C19	1146 (2)	4036 (23)	2200 (5)	133 (17)
C20	919 (2)	4606 (23)	2401 (5)	97 (14)
F201	954 (1)	6487 (16)	2790 (4)	185 (12)
F202	866 (2)	2860 (22)	2773 (5)	240 (17)
C21	717 (2)	5215 (32)	1813 (6)	134 (20)
F211	673 (2)	3172 (17)	1412 (4)	204 (14)
F212	788 (1)	6954 (19)	1445 (5)	220 (16)
C22	478 (2)	5881 (26)	1948 (6)	175 (32)
F221	425 (2)	3955 (25)	2259 (7)	284 (25)
F222	513 (2)	7960 (28)	2269 (6)	271 (22)
F223	336 (2)	6123 (20)	1352 (5)	244 (17)
O30	3009 (1)	-539 (8)	7695 (2)	58 (5)
C31	3071 (1)	-2520 (12)	8159 (3)	59 (8)
C32	3309 (1)	-2046 (13)	8612 (3)	58 (8)
C33	3394 (1)	-4294 (12)	9023 (3)	56 (7)
C34	3634 (1)	-3970 (14)	9497 (4)	68 (9)
C35	3723 (2)	-6214 (16)	9857 (4)	73 (10)
F351	3551 (1)	-7221 (10)	10144 (3)	111 (7)
F352	3761 (1)	-7955 (9)	9417 (3)	102 (6)
C36	3946 (2)	-6125 (17)	10431 (5)	82 (12)
F361	3903 (1)	-4575 (12)	10892 (2)	129 (8)
F362	3983 (1)	-8316 (11)	10711 (3)	129 (8)
C37	4168 (2)	-5347 (19)	10261 (5)	92 (13)
F371	4136 (1)	-3242 (17)	9969 (5)	199 (14)
F372	4218 (1)	-6782 (21)	9787 (5)	255 (18)
C38	4396 (2)	-5099 (23)	10787 (6)	139 (21)
F381	4408 (1)	-6794 (21)	11233 (5)	229 (17)
F382	4378 (2)	-3147 (25)	11164 (6)	281 (22)
C39	4631 (2)	-4785 (24)	10586 (8)	197 (34)
F391	4599 (1)	-3055 (25)	10136 (7)	270 (21)
F392	4693 (3)	-6961 (27)	10417 (9)	391 (24)
C40	4846 (3)	-4292 (31)	11147 (8)	253 (52)
F401	4860 (2)	-5773 (26)	11659 (8)	315 (26)
F402	4820 (2)	-2156 (31)	11414 (10)	330 (19)
F403	5026 (2)	-3932 (22)	10869 (8)	297 (18)

is equal to $151.0(7)^\circ$. In molecule **II**, each benzoate group is planar, but the angle between their mean planes is equal to $61.4(2)^\circ$, the torsion angle C7–O9–C10–C11 being equal to $123.5(7)^\circ$. The total length of the core (C1...O18) is equal to $11.09(1)$ and $11.21(1)$ Å, respectively, for **I** and **II**.

(2) The semi-perfluorinated chain $\text{CH}_2\text{C}_3\text{F}_7$ (atoms C19 to F223) is quite planar for both molecules **I** and **II**. There is only one significant torsion angle (differing by more than 10° from the *trans*-(180°))

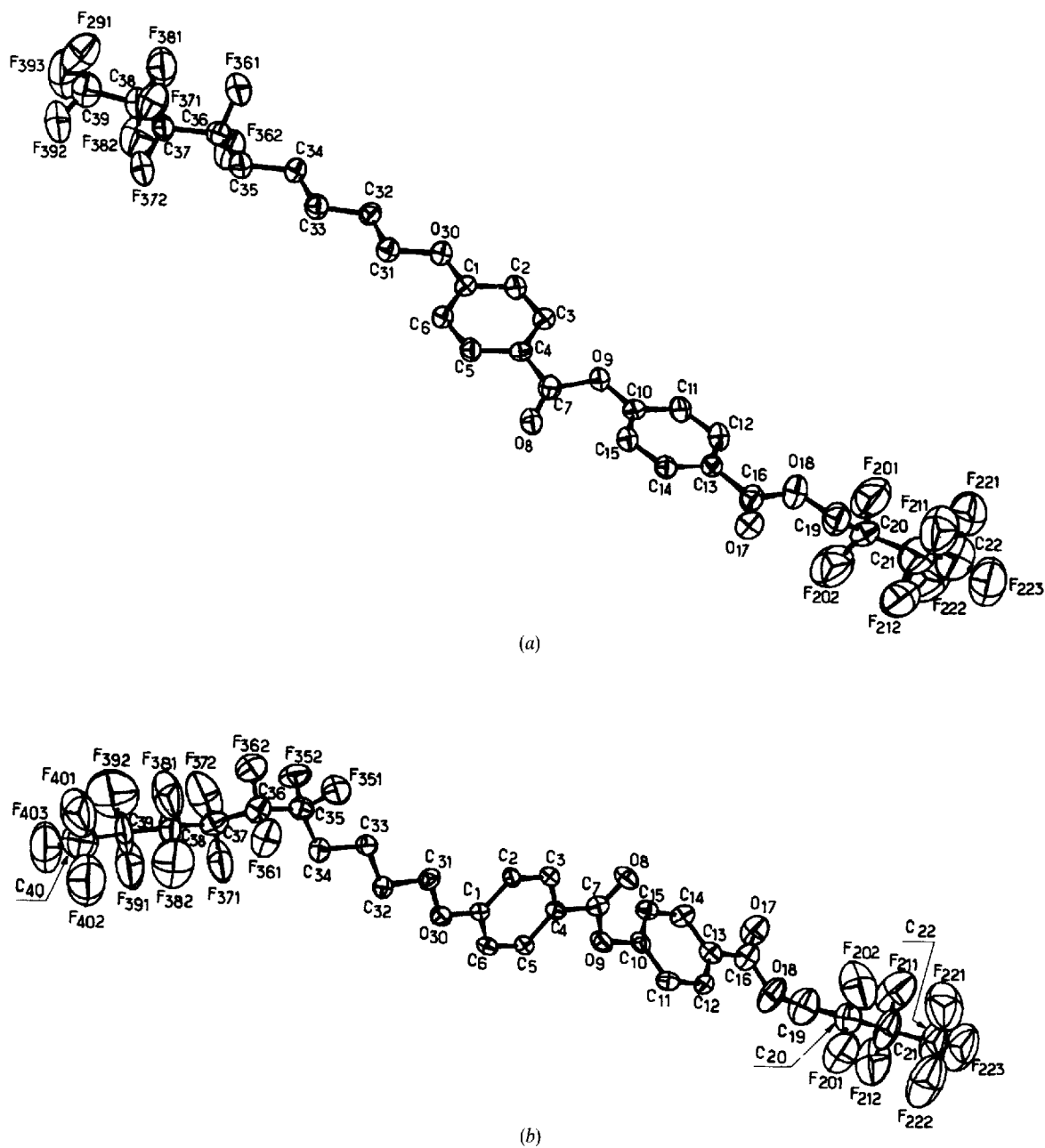


Figure 1(a), (b). SNOOPI drawing and atom labelling of molecules **I** and **II** respectively (displacement ellipsoids are shown at 50% probability levels).

conformation) which corresponds to the transition from the central core to the semi-perfluorinated chain. This angle, C16–O18–C19–C20 is equal to $143.3(9)^\circ$ and $131.4(9)^\circ$ for **I** and **II**, respectively. There is a bend at the C19 level (angle C1...C19...C22, respectively equal to $130.8(4)$ and $135.5(3)^\circ$ for molecules **I** and **II**). The distance between C19 and F223 is, respectively, equal to $4.54(2)$ and $4.77(2)$ Å for **I** and **II**.

(3) The semi-perfluorinated chains $\text{OC}_5\text{H}_{10}\text{C}_4\text{F}_9$ (atoms O30 to F393) for **I** and $\text{OC}_4\text{H}_8\text{C}_6\text{F}_{13}$ (atoms O30 to F403) for **II**, can be analysed as being composed of an alkoxy chain followed by a perfluorinated chain. The alkoxy chains and the perfluorinated chains are fully extended in both compounds, with torsion differing by less than 10° from 180° . But, while in compound **I** the $\text{OC}_5\text{H}_{10}\text{C}_4\text{F}_9$ is fully extended, there is a bend at

Table 3(a), (b). Bond lengths (Å) with their standard deviations in brackets for compounds **I** and **II**, respectively.

Compound I			
C1–C2	1.36 (1)	C21–F211	1.37 (2)
C1–C6	1.37 (1)	C21–F212	1.34 (2)
C1–O30	1.36 (1)	C21–C22	1.51 (3)
C2–C3	1.36 (1)	C22–F221	1.34 (2)
C3–C4	1.43 (1)	C22–F222	1.32 (3)
C4–C5	1.37 (1)	C22–F223	1.34 (2)
C4–C7	1.48 (1)	O30–C31	1.45 (1)
C5–C6	1.40 (1)	C31–C32	1.49 (1)
C7–O8	1.21 (1)	C32–C33	1.48 (1)
C7–O9	1.36 (1)	C33–C34	1.52 (1)
O9–C10	1.38 (1)	C34–C35	1.51 (1)
C10–C11	1.39 (1)	C35–C36	1.47 (1)
C10–C15	1.39 (1)	C36–F361	1.35 (1)
C11–C12	1.37 (1)	C36–F362	1.34 (1)
C12–C13	1.37 (1)	C36–C37	1.52 (1)
C13–C14	1.39 (1)	C37–F371	1.37 (1)
C13–C16	1.49 (1)	C37–F372	1.31 (1)
C14–C15	1.36 (1)	C37–C38	1.49 (1)
C16–O17	1.17 (1)	C38–F381	1.28 (1)
C16–O18	1.37 (1)	C38–F382	1.36 (1)
O18–C19	1.42 (1)	C38–C39	1.45 (2)
C19–C20	1.57 (2)	C39–F391	1.33 (2)
C20–F201	1.28 (2)	C39–F392	1.31 (2)
C20–F202	1.39 (2)	C39–F393	1.27 (2)
C20–C21	1.63 (2)		

Table 3(b).

Compound II			
C1–C2	1.38 (1)	C21–C22	1.52 (2)
C1–C6	1.39 (1)	C22–F221	1.31 (2)
C1–O30	1.36 (1)	C22–F222	1.32 (2)
C2–C3	1.39 (1)	C22–F223	1.31 (2)
C3–C4	1.39 (1)	O30–C31	1.44 (1)
C4–C5	1.39 (1)	C31–C32	1.50 (1)
C4–C7	1.48 (1)	C32–C33	1.52 (1)
C5–C6	1.36 (1)	C33–C34	1.52 (1)
C7–O8	1.19 (1)	C34–C35	1.47 (1)
C7–O9	1.38 (1)	C35–F351	1.39 (1)
O9–C10	1.42 (1)	C35–F352	1.37 (1)
C10–C11	1.39 (1)	C35–C36	1.54 (1)
C10–C15	1.38 (1)	C36–F361	1.34 (1)
C11–C12	1.39 (1)	C36–F362	1.34 (1)
C12–C13	1.38 (1)	C36–C37	1.47 (2)
C13–C14	1.37 (1)	C37–F371	1.30 (1)
C13–C16	1.47 (1)	C37–F373	1.33 (2)
C14–C15	1.37 (1)	C37–C38	1.51 (2)
C16–O17	1.22 (1)	C38–F381	1.30 (2)
C16–O18	1.33 (1)	C38–F382	1.34 (2)
O18–C19	1.44 (1)	C38–C39	1.52 (2)
C19–C20	1.50 (2)	C39–F391	1.31 (2)
C20–F20	1.30 (1)	C39–F392	1.32 (2)
C20–F20	1.31 (2)	C39–C40	1.52 (2)
C20–C21	1.51 (2)	C40–F401	1.31 (2)
C21–F211	1.39 (2)	C40–F402	1.32 (2)
C21–F212	1.34 (2)	C40–F403	1.32 (2)

Table 4(a), (b). Bond angles (°) with their standard deviations in brackets for compounds **I** and **II**, respectively.

Compound I			
C2–C1–C6	120.7 (6)	O17–C16–O18	121.4 (8)
C2–C1–O30	115.2 (6)	C16–O18–C19	115.6 (7)
C6–C1–O30	124.1 (6)	O18–C19–C20	104.3 (8)
C1–C2–C3	121.2 (6)	C19–C20–C21	103.1 (9)
C2–C3–C4	119.2 (6)	F201–C20–F202	109.4 (11)
C3–C4–C5	118.9 (6)	C20–C21–C22	109.9 (11)
C3–C4–C7	121.6 (6)	F211–C21–F212	112.0 (11)
C5–C4–C7	119.4 (6)	F221–C22–F222	112.2 (15)
C4–C5–C6	120.4 (6)	F221–C22–F223	115.9 (15)
C1–C6–C5	119.6 (6)	F222–C22–F223	124.0 (16)
C4–C7–O8	123.3 (6)	C1–O30–C31	118.6 (5)
C4–C7–O9	112.3 (6)	O30–C31–C32	108.6 (5)
O8–C7–O9	124.3 (6)	C31–C32–C33	112.2 (6)
C7–O9–C10	122.7 (5)	C32–C33–C34	115.1 (6)
O9–C10–C11	114.8 (6)	C33–C34–C35	112.3 (6)
O9–C10–C15	126.6 (6)	C34–C35–C36	113.6 (6)
C11–C10–C15	118.6 (6)	C35–C36–C37	117.5 (6)
C10–C11–C12	121.4 (6)	F361–C36–F362	103.1 (6)
C11–C12–C13	119.3 (7)	C36–C37–C38	120.4 (7)
C12–C13–C14	120.2 (6)	F371–C37–F372	99.8 (6)
C12–C13–C16	123.6 (6)	C37–C38–C39	120.4 (8)
C14–C13–C16	116.2 (6)	F381–C38–F382	104.9 (8)
C13–C14–C15	120.2 (6)	F391–C39–F392	101.1 (9)
C10–C15–C14	120.2 (6)	F391–C39–F393	101.0 (9)
C13–C16–O17	129.2 (8)	F392–C39–F393	107.6 (9)
C13–C16–O18	109.4 (6)		

the level of the C35–C36 bond for compound **II**; the C34–C35–C36–C37 torsion angle is equal to $-62.1(9)^\circ$. The C1...C35...C39 angle is equal to $-175.3(2)^\circ$ for **I** and the C1...C35...C40 angle is equal to $136.0(2)^\circ$ for **II**. This is in agreement with the preceding results. The total length of the OC₅H₁₀C₄F₉ semi-fluorinated chain in **I** is equal to 12.34(1) Å, while the total length of the OC₄H₈C₆F₁₃ semi-perfluorinated chain in **II** is equal to 12.19(2) Å.

Summarising, the molecules **I** and **II** differ by three torsion angles. The molecular length F223...F393 is equal to 29.81(2) Å for **I** and the molecular length F223...F403 is equal to 30.18(2) Å for **II**.

The plots for structures **I** and **II** along *Ox* and *Oy*, respectively are shown in figures 2(a) and 2(b). In both structures the molecules give rise to sheets parallel to (*xOy*) for **I** and to (*yOz*) for **II**. The thickness of the sheets is equal to the *c* parameter (23.55 Å) for **I** and to the *a*/2 parameter (29.1 Å) for **II**, comparing with a molecular length close to 29.8 Å for **I** and 30.2 Å for **II**. The tilt angle, corresponding to the angle between the core axis and the perpendicular to the sheet, is equal to 55.2° for **I** and 41.6° for **II**. Contiguous molecules are arranged in a smectic C-like fashion through numerous van der Waals interactions and dipole-dipole inter-

Table 4(b).

Compound II			
C2-C1-C6	119.5 (6)	O17-C16-O18	121.8 (8)
C2-C1-O30	124.7 (6)	C16-O18-C19	118.5 (8)
C6-C1-O30	115.8 (6)	O18-C19-C20	105.1 (9)
C1-C2-C3	119.7 (6)	C19-C20-C21	113.7 (10)
C2-C3-C4	120.2 (6)	F201-C20-F202	105.2 (10)
C3-C4-C5	119.8 (6)	C20-C21-C22	119.0 (11)
C3-C4-C7	115.9 (6)	F211-C21-F212	107.2 (11)
C5-C4-C7	124.3 (6)	F221-C22-F222	119.9 (13)
C4-C5-C6	119.5 (6)	F221-C22-F223	111.3 (12)
C1-C6-C5	121.2 (6)	F222-C22-F223	111.4 (12)
C4-C7-O8	127.0 (7)	C1-O30-C31	117.2 (5)
C4-C7-O9	111.2 (6)	O30-C31-C32	109.2 (5)
O8-C7-O9	121.7 (7)	C31-C32-C33	109.5 (6)
C7-O9-C10	117.4 (5)	C32-C33-C34	113.0 (6)
O9-C10-C11	115.1 (6)	C33-C34-C35	112.8 (6)
O9-C10-C15	121.1 (6)	C34-C35-C36	119.5 (7)
C11-C10-C15	123.4 (7)	F351-C35-F352	103.5 (6)
C10-C11-C12	116.5 (7)	C35-C36-C37	117.5 (8)
C11-C12-C13	121.4 (7)	F361-C36-F362	108.7 (8)
C12-C13-C14	119.5 (7)	C36-C37-C38	122.5 (9)
C12-C13-C16	122.0 (7)	F371-C37-F372	103.4 (9)
C14-C13-C16	118.5 (7)	C37-C38-C39	121.2 (10)
C13-C14-C15	121.5 (7)	F381-C38-F382	100.3 (10)
C10-C15-C14	117.7 (7)	C38-C39-C40	117.1 (12)
C13-C16-O17	124.9 (8)	F391-C39-F392	119.1 (14)
C13-C16-O18	113.3 (7)	F401-C40-F402	102.8 (8)
O17-C16-O18	121.8 (8)	F401-C40-F403	121.7 (15)
C16-O18-C19	118.5 (8)	F402-C40-F403	102.8 (15)

actions between antiparallel carbonyl groups in neighbouring molecules related through the centres of symmetry. On the other hand, the interactions between the parallel sheets are very weak.

Generally speaking, the molecules of mesogenic compounds with semi-perfluorinated chains are not linear because a greater or lesser bend is present between the fluorinated and hydrogenated segments. It can be verified that the core of such molecules is strongly tilted within the crystalline sheet. In that event, if the value of n (number of hydrogenous carbon atoms in the second perfluorinated chain) is odd, the chain is roughly a prolongation of the central core. The entire molecule is then tilted and can be considered as a precursor of the smectic C mesophase. On the other hand, if the number n is even, the molecule adopts a zig-zag conformation, which then preferentially favours a smectic A mesophase.

4. Mesomorphic properties

4.1. DSC measurement and optical properties

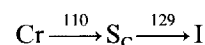
The textures were observed with a polarizing microscope equipped with a heating and cooling stage (Mettler FP52). Transition temperatures and enthalpies were determined by calorimetry using a DSC7 (Perkin-Elmer). Transition temperatures ($^{\circ}\text{C}$) and enthalpies

(kJ mol^{-1}) are reported in tables 5, 6 and 7, respectively for series 1A, 1B and 1C.

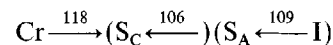
The analysis of these tables shows the exclusive presence of lamellar smectic A and C mesophases, stabilized by the introduction of perfluorinated fragments and the presence of the dibenzoate core. The increase in fluorinated carbons in a given family is accompanied by an increase in the clearing temperature, partly due to the increase in the molecular weight of the compounds.

An even and odd effect is observed for series 1C, which entails the disappearance of the smectic A phase, to the advantage of the smectic C mesophase. It is emphasized that the even and odd effect is not due to the total number of carbons $m+n$ in the chain, but simply to the value of n . When n is even, both S_A and S_C mesophases exist, whereas when n is odd, there is only the S_C mesophase. This effect is illustrated below:

series 1C $m=7$ $n=5$



series 1C $m=3$ $n=6$



The effect is not obvious for the other two series 1A and 1B for which the length of the R_F chain is shorter. It can however be verified that for an even value of n , the S_C mesophase is always monotropic. These observations are in agreement with the crystal structures of these compounds (n even corresponds to an S_C phase, n odd corresponds to a zig-zag conformation of the molecule and an S_A phase).

4.2. X-ray diffraction

X-ray measurements were made as a function of temperature using an 'Imaging Plate Scanner' system (Marresearch). This was equipped with a graphite monochromator (CuK_α radiation) and a heated sample holder.

An X-ray diffraction study on the mesophase was performed for several compounds for the three series. Table 8 gives the thickness d (\AA) of the smectic layers, as well as two other parameters: the molecular length L (\AA) (evaluated from molecular models with a fully extended conformation; the difference between these values and those found for the crystal was due to the zig-zag conformation) and the d/L ratio in the smectic A mesophase. The measured values for the S_C and S_A sheets are relatively close for a given compound, which means that it is not possible to determine the tilt angle θ using the relationship $\cos \theta = d_{S_C}/d_{S_A}$. This agrees with the optical microscopic observations, which show that

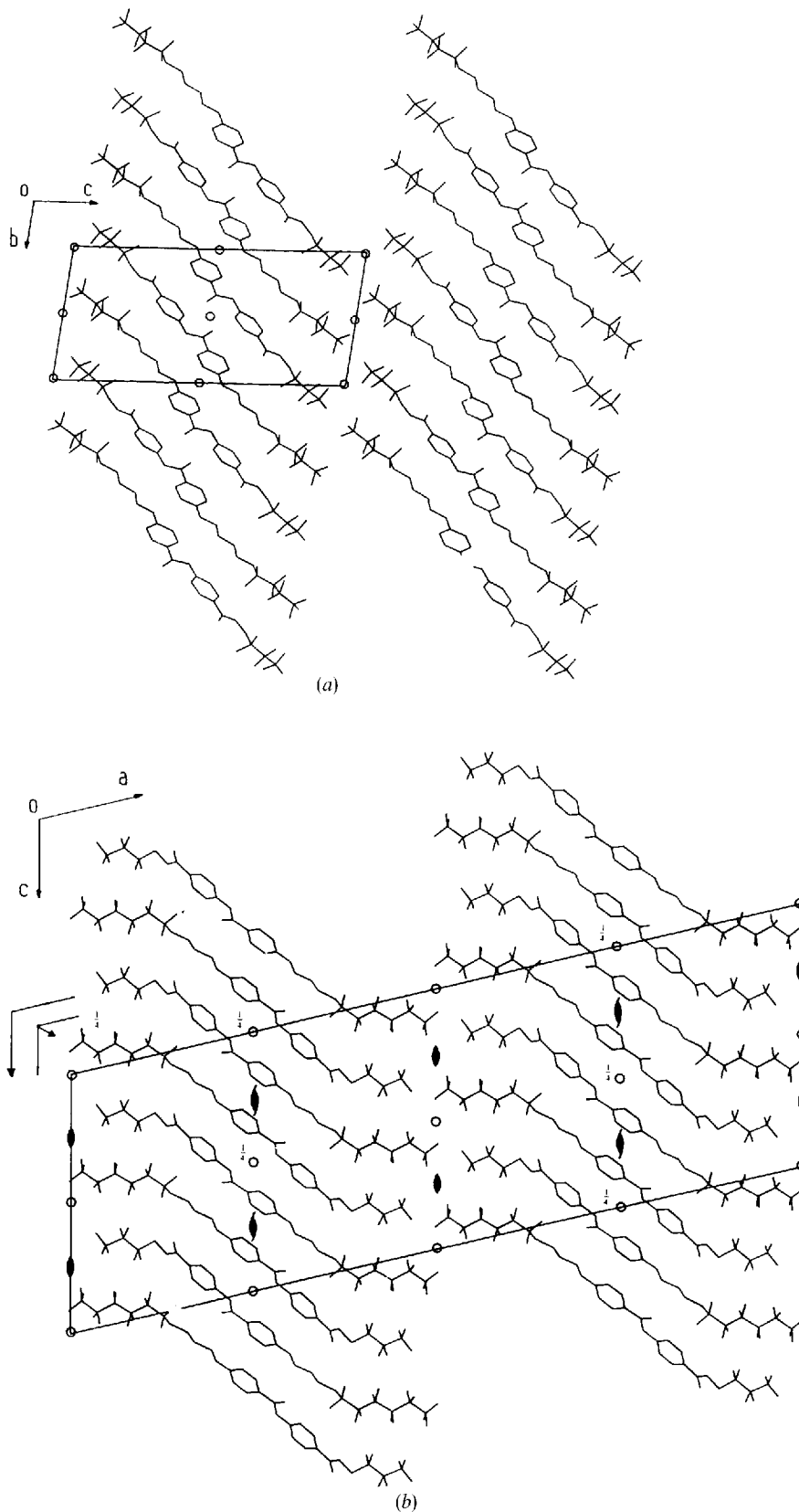


Figure 2(a), (b). Projection of (a) structure I parallel to a on the (yOz) plane, and (b) structure II parallel to b on the (xOz) plane.

Table 5. Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kJ mol^{-1}) for series **1A**. Cr = crystal; S_C, S_A = smectic phases C and A; I = isotropic liquid; \bullet = the phase exists; () = monotropic phase; [] = ΔH .

<i>m</i>	<i>n</i>	Cr	S_C	S_A	I
4	3	\bullet 80.5 [22.17]	\bullet 87.4 [1.05]	\bullet 90.9 [3.28]	\bullet
4	4	\bullet 88.4 [43.43]	(\bullet 82.2 [0.54])	\bullet 95.1 [3.83]	\bullet
4	5	\bullet 70.9 [33.23]	\bullet 80.9 [0.68]	\bullet 89.6 [3.31]	\bullet
6	4	\bullet 98.4 [46.32]	(\bullet 93.4 [0.40])	\bullet 111.3 [4.29]	\bullet
6	5	\bullet 73.7 [35.80]	\bullet 92.3 [0.73]	\bullet 104.0 [3.73]	\bullet
6	6	\bullet 104.8 [47.24]	(\bullet 87.4 [0.83])	\bullet 107.1 [4.35]	\bullet

Table 6. Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kJ mol^{-1}) for series **1B**. Cr = crystal; S_C, S_A = smectic phases C and A; I = isotropic liquid; \bullet = the phase exists; () = monotropic phase; [] = ΔH .

<i>m</i>	<i>n</i>	Cr	S_C	S_A	I
4	3	\bullet 67.9 [20.82]	(\bullet 59.3 [0.70])	(\bullet 65.6 [2.76])	\bullet
4	4	\bullet 90.1 [41.88]	(\bullet 65.0 [0.16])	(\bullet 76.2 [3.66])	\bullet
4	5	\bullet 69.5 [40.09]	(\bullet 63.2 [0.42])	\bullet 73.4 [3.37]	\bullet
6	4	\bullet 91.8 [45.04]	(\bullet 76.8 [0.21])	\bullet 99.7 [4.56]	\bullet
6	5	\bullet 76.3 [32.20]	\bullet 77.7 [0.34]	\bullet 95.2 [4.32]	\bullet
6	6	\bullet 95.5 [45.99]	(\bullet 77.1 [0.17])	\bullet 100.1 [5.17]	\bullet

Table 7. Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kJ mol^{-1}) for series **1C**. Cr = crystal; S_C, S_A = smectic phases C and A; I = isotropic liquid; \bullet = the phase exists; — = the phase does not exist; () = monotropic phase; [] = ΔH .

<i>m</i>	<i>n</i>	Cr	S_C	S_A	I
4	3	\bullet 104.1 [32.41]	\bullet 115.8 [6.44]	—	\bullet
4	4	\bullet 126.3 [53.02]	(\bullet 114.7 [1.26])	(\bullet 118.5 [4.35])	\bullet
4	5	\bullet 92.8 [29.12]	\bullet 114.7 [6.72]	—	\bullet
6	4	\bullet 126.0 [49.33]	\bullet 126.4 [1.86]	\bullet 131.1 [4.11]	\bullet
6	5	\bullet 102.9 [34.11]	\bullet 126.6 [7.90]	—	\bullet
6	6	\bullet 120.3 [41.60]	\bullet 122.7 [2.25]	\bullet 126.3 [3.84]	\bullet

Table 8. Characteristics of the S_C and the S_A phases for the series of polyphilic compounds **1A**, **1B** and **1C**. d_{S_C}, d_{S_A} = layer thickness (\AA) of the smectic C and A phases ($\pm 0.1 \text{\AA}$); L = molecular length (\AA); d/L = layer thickness in the S_A phase/molecular length.

Series	<i>m</i>	<i>n</i>	d_{S_C}	d_{S_A}	L	d_{S_A}/L
1A	4	4	25.3	25.8	33.7	0.76
	4	5	26.8	27.5	34.8	0.79
	6	4	28.3	30.9	36.6	0.84
	6	5	29.1	30.1	37.7	0.80
1B	4	4	22.6	22.9	34.9	0.66
	6	5	31.3	34.1	38.7	0.88
	6	6	27.2	27.5	39.8	0.69
1C	4	4	26.6	26.9	38.9	0.67
	6	5	30.1	—	42.9	—

the birefringence increases when going from the S_A to the S_C mesophase; the tilt angle measurements when saturation occurs give values around 27° which are well above the value obtained from the d_{S_C}/d_{S_A} ratio ($\theta \approx 14^{\circ}$). The thickness evolution of the smectic A and C sheets as a function of temperature is shown in figure 3 for the compound with $m = 6$ and $n = 6$ of series **1B**. This shows a sharp transition between the two dimensions.

The d/L values show that the sheets observed for these polyphilic compounds are monomolecular. The fact that the d/L ratio is much smaller than 1 in most cases suggests that the molecules are not linear, but bent in the smectic A phase.

All the physicochemical results (DSC, light microscopy and X-ray diffraction) are in agreement with the crystal structure, which shows that molecules are not linear and that the central cores are greatly tilted within the sheets. Therefore we propose a structural model for the smectic A and C phases, in the case of polyphilic compounds, in which the molecular conformation is of a zig-zag type (figure 4).

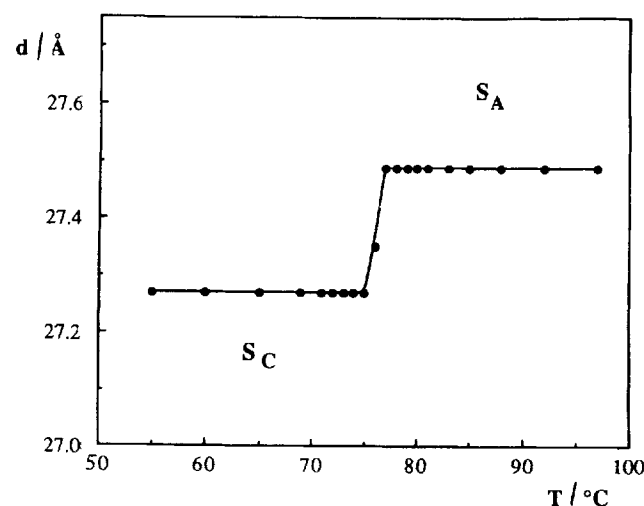


Figure 3. Evolution of the layer thickness of the S_A and S_C phases (\AA) of the polyphile $m = 6, n = 6$ of series **1B** as a function of temperature ($^{\circ}\text{C}$).

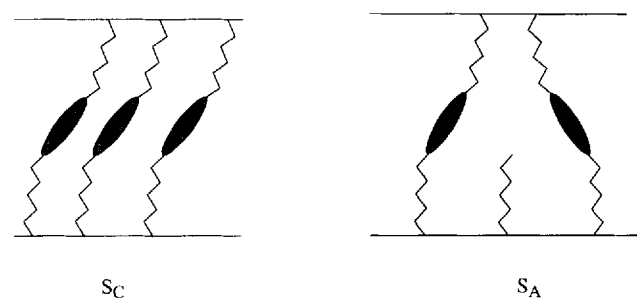


Figure 4. Polyphilic compounds: structural model for the S_A and S_C mesophases.

5. Conclusion

Three new series of semi-perfluorinated polyphilic compounds were synthesized. All compounds exhibit S_A and/or S_C phases with a marked odd and even effect, relative to the number n of CH_2 groups, for long chain lengths. Crystal structures of two compounds from one series have been investigated. In the S_A mesophases, the layer spacings are much smaller than the molecular lengths and this suggests a bent conformation for the molecules. Both structures show a smectic C-like arrangement arising through numerous van der Waals and dipole-dipole interactions. But if contiguous molecules are strictly antiparallel in structure **I**, they are only roughly antiparallel in structure **II** because of the presence of a 2_1 axis. Moreover, the perfluorinated terminal chains are quasi-parallel to the normal of the sheet in structure **II**, which is not the case in structure **I**. Both dibenzoate cores are tilted to the layer. However, while the $\text{C}_6\text{F}_{13}\text{-C}_4\text{H}_8\text{O}$ semi-perfluorinated chain in **I** is a roughly linear prolongation of the central core, the $\text{C}_4\text{F}_9\text{-C}_5\text{H}_{10}\text{O}$ semi-perfluorinated chain in **II** is largely bent at the C35 level. In consequence, the molecular conformation of **II** is of the zig-zag type. The differences between the molecular conformations and arrangements may be related to the odd/even effect. These results permit us to propose a structural model with zig-zag molecules for smectic A and C mesophases.

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 purities of intermediates and final products were checked by thin layer chromatography and by normal-phase HPLC. 2,2,3,3,4,4,4-heptafluorobutyl, 2,2,3,3,4,4,5,5-octafluoropentyl and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorooctyl 4-hydroxybenzoates were prepared following the well known method [4, 21].

6.1. Ethyl 4-(5-hexenyloxy)benzoate

33.2 g (0.2 mol) of ethyl 4-hydroxybenzoate was added to a solution of 12.3 g (0.22 mol) of KOH and 30 ml of water in 300 ml of ethanol. The mixture was stirred until complete solubility was obtained. Then 32.6 g (0.2 mol) of 6-bromo-1-hexene was added dropwise and the solution was refluxed for 4 h. The solvent (ethanol) was evaporated, and the residue was hydrolysed with 15 ml of concentrated hydrochloric acid in 100 g of crushed ice and 100 ml of water. The organic material was extracted into diethyl ether (300 ml) and the organic phase was washed with water and dried over anhydrous sodium sulphate. After filtration, the solvent was evaporated under reduced pressure and the product was

chromatographed on silica gel with toluene as solvent. This afforded a colourless oil. Yield: 66 per cent. IR (KBr): 2940, 1713, 1607, 1514, 1253, 1168 cm^{-1} . ^1H NMR (CDCl_3 , TMS): 1.3 (t, 3H, CH_3), 1.5 (m, 2H, $\text{CH}_2\beta$), 2.1 (m, 2H, $\text{CH}_2\text{-CH=CH}_2$), 4.0 (t, 2H, CH_2O), 4.3 (q, 2H, $\text{CO}_2\text{-CH}_2$), 5.0 (m, 2H, $\text{CH}_2=$), 5.8 (m, 1H, CH=), 6.9 (d, 2H, aromatic), 8.0 (d, 2H, aromatic).

6.2. Ethyl 4-[(5-iodo-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro)dodecyloxy]benzoate

A mixture of 26.8 g (0.11 mol) of ethyl 4-(5-hexenyloxy)benzoate and 66.3 g (0.15 mol) of 1-iodoperfluorohexane was stirred at room temperature under nitrogen for 30 min. Then 100 mg of azoisobutyronitrile (AIBN) was added and the mixture was heated at 110°C for 15 min. The progress of the reaction was monitored by TLC. If the reaction was not finished, a further 100 mg of AIBN was added to the mixture and the operation was started again. When the starting material had disappeared, the solution was cooled to room temperature and the compound recrystallized from heptane at -20°C . The desired compound was filtered off and washed with cool heptane. Yield: 77 per cent, m.p. = 47°C . IR (KBr): 1706, 1287, 1270, 1251, 1212, 1170 cm^{-1} . ^1H NMR (CDCl_3 , TMS): 1.2 (t, 3H, CH_3), 1.8 (m, 6H, $\text{CH}_2\beta\gamma\delta$), 2.9 (m, 2H, $\text{CF}_2\text{-CH}_2$), 4.1 (t, 2H, $\text{CH}_2\alpha$), 4.4 (m, 3H, CH-I , $\text{CO}_2\text{-CH}_2$), 6.9 (d, 2H, aromatic), 8.0 (d, 2H, aromatic).

6.3. Ethyl 4-[(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro)dodecyloxy]benzoate

HCl gas was injected into a mixture of 34.5 g (0.05 mol) of ethyl 4-[(5-iodo-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro)dodecyloxy]benzoate in 600 ml of absolute ethanol. 14 g (0.2 mol) of zinc powder was added in small portions during 30 min. Passage of HCl gas was continued for 15 min more. Then the solvent was evaporated. The residue was hydrolysed and the organic product extracted into diethyl ether. After evaporation, the product was recrystallized from absolute ethanol. Yield: 72 per cent, Cr 42 S_A 45 I. IR (KBr): 1720, 1710, 1278, 1252, 1208, 1167 cm^{-1} . ^1H NMR (CDCl_3 , TMS): 1.3 (t, 3H, CH_3), 1.7 (m, 8H, $\text{CH}_2\beta\gamma\delta\epsilon$), 2.1 (m, $\text{CF}_2\text{-CH}_2$), 4.0 (t, 2H, $\text{CH}_2\alpha$), 4.4 (q, 2H, $\text{CO}_2\text{-CH}_2$), 6.9 (d, 2H, aromatic), 8.0 (d, 2H, aromatic).

6.4. 4-[(7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluoro)-dodecyloxy]benzoic acid

16.7 g (0.036 mol) of ethyl 4-[(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro)dodecyloxy]benzoate were dissolved in 100 ml of ethanol. To this mixture a solution of 5 g KOH in 25 ml of water was added. The mixture was refluxed for 2 h. The solvent was evaporated and the residue hydrolysed with 5 ml of concentrated HCl,

50 g of crushed ice and 100 ml of water. The solid was filtered off and recrystallized from absolute ethanol. Yield: 92 per cent, Cr 160 S_C 178 I. IR (KBr): 2900, 1675, 1590, 1262 cm⁻¹. ¹H NMR (CDCl₃, TMS): 1.3 (s, 1H, CO₂H), 1.7 (m, 8H, CH₂βγδϵ), 2.1 (m, 2H, CF₂-CH₂), 4.1 (t, 2H, CH₂α), 6.9 (d, 2H, aromatic), 8.0 (d, 2H, aromatic).

6.5. 2,2,3,3,4,4,4-Heptafluorobutyloxycarbonylphenyl 4-[(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro)dodecyloxy]benzoate

To a mixture of 0.32 g (1.0 mmol) of 2,2,3,3,4,4,4-heptafluorobutyl 4-hydroxybenzoate [21], 0.22 g (1.0 mmol) of DCC, 10 mg of DMAP in 10 ml of dichloromethane was added 0.54 g (1.0 mmol) of 4-[(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro)dodecyloxy]benzoic 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. ¹H NMR (CDCl₃, TMS): 1.9 (m, 2H, CH₂βδϵ), 2.2 (m, 2H, CH₂γ), 4.1 (t, 2H, CH₂α), 4.9 (t, 2H, CO₂-CH₂), 6.9 (d, 2H, aromatic), 7.4 (d, 2H, aromatic), 8.1 (m, 4H, aromatic).

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