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Structure of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorodecyl 1,10-ditosylate by X-ray crystallography and ¹⁹F-NMR spectroscopy

Soma De^a, N.K. Lokanath^b, M.A. Sridhar^b, J. Shashidhara Prasad^b, K. Venkatesan^a, Santanu Bhattacharya^{a,1,*}

^aDepartment of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India ^bSchool of Physics, Mysore University, Mysore 570 013, India

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Abstract

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorodecyl 1,10-ditosylate and its precursors were synthesized and characterized by ¹H- and ¹⁹F-NMR spectroscopic methods and X-ray crystallography. These compounds are building blocks for the syntheses of the surfactants containing polyperfluoromethylene spacer. The molecule has extended all-trans conformation with molecular symmetry \overline{I} (C_i). There is a reasonably strong C–H...O interaction in the crystal and there are two F...F intermolecular contact distances less than the sum of van der Waals radii. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: X-ray crystallography; NMR spectroscopy; Surfactant; Polyperfluoromethylene spacer

1. Introduction

This group has been interested in the design of novel gemini surfactants, see (1) below, owing to their interesting physical and chemical properties like low critical micellar concentration, high viscoelasticity and an enhanced propensity for lowering oil-water interfacial tension in comparison to their conventional single-chain analogues e.g., cetyltrimethylammonium bromide. It has been demonstrated [1-3] that their micellar properties solely depend on the nature and length of the spacer unit connecting the two head groups. It has been deemed worthwhile to examine the role of the replacement of the polymethylene spacer by the polyperfluoromethylene spacer. This should be interesting because of the following reasons, a) it is more hydrophobic and stiffer in nature than a hydrocarbon chain [4,5]; b) larger Van der Waals radii for F than that of H; which should generate greater inter-chain contacts upon selfassembly in a micellar or related aggregates [6-9]; c) enhanced thermal stability; d) chemical inertness and e) biocompatibility. Indeed compounds with a long perfluoroalkyl chain connected by a suitable functional group show unusual surface properties [10]. In addition surfaces coated with compounds possessing perfluorinated chains become nonwettable. For these reasons, various perfluorinated compounds are receiving increased attention [11]. Unfortunately, very little reliable structural information is available on such compounds. Therefore,

^{*} Corresponding author. Fax: 00 91 080 334 1683; e-mail: sb@orgchem.iisc.ernet.in

¹ Also at the Chemical Biology Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064.

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before undertaking an elaborate program for their synthesis, we sought to secure information on simple structural perfluorocarbon derivatives in terms of conformational details. In this article, the crystal structure of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadeca-fluorodecyl 1,10-ditosylate (2) is reported, a precursor for surfactant synthesis.



2. Experimental

2.1. Materials

Perfluorosebacic acid was purchased from Aldrich Chemical Co. Thin layer chromatography was performed on silica gel-G purchased from Merck. The plates were visualized by putting them in iodine chamber. Column chromatography was done on silica gel (60–120 mesh) obtained from Acme Synthetic Chemicals. All the reagents and solvents were obtained from commercial source and were purified, dried or freshly distilled as required according to a literature procedure [12].

2.2. Synthesis

Melting points were recorded in open capillary tubes and are uncorrected. ¹H-NMR spectra (TMS as an internal standard) were recorded on either a JEOL-FX-90Q (90 MHz), a 200 MHz or a 270 MHz Bruker NMR spectrometer. ¹H-decoupled ¹⁹F-NMR spectra were recorded in 400 MHz Bruker NMR spectrometer. Chemical shifts (δ) are reported in ppm downfield from the internal standard. IR spectra were recorded in a Perkin Elmer Model 781 spectrometer and are reported in wave numbers (cm⁻¹). Microanalyses were performed on a Carlo Erba elemental analyzer model 1106.

