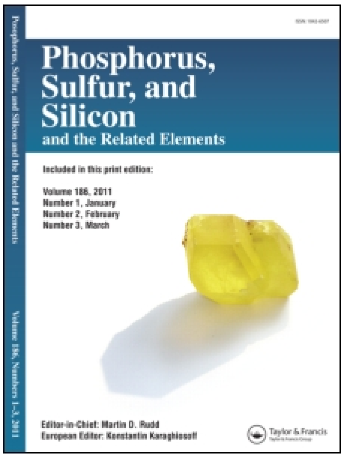

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PHASE TRANSFER SYNTHESIS OF SYMMETRICAL DI-*TERMINALLY* PERFLUORINATED ALKYL TRITHIOCARBONATES

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PHASE TRANSFER SYNTHESIS OF SYMMETRICAL DI-*TERMINALLY* PERFLUORINATED ALKYL TRITHIOCARBONATES

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Symmetrical di-terminally perfluorinated alkyl trithiocarbonates having the formula $[F(CF_2)_n(CH_2)_mS]_2CS$ (n = 4,6,8 m = 2 and n = 6,8 m = 11) were prepared in good yield under phase-transfer catalytic conditions starting from perfluoroalkyl alkyl iodides $F(CF_2)_n(CH_2)_mI$.

Keywords: di-terminally perfluorinated alkyl trithiocarbonates

INTRODUCTION

Symmetrical dialkyltrithiocarbonates constitude an important class of compounds which have been claimed for various applications, especially as pesticides, lubricating additives[1] in the synthesis of dithiocarboxylate derivatives[2] and of thiols[3], and for their absorption properties on metals[4]. Apart from other less important methods, the usual syntheses of dialkyltrithiocarbonates involve reactions of thiols with thiophosgene[5–6], chlorodithioformates[7], carbon disulfide and alkyl halides in phase transfer conditions[1], or carbon disulfide KOH and alkyl halides in anhydrous THF[8]. An original synthesis involving (imidazol-1-yl)acetonitrile and carbon disulfide has been reported[9]. Recently a synthesis of trithiocarbonates based on bis(thiocarbonyl)disulfide and an azo-compound has been

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described[10]. In the field of perfluoroalkyl derivatives of sulfur, ditrifluoromethyltrithiocarbonate prepared unexpectedly from trifluoromethanethiol and ammonia[11] or from bis(perfluoroisopropyl)mercury and sulfur[12], has been first reported. The butyl F-hexyltrithiocarbonate has been prepared from sodium n-butyltrithiocarbonate in the presence of zinc copper in DMSO[4]. Thiols, thioethers and disulfides[13–15] and particulaly terminally perfluorinated ones[13,16,17] have been extensively studied relatively to their ability to produce self-assembled monolayers on gold surfaces. Trithiocarbonates have not yet been used in this area. We consider the are interesting candidates in this field, owing to their strong affinity for metals, as cited in the above. Consequently the aim of this work is to describe the synthesis of symmetrical di-terminally perfluorinated alkyl trithiocarbonates corresponding to the general formula $[F(CF_2)_n(CH_2)_mS]_2CS$ (n = 4,6,8 m = 2 and n = 6,8 m = 11).

RESULTS AND DISCUSSION

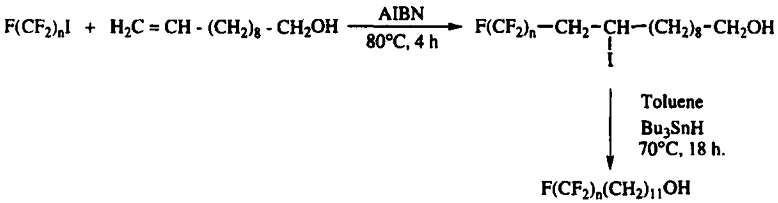
Symmetrical di-terminally perfluorinated alkyl trithiocarbonates have been prepared under phase-transfer catalytic conditions starting from perfluoroalkyl alkyl iodides $F(CF_2)_n(CH_2)_mI$. Terminally fluorinated alkyl iodides corresponding to the general formula $F(CF_2)_n(CH_2)_mI$ with n=4,6,8,10; m=2 have been supplied by Elf-ATOCHEM, the ones for m = 11 have been prepared through the synthesis of 11-perfluoroalkylundecanols followed by their conversion to iodides. For the synthesis of such alcohols we have choosen the route depicted in scheme 1[18]. Other possible routes have been reported recently[19]. Their conversion to iodides has been adapted from[20] (scheme 1). The expected trithiocarbonates have been formed by reaction of the corresponding halides with sodium thiocