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A Mesogenic Perfluorinated Compound

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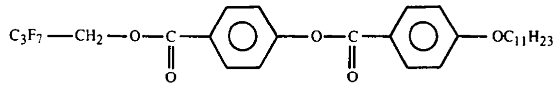
(*Received* 4 *July* 1994; *accepted* 23 *November* 1994)

Abstract

The structure of 4-(2,2,3,3,4,4,4-heptafluorobutyloxycarbonyl)]phenyl 4-undecyloxybenzoate, $C_{29}H_{33}F_7O_5$, adopts a slightly bent conformation. Molecules are aligned in the same direction and orientation as in an S_A smectic-like molecular arrangement. It is, therefore, a precursor of a ferroelectric phase.

Comment

Liquid crystals play an important role in a wide variety of electro-optical display devices and their development is currently of great interest (Kaneko, 1987). Recently, liquid crystals incorporating F atoms have shown very interesting results for such displays (Schad & Kelly, 1985; Goto, Ogawa, Sawada & Sugimori, 1991). There are numerous ways to introduce fluorine into liquid crystals; one is discussed in a recent paper regarding the 4-cyanophenyl 4-perfluoroheptylbenzoate with a cyano group on one side and a perfluoroheptyl chain on the other (Kromm, Bideau, Cotrait, Destrade & Nguyen, 1994), which gives an S_{A_2}-like arrangement. For the present compound, structural characterization shows that the material has a monolayer S_A phase. In order to clarify the precise relationship between the S_A structure and the molecular interactions, we solved the crystal structure of the present compound (1).



(1)

The molecule can be analysed as consisting of three parts, the alkoxy chain, the central core and the semi-perfluorinated chain. The title compound crystallizes in the *P*1 space group with two independent molecules in the cell, (I) and (II). The atom labelling, along with the molecular conformations, are given in a *SNOOPI* drawing (Davies, 1983) (Fig. 1). Both alkoxy chains (O30–C41) for (I) and (O80–C91) for (II) are planar with torsion angles differing by less than 5° from 180°. Both semi-perfluorinated chains O18–C22 for (I) and O68–C72 for (II) are fully extended. The only conformational differences between molecules (I) and (II) are relative to the central core: C1–O18 and C51–O68 for (I) and (II), respectively. The torsion angles which differentiate molecules are as follows: C3—C4—C7—O9 −10.3 (12), C53—C54—C57—O59 −167.2 (7), C7—O9—C10—C11 −121.0 (9) and C57—O59—C60—C61 −71.1 (11)°.

Both molecules are bent at the homologous C16 and C66 level: C(22)···C(16)···C(41) and C(72)···C(66)···C(91) are 131.7 and 127.8°, respectively. The two phenyl rings of the cores make angles of 52.5 and

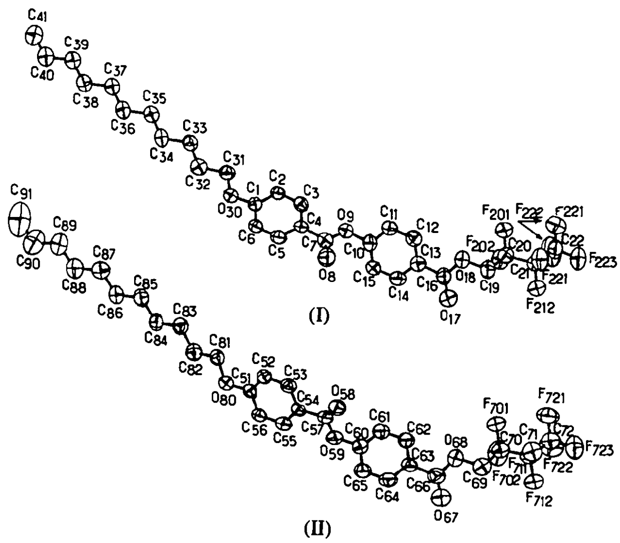


Fig. 1. View of $C_{29}H_{33}F_7O_5$ showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels (the projection of the structure is along the *z* axis).

ISSN 0108-2701 ©1995

58.5° for (I) and (II), respectively. The distances and angles in the core are in agreement with those found in similar structures (Bideau, Bravic, Cotrait, Nguyen & Destrade, 1991). The semi-perfluorinated chains are characterized by an average C—F distance of 1.33 Å and F—C—F and C—C—F angles of 107.1 and 108.5°, respectively. These values are in full agreement with those found in the 4-cyanophenyl 4-perfluoroheptylbenzoate. The lengths of molecules (I) and (II) are 30.8 and 30.7 Å, respectively. This is in agreement with the X-ray measurement on the mesophase of 28.86 Å for the S_C phase and 29.78 Å for the S_A phase.

Molecules form monomolecular sheets almost parallel to the $y0z$ plane. The thickness of the layers is close to the value of the a parameter. The interactions between the end of the alkoxy chain of one molecule and the end of the perfluorinated chain of another are very weak. The interactions between neighbouring molecules in a layer are also very weak, particularly in the vicinity of the perfluorinated chains. Because of the absence of centres of symmetry (space group $P1$), the two independent molecules are slightly different and approximately parallel (see the torsion angles given above). Such compounds may eventually give rise to ferroelectric properties which will be studied later.

Experimental

Crystal data

$C_{29}H_{33}F_7O_5$
$M_r = 594.60$
Triclinic
$P1$
$a = 30.912\,(7)$ Å
$b = 7.719\,(2)$ Å
$c = 6.184\,(6)$ Å
$\alpha = 95.40\,(7)°$
$\beta = 87.16\,(7)°$
$\gamma = 94.85\,(2)°$
$V = 1462\,(2)$ Å^3
$Z = 2$
$D_x = 1.350$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 17 reflections
$\theta = 12\text{–}19°$
$\mu = 0.114$ mm^{-1}
$T = 293$ K
Prism
$0.50 \times 0.25 \times 0.10$ mm
Colourless
Crystal source: crystallized from toluene

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5100 measured reflections
3169 independent reflections
2386 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.016$
$\theta_{max} = 22°$
$h = -32 \rightarrow 32$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 6$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.0452$
$wR = 0.0459$
$S = 1.229$
2387 reflections
739 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.30$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
C1	1.2494 (3)	0.8429 (10)	0.3677 (13)	4.2 (4)
C2	1.2114 (3)	0.7824 (10)	0.4770 (13)	4.3 (4)
C3	1.1714 (3)	0.8095 (11)	0.3970 (13)	4.8 (4)
C4	1.1700 (3)	0.8941 (10)	0.2077 (12)	4.0 (4)
C5	1.2078 (3)	0.9521 (12)	0.1018 (13)	5.2 (4)
C6	1.2470 (3)	0.9293 (11)	0.1809 (13)	4.5 (4)
C7	1.1285 (3)	0.9234 (11)	0.1081 (14)	5.1 (4)
O8	1.1250 (2)	1.0106 (9)	−0.0353 (11)	7.7 (4)
O9	1.0940 (2)	0.8314 (8)	0.2039 (9)	5.2 (3)
C10	1.0526 (3)	0.8361 (11)	0.1157 (14)	4.9 (4)
C11	1.0209 (3)	0.9000 (13)	0.2558 (14)	5.5 (5)
C12	0.9793 (3)	0.8961 (13)	0.1832 (15)	6.0 (5)
C13	0.9708 (3)	0.8351 (11)	−0.0296 (14)	5.0 (4)
C14	1.0035 (3)	0.7686 (13)	−0.1677 (14)	5.8 (5)
C15	1.0454 (3)	0.7697 (13)	−0.0933 (14)	5.5 (5)
C16	0.9274 (3)	0.8331 (13)	−0.1198 (15)	5.8 (5)
O17	0.9184 (2)	0.7886 (10)	−0.3045 (11)	7.9 (4)
O18	0.8974 (2)	0.8897 (9)	0.0347 (10)	6.8 (4)
C19	0.8546 (3)	0.8999 (14)	−0.0319 (17)	6.8 (6)
C20	0.8253 (3)	0.7855 (12)	0.0994 (15)	5.3 (5)
C21	0.7773 (3)	0.7919 (13)	0.0526 (14)	5.6 (5)
C22	0.7431 (3)	0.6905 (14)	0.1867 (17)	7.0 (6)
O30	1.2905 (2)	0.8260 (7)	0.4235 (8)	5.0 (3)
C31	1.2979 (3)	0.7475 (11)	0.6188 (13)	5.1 (4)
C32	1.3461 (3)	0.7815 (13)	0.6495 (16)	6.3 (5)
C33	1.3618 (3)	0.7093 (12)	0.8453 (14)	5.7 (5)
C34	1.4110 (3)	0.7475 (13)	0.8695 (17)	6.2 (5)
C35	1.4293 (3)	0.6826 (13)	1.0627 (15)	6.2 (5)
C36	1.4776 (3)	0.7221 (13)	1.0813 (16)	6.1 (5)
C37	1.4971 (3)	0.6572 (14)	1.2720 (16)	6.6 (5)
C38	1.5447 (3)	0.6969 (14)	1.2874 (16)	6.9 (6)
C39	1.5656 (3)	0.6347 (15)	1.4766 (17)	7.3 (6)
C40	1.6123 (3)	0.6745 (17)	1.4911 (19)	8.7 (7)
C41	1.6337 (4)	0.615 (2)	1.672 (2)	11.2 (9)
F201	0.8297 (2)	0.8248 (7)	0.3145 (8)	6.8 (3)
F202	0.8347 (2)	0.6178 (7)	0.0610 (9)	6.9 (3)
F211	0.7679 (2)	0.9609 (8)	0.0892 (11)	8.3 (4)
F212	0.7716 (2)	0.7419 (9)	−0.1573 (9)	8.4 (3)
F221	0.7437 (2)	0.7419 (12)	0.3899 (10)	12.0 (5)
F222	0.7498 (2)	0.5234 (10)	0.1614 (15)	12.4 (5)
F223	0.7047 (2)	0.7049 (10)	0.1208 (12)	10.2 (4)
C51	0.2834 (2)	0.3040 (10)	0.9244 (12)	4.0 (4)
C52	0.2602 (3)	0.4211 (10)	1.0500 (13)	4.2 (4)
C53	0.2203 (3)	0.4534 (11)	0.9848 (13)	4.8 (4)
C54	0.2034 (3)	0.3761 (10)	0.7920 (12)	3.7 (4)
C55	0.2281 (3)	0.2609 (10)	0.6665 (12)	4.3 (4)
C56	0.2681 (3)	0.2244 (11)	0.7275 (12)	4.4 (4)
C57	0.1592 (3)	0.4152 (10)	0.7401 (12)	4.4 (4)
O58	0.1397 (2)	0.5298 (8)	0.8276 (9)	5.5 (3)
O59	0.1438 (2)	0.3037 (8)	0.5730 (8)	5.3 (3)
C60	0.1011 (3)	0.3255 (12)	0.5136 (14)	5.2 (5)
C61	0.0670 (3)	0.2805 (13)	0.6464 (14)	5.7 (5)
C62	0.0255 (3)	0.3041 (12)	0.5853 (14)	5.4 (5)
C63	0.0198 (3)	0.3615 (11)	0.3849 (12)	4.4 (4)
C64	0.0552 (3)	0.4019 (12)	0.2500 (14)	5.9 (5)
C65	0.0968 (3)	0.3823 (12)	0.3138 (13)	5.5 (5)
C66	−0.0232 (3)	0.3860 (13)	0.3052 (15)	6.0 (5)
O67	−0.0311 (2)	0.4088 (12)	0.1251 (11)	9.3 (5)
O68	−0.0542 (2)	0.3746 (10)	0.4615 (10)	7.7 (4)
C69	−0.0972 (4)	0.4051 (16)	0.4035 (17)	7.9 (6)
C70	−0.1273 (3)	0.3109 (12)	0.5486 (14)	5.8 (5)
C71	−0.1747 (3)	0.3391 (12)	0.5149 (15)	6.0 (5)
C72	−0.2100 (3)	0.2480 (13)	0.6470 (15)	6.3 (5)
O80	0.3225 (2)	0.2511 (7)	0.9795 (8)	4.9 (3)

C81	0.3376 (3)	0.3075 (11)	1.1906 (14)	4.8 (4)
C82	0.3766 (3)	0.2064 (12)	1.2252 (15)	5.7 (5)
C83	0.3989 (3)	0.2674 (12)	1.4347 (15)	5.5 (5)
C84	0.4392 (3)	0.1745 (13)	1.4587 (15)	5.8 (5)
C85	0.4642 (3)	0.2386 (13)	1.6568 (16)	6.1 (5)
C86	0.5060 (3)	0.1479 (14)	1.6710 (16)	6.5 (5)
C87	0.5317 (3)	0.2089 (15)	1.8709 (17)	7.2 (6)
C88	0.5738 (3)	0.1251 (15)	1.8775 (19)	7.6 (6)
C89	0.6005 (4)	0.1918 (16)	2.071 (2)	8.8 (7)
C90	0.6422 (4)	0.1078 (18)	2.077 (3)	11.2 (9)
C91	0.6675 (5)	0.171 (3)	2.257 (4)	17.6 (16)
F701	−0.1202 (2)	0.3562 (9)	0.7611 (8)	8.6 (4)
F702	−0.1233 (2)	0.1382 (8)	0.5182 (12)	9.3 (4)
F711	−0.1794 (2)	0.5111 (7)	0.5503 (9)	7.1 (3)
F712	−0.1824 (2)	0.2918 (8)	0.3016 (8)	7.5 (3)
F721	−0.2049 (2)	0.2821 (9)	0.8554 (9)	9.0 (4)
F722	−0.2109 (2)	0.0771 (8)	0.6051 (11)	9.7 (4)
F723	−0.2487 (2)	0.2931 (11)	0.6044 (12)	10.9 (5)

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.39 (1)	C51—C52	1.36 (1)
C1—C6	1.39 (1)	C51—C56	1.39 (1)
C1—O30	1.35 (1)	C51—O80	1.38 (1)
C2—C3	1.40 (1)	C52—C53	1.36 (1)
C3—C4	1.39 (1)	C53—C54	1.39 (1)
C4—C5	1.37 (1)	C54—C55	1.38 (1)
C4—C7	1.49 (1)	C54—C57	1.48 (1)
C5—C6	1.36 (1)	C55—C56	1.37 (1)
C7—O8	1.18 (1)	C57—O58	1.19 (1)
C7—O9	1.37 (1)	C57—O59	1.36 (1)
O9—C10	1.42 (1)	O59—C60	1.42 (1)
C10—C11	1.37 (1)	C60—C61	1.34 (1)
C10—C15	1.37 (1)	C60—C65	1.36 (1)
C11—C12	1.38 (1)	C61—C62	1.39 (1)
C12—C13	1.39 (1)	C62—C63	1.38 (1)
C13—C14	1.39 (1)	C63—C64	1.37 (1)
C13—C16	1.48 (1)	C63—C66	1.47 (1)
C14—C15	1.40 (1)	C64—C65	1.39 (1)
C16—O17	1.20 (1)	C66—O67	1.18 (1)
C16—O18	1.37 (1)	C66—O68	1.33 (1)
O18—C19	1.42 (1)	O68—C69	1.44 (1)
C19—C20	1.48 (1)	C69—C70	1.46 (2)
C20—C21	1.53 (1)	C70—C71	1.53 (1)
C20—F201	1.35 (1)	C70—F701	1.35 (1)
C20—F202	1.34 (1)	C70—F702	1.34 (1)
C21—C22	1.52 (1)	C71—C72	1.50 (1)
C21—F211	1.36 (1)	C71—F711	1.34 (1)
C21—F212	1.34 (1)	C71—F712	1.36 (1)
C22—F221	1.28 (1)	C72—F721	1.31 (1)
C22—F222	1.32 (1)	C72—F722	1.32 (1)
C22—F223	1.29 (1)	C72—F723	1.32 (1)
O30—C31	1.44 (1)	O80—C81	1.43 (1)
C31—C32	1.51 (1)	C81—C82	1.53 (1)
C32—C33	1.50 (1)	C82—C83	1.52 (1)
C33—C34	1.54 (1)	C83—C84	1.51 (1)
C34—C35	1.49 (1)	C84—C85	1.50 (1)
C35—C36	1.51 (1)	C85—C86	1.53 (1)
C36—C37	1.50 (1)	C86—C87	1.52 (2)
C37—C38	1.48 (2)	C87—C88	1.51 (2)
C38—C39	1.50 (2)	C88—C89	1.52 (2)
C39—C40	1.46 (2)	C89—C90	1.49 (2)
C40—C41	1.46 (2)	C90—C91	1.42 (3)
C2—C1—C6	119.9 (8)	C52—C51—C56	121.5 (8)
C2—C1—O30	126.3 (8)	C52—C51—O80	124.0 (7)
C6—C1—O30	113.8 (7)	C56—C51—O80	114.5 (7)
C1—C2—C3	118.9 (8)	C51—C52—C53	118.4 (8)
C2—C3—C4	119.8 (8)	C52—C53—C54	122.4 (8)
C3—C4—C5	120.3 (8)	C53—C54—C55	117.7 (8)
C3—C4—C7	123.0 (8)	C53—C54—C57	118.1 (7)
C5—C4—C7	116.7 (8)	C55—C54—C57	124.1 (8)
C4—C5—C6	120.4 (8)	C54—C55—C56	121.4 (8)
C1—C6—C5	120.5 (8)	C51—C56—C55	118.5 (8)
C4—C7—O8	125.9 (9)	C54—C57—O58	125.4 (8)
C4—C7—O9	110.8 (7)	C54—C57—O59	110.9 (7)
O8—C7—O9	123.3 (9)	O58—C57—O59	123.7 (8)
C7—O9—C10	117.5 (7)	C57—O59—C60	115.6 (7)
O9—C10—C11	116.0 (8)	O59—C60—C61	120.0 (8)
O9—C10—C15	120.4 (8)	O59—C60—C65	116.8 (8)
C11—C10—C15	123.5 (9)	C61—C60—C65	123.1 (9)
C10—C11—C12	118.3 (9)	C60—C61—C62	119.0 (9)
C11—C12—C13	120.1 (9)	C61—C62—C63	119.6 (9)
C12—C13—C14	120.3 (9)	C62—C63—C64	120.2 (8)
C12—C13—C16	122.8 (9)	C62—C63—C66	123.1 (8)
C14—C13—C16	116.9 (8)	C64—C63—C66	116.7 (8)
C13—C14—C15	119.5 (9)	C63—C64—C65	120.0 (9)
C10—C15—C14	118.2 (9)	C60—C65—C64	118.1 (9)
C13—C16—O17	126.0 (9)	C63—C66—O67	127 (1)
C13—C16—O18	111.5 (8)	C63—C66—O68	111.7 (8)
O17—C16—O18	122.6 (9)	O67—C66—O68	122 (1)
C16—O18—C19	117.2 (8)	C66—O68—C69	116.3 (8)
O18—C19—C20	107.3 (8)	O68—C69—C70	106.5 (9)
C19—C20—C21	112.9 (8)	C69—C70—C71	112.6 (9)
F201—C20—F202	105.2 (7)	F701—C70—F702	105.7 (8)
C20—C21—C22	119.0 (8)	C70—C71—C72	119.6 (9)
F211—C21—F212	107.6 (8)	F711—C71—F712	107.0 (8)
F221—C22—F222	108.6 (9)	F721—C72—F722	107.1 (9)
F221—C22—F223	108.5 (9)	F721—C72—F723	108.0 (9)
F222—C22—F223	106.9 (9)	F722—C72—F723	106.6 (9)
C1—O30—C31	119.8 (7)	C51—O80—C81	118.1 (6)
O30—C31—C32	104.7 (7)	O80—C81—C82	107.3 (7)
C31—C32—C33	114.4 (8)	C81—C82—C83	112.9 (8)
C32—C33—C34	112.7 (8)	C82—C83—C84	112.4 (8)
C33—C34—C35	116.4 (9)	C83—C84—C85	114.3 (8)
C34—C35—C36	114.8 (9)	C84—C85—C86	113.0 (9)
C35—C36—C37	116.1 (9)	C85—C86—C87	114.3 (9)
C36—C37—C38	115.2 (9)	C86—C87—C88	113.8 (9)
C37—C38—C39	117.0 (9)	C87—C88—C89	114 (1)
C38—C39—C40	117 (1)	C88—C89—C90	114 (1)
C39—C40—C41	118 (1)	C89—C90—C91	114 (1)

H atoms were introduced at theoretical positions (Lehman, Koetzel & Hamilton, 1972).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (B. A. Frenz & Associates, Inc., 1982). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *CRISAF* (local program). Molecular graphics: *SNOOPI* (Davies, 1983); private communication.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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