Empirical formula	$C_{24}H_{18}F_{16}O_6S_2$
Formula weight	770.5
Temperature	293 (2) K
Crystal system, space group	Triclinic, P1
Unit cell dimensions	$a = 7.915 (3) A, \alpha = 91.93 (3)^{\circ}$
	$b = 17.800(5) \text{ Å}, \beta = 104.94(3)^{\circ}$
	$c = 5.371 (3) \text{ Å}, \gamma = 99.49 (2)^{\circ}$
Volume	718.8 (5) Å ³
Z, calculated density	1, 1.780 Mg/m^3
Absorption coefficient	0.330 mm^{-1}
F (000)	386
Crystal shape	Rectangular
Crystal color	Colorless
Crystal size	$0.3 \times 0.25 \times 0.2 \text{ mm}$
On the diffractometer:	
θ range for accurate cell	2.33-22.50°
dimensions (°)	
Index ranges	$0<=h<=8,\;-19<=k<=$
	18, -5 < = 1 < = 5
Reflections collected/unique	2052/1885 [R(int) = 0.0178]
Completeness to $2\theta = 22.50$	99.9%
Standard reflections	
Number	3
Interval	200
Decay	- 4.2
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	1885/0/218
Goodness-of-fit on F ²	1.025
Final R indices $[I > 2\sigma_1]$	R1 = 0.0422, $wR2 = 0.1224$
R indices (all data)	R1 = 0.0466, wR2 = 0.1260
Extinction coefficient	0.012 (3)
Max. shift/ σ	0.001
Largest diff. Peak and hole	0.371 and -0.276 e.A^{-3}

Table 1

Crystal data and experimental crystallographic details

2.2.1. Diethyl perfluorosebacate (4)

Perfluorosebacic acid **3** (1.5 g, 4.08 mmol) was refluxed with excess dry EtOH in presence of one drop of conc. H₂SO₄ for 24 h. After removal of EtOH, the organic layer was dissolved in CHCl₃ and washed successively with water and NaHCO₃ (sat.). The product was passed through anhydrous Na₂SO₄ and upon concentration, a colorless liquid was obtained (yield *ca.* 99%). IR (nujol) 1770 cm⁻¹; ¹H-NMR (CDCl₃, 90 MHz) δ 1.33 (t, 6H), 4.4 (q, 4H); ¹⁹F-NMR (CDCl₃, 376.5 MHz) δ -86.51 (t), -83.48 (br s), -83.3 (br s), -82.41 (br s); ¹³C-NMR (CDCl₃, 22.5 MHz) δ 13:75, 64.82; LRMS, EI, m/z (%) 547 (20).

Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor^a

	х	У	Z	U_{eq}	
C (1)	14119 (6)	4296 (3)	1998 (9)	0.0964 (15)	
C (2)	12659 (4)	3981 (2)	3210 (7)	0.0614 (9)	
C (3)	12795 (5)	3375 (2)	4707 (9)	0.0730 (11)	
C (4)	11460 (4)	3082 (2)	5799 (7)	0.0635 (10)	
C (5)	9966 (4)	3402 (17)	5393 (6)	0.0443 (7)	
C (6)	9789 (5)	4010 (2)	3894 (7)	0.0631 (9)	
C (7)	11151 (5)	4296 (2)	2836 (7)	0.0714 (11)	
S (8)	8259 (10)	3033.9 (5)	6779.7 (15)	0.0531 (3)	
O (9)	8845 (3)	2482.1 (15)	8482 (4)	0.0704 (7)	
O (10)	7493 (3)	3631.8 (15)	7612 (5)	0.0743 (8)	
O (11)	6714 (3)	2606.7 (12)	4387 (4)	0.0517 (6)	
C (12)	7048 (4)	1953.4 (17)	3097 (6)	0.0494 (8)	
C (13)	5365 (4)	1614.2 (17)	1045 (6)	0.0466 (7)	
F (14)	5823 (3)	1152.7 (12)	-625 (4)	0.0714 (6)	
F (15)	4675 (3)	2164.8 (11)	-305 (4)	0.0696 (6)	
C (16)	3906 (4)	1134.7 (16)	2043 (5)	0.0439 (7)	
F (17)	4672 (2)	606 (11)	3444 (4)	0.0691 (6)	
F (18)	3390 (3)	1581.2 (12)	3632 (4)	0.0733 (6)	
C (19)	2248 (4)	707.4 (16)	-14 (6)	0.0440 (7)	
F (20)	2765 (3)	234.3 (13)	-1529 (4)	0.0780 (7)	
F (21)	1533 (3)	1217.6 (13)	-1511 (5)	0.0904 (8)	
C (22)	781 (4)	246.5 (17)	1018 (6)	0.0464 (7)	
F (23)	1517 (3)	-215.2 (14)	2715 (4)	0.0937 (9)	
F (24)	143 (3)	734.9 (14)	2298 (5)	0.1031 (10)	

^a Coordinates are fractional \times 10⁴; isotropic thermal parameters are U_{eq} (Å²). The ESD values are given in parentheses.

2.2.2. 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9hexadecafluorodecane-1,10-diol (5)

Table 2

To an ice-cold solution of 4 (1.1 g, 2.01 mmol) in dry THF (15 mL), LiAlH₄ (0.306 g, 8.06 mmol) was added and stirred at 0°C for 1 h. Then the mixture was refluxed for 12 h. After this the reaction mixture was cooled and carefully quenched with cold EtOAc first and then with water. The organic layer was extracted with CHCl₃ and passed through anhydrous Na₂SO₄. The solution was concentrated by rotary evaporation to leave a colorless solid (yield 90%). The solid was highly soluble in acetone, but sparingly soluble in CHCl₃. So, it was recrystallized from a mixture of acetone CHCl₃. Mp 128°C (sharp); IR (nujol) 3300, 1700 cm⁻¹; ¹H-NMR (CD₃COCD₃, 90 MHz) δ 4.2 (m, 4H), 5.18 (t, 2H); ¹⁹F-NMR (CD₃COCD₃, 376.5 MHz) δ -93.1 (br s), -91.55 (s). Elemental Analysis-found: C = 25.44%, H = 1.3%; calculated C = 25.5%, H = 1.39% with 0.5 H₂O.

2.2.3. 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9hexadecafluorodecyl 1,10-ditosylate (2)

Alcohol 5 (0.26 g, 0.563 mmol) dissolved in pyridine (1.4 mL) was treated with tosyl chloride (0.644 g, 3.376 mmol) at 0°C. Diethyl ether (25 mL) was added and the solution was washed successively with 1.5 M HCl, 3% NaHCO₃ and water. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under vacuum. A white solid was obtained. It was purified by passing through a silica gel (60-120)mesh) column using 10:1-7:1 hexane/EtOAc as the eluent to obtain a colorless crystal (yield 80%). Mp 77-78°C; TLC (10:1 hexane/EtOAC, Rf 0.2); IR 1590, 1235 cm^{-1} ; ¹H-NMR (CDCl₃, (nuiol) 90 MHz) δ 2.43 (s, 6H), 4.43 (t, 4H), 7.36 (d, 4H), 7.8 (d, 4H); ¹⁹F-NMR (CDCl₃, 376.5 MHz) δ -124.1 (s), -123.0 (s), -120.5 (s); ¹³C-NMR (CDCl₃, 22.5 MHz) δ 21.6, 62.72, 63.94, 65.27, 128.17, 130.16, 132.04, 146.08. Elemental Analysis-found:

Table 3				
Bond lengths	[Å]	and	angles	[°]

Table 3 (continued)

bolid lengths [A] and an	gies []
C1-C2	1.507 (5)
C1-H1B	0.9600
C1-H1C	0.9600
C2-C3	1.368 (5)
C2-C7	1.372 (5)
C3-C4	1.376 (5)
C3-H3	0.9300
C4-C5	1.366 (5)
C4-H4	0.9300
C5-C6	1.375 (5)
C5-S8	1.752 (3)
C6-C7	1.379 (5)
C6-H6	0.9300
C7-H7	0.9300
S8-O9	1.417 (3)
S8-O10	1.421 (3)
S8-O11	1.594 (2)
O11-C12	1.429 (4)
C12-C13	1.512 (4)
C12-H12A	0.9700
C12-H12B	0.9700
C13-F15	1.343 (4)
C13-F14	1.352 (4)
C13-C16	1.541 (4)
C16–F18	1.330 (3)
C16–F17	1.349 (3)
C16-C19	1.546 (4)
C19-F21	1.332 (3)
C19–F20	1.334 (4)
C19-C22	1.542 (4)
C22-F24	1.329 (4)
C22-F23	1.334 (4)
C22-C22 (xyz)	1.541 (6)
C2-CI-HIA	109.5
$U_2 - U_1 - \Pi ID$	109.5
$\Pi A - CI - \Pi ID$	109.5
	109.5
	109.5
C_{3} C_{2} C_{7}	118.2 (3)
$C_{3}-C_{2}-C_{1}$	110.2(3) 121.2(4)
$C_{7}-C_{7}-C_{1}$	121.2(4) 120.6(4)
$C_{2}-C_{3}-C_{4}$	120.0(4) 121.4(3)
С2-С3-С4	110.3
C4_C3_H3	119.3
$C_{5} = C_{4} = C_{3}$	119.5
C5-C4-H4	120.3
C3-C4-H4	120.3
C4 - C5 - C6	120.5
C4-C5-S8	119.9 (2)
C6-C5-S8	119.6 (2)
C5-C6-C7	118.8 (3)
C5-C6-H6	120.6
C7-C6-H6	120.6
C2-C7-C6	121.6 (3)
	· /

С2-С7-Н7	119.2
C6-C7-H7	119.2
O9-S8-O10	120.63 (17)
O9-S8-O11	108.38 (14)
O10-S8-O11	102.92 (14)
O9-S8-C5	108.86 (15)
O10-S8-C5	110.73 (15)
O11-S8-C5	103.87 (13)
C12-O11-S8	117.47 (18)
O11-C12-C13	107.9 (2)
O11-C12-H12A	110.1
C13-C12-H12A	110.1
O11-C12-H12B	110.1
C13-C12-H12B	110.1
H12A-C12-H12B	108.4
F15-C13-F14	107.1 (2)
F15-C13-C12	110.6 (2)
F14-C13-C12	107.2 (2)
F15-C13-C16	108.7 (2)
F14-C13-C16	107.7 (2)
C12-C13-C16	115.3 (3)
F18-C16-F17	107.6 (2)
F18-C16-C13	109.0 (2)
F17-C16-C13	109.6 (2)
F18-C16-C19	108.9 (2)
F17-C16-C19	107.5 (2)
C13-C16-C19	116.9 (2)
F21-C19-F20	106.8 (3)
F21-C19-C22	108.0 (2)
F20-C19-C22	108.4 (2)
F21-C19-C16	108.3 (2)
F20-C19-C16	108.7 (2)
C22-C19-C16	116.2 (2)
F24-C22-F23	107.2 (3)
F24-C22-C19	108.0 (2)
F23-C22-C19	108.6 (2)
F24-C22-C22 (xxjz)	108.7 (3)
F23-C22-C22 (xxjz)	107.8 (3)
C19-C22-C22 (xxyz)	116.2 (3)

C=37.75%, H=2.5%; calculated C=37.42%, H=2.35%.

2.3. X-ray crystallography

Single crystals suitable for X-ray diffraction analysis were grown from CHCl₃/MeOH mixture at room temperature by slow evaporation. Crystal data and details of the experimental crystallographic work for **2** are recorded in Table 1. Diffraction data were

	F F F					1
	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C1	0.087 (3)	0.0105 (3)	0.095 (3)	-0.003 (3)	0.052 (3)	-0.028 (3)
C2	0.050 (2)	0.063 (2)	0.065 (2)	-0.0036 (18)	0.0204 (17)	-0.0123 (17)
C3	0.049 (2)	0.072 (2)	0.106 (3)	0.018 (2)	0.033 (2)	0.0101 (18)
C4	0.049 (2)	0.060 (2)	0.084 (3)	0.0251 (19)	0.0203 (18)	0.0094 (16)
C5	0.0396 (16)	0.0466 (17)	0.0432 (16)	0.0024 (14)	0.0100 (13)	-0.0005 (13)
C6	0.0507 (19)	0.064 (2)	0.075 (2)	0.0200 (19)	0.0146 (17)	0.0117 (17)
C7	0.075 (3)	0.064 (2)	0.071 (2)	0.0269 (19)	0.019 (2)	-0.0023 (19)
S 8	0.0430 (5)	0.0628 (6)	0.0492 (5)	-0.0021 (4)	0.0149 (4)	-0.0056 (4)
09	0.0676 (15)	0.0849 (17)	0.0528 (14)	0.0232 (13)	0.0158 (12)	-0.0066 (13)
O10	0.0587 (14)	0.0826 (17)	0.0811 (17)	-0.0261 (14)	0.0304 (13)	-0.0005 (13)
011	0.0385 (11)	0.0527 (13)	0.0591 (13)	-0.0048 (10)	0.0115 (10)	-0.0010 (9)
C12	0.0422 (17)	0.0517 (18)	0.0536 (18)	0.0019 (15)	0.0162 (14)	0.0009 (14)
C13	0.0477 (17)	0.0475 (17)	0.0441 (17)	0.0048 (14)	0.0165 (14)	0.0001 (14)
F14	0.0696 (13)	0.0798 (14)	0.0659 (13)	-0.0161 (10)	0.0372 (10)	-0.0096 (10)
F15	0.0638 (12)	0.0652 (12)	0.0661 (12)	0.0287 (10)	0.0012 (10)	-0.0062 (10)
C16	0.0476 (17)	0.0444 (16)	0.0389 (16)	0.0032 (13)	0.0137 (13)	0.0029 (14)
F17	0.0560 (12)	0.0735 (13)	0.0663 (12)	0.0330 (11)	0.0012 (9)	-0.0023 (10)
F18	0.0655 (13)	0.0744 (13)	0.0785 (14)	-0.0304 (11)	0.0391 (11)	-0.0164 (10)
C19	0.0468 (17)	0.0415 (16)	0.0427 (16)	0.0078 (13)	0.0125 (14)	0.0038 (13)
F20	0.0684 (13)	0.0879 (15)	0.0745 (14)	-0.0323 (12)	0.0392 (11)	-0.0194 (11)
F21	0.0625 (13)	0.0809 (15)	0.1021 (17)	0.0528 (13)	-0.0144(12)	-0.0110 (11)
C22	0.0479 (17)	0.0489 (17)	0.0419 (16)	0.0005 (14)	0.0169 (14)	0.0004 (14)
F23	0.0674 (14)	0.1109 (18)	0.0760 (15)	0.0542 (14)	-0.0080 (11)	-0.0262 (13)
F24	0.0735 (15)	0.1038 (18)	0.128 (2)	-0.0684 (17)	0.0601 (15)	-0.0313 (13)

Anisotropic displacement parameters (Å²). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11} + ... + 2hkabU_{12}]$

measured on a Rigaku AFC75 Diffractometer with monochromated Mo radiation ($\lambda = 0.71073$ Å). The intensities of three control reflections ($2\ \bar{6}\ 0, 2\ \bar{3}\ 0$ and $2\ \bar{5}\ \bar{1}$) monitored every 150 reflections were used for checking the stability of the crystal. The small deterioration was corrected and data reduced using the program developed by Molecular Structure

Table 4

Table 5 Hydrogen coordinates and isotropic displacement parameters $(\mathring{A}^2)^a.$

	х	Y	Z	U_{eq}
H (1A)	14160	3934	661	0.145
H (1B)	15238	4390	3293	0.145
H (1C)	13888	4766	1269	0.145
H (3)	13812	3157	4991	0.088
H (4)	11572	2668	6806	0.076
H (6)	8767	4225	3600	0.076
H (7)	11046	4712	1843	0.086
H (12A)	7379	1580	4323	0.059
H (12B)	8014	2102	2310	0.059

^a Coordinates are fractional $\times 10^4$; isotropic thermal parameters are U_{eq} (Å²). The ESD values are given in parentheses.

Corporation [13]. Statistical tests favored the choice of the space group P $\overline{1}$. As the number of molecules with unit cell is one, the molecular symmetry must be $\overline{1}$ (C_i) and it must coincide with a centre of inversion in the unit cell. The structure was solved by using direct method SHELXS-86 [14] and refined by the full-matrix least squares method using SHELXL-97 [15]. All the hydrogen atoms were fixed at the stereochemically expected positions (C–H = 0.93 Å) and refined as riding hydrogens. The final atomic positions and selected molecular dimensions are recorded in Tables 2–5. Fig. 1 portrays on ORTEP diagram [16]



Scheme 1.



Fig. 1. ORTEP [16] plot of 2 with the atom-numbering scheme.

of the molecule with atom numbering. The molecular packing looking down the c-axis is presented in Fig. 2.

3. Results and discussion

The target molecule (2) has been synthesized according to a procedure summarized in Scheme 1. The details of each synthetic step have been presented in the Experimental.

The molecule adopts an extended conformation. It also reveals that bond lengths and angles are normal with the exception of C–C–C and F–C–F angles which have average values of 116.2(1) and 107.2(1)° respectively. The widening of the C–C–C angle from the expected value is accompanied by a decrease in the F–C–F angle. However, there are no

report of X-ray results on polyfluoromethylene system, as seen from the Cambridge Database [17]. In the crystal lattice, molecules translated along the c-axis (x, y, z-1) are linked by a reasonably strong C-H...O hydrogen bond [O9...H12 = 2.400 Å and $C12-H12B...O9 = 146.5^{\circ}$]. It is noteworthy that with an excess of F acceptors, there is no trace of intermolecular C-H...F hydrogen bonding although there is a short intramolecular F18...H12B contact of 2.454 Å. There are two intermolecular F...F contacts less than the sum of van der Waals radii of 2.84 Å (F21...F23: 2.670 Å; F17...F17: 2.808 Å). There are at least ten intermolecular F...F, F...H, O...H and F...C contacts less than 3.0 Å which may partly account for the high crystal density (1.78 Mg/ m^3) . It is to be expected that the energy contribution from electrostatic interaction arising from F...H would also contribute to the stability of the crystal structure.



Fig. 2. Molecular packing looking down the c-axis.

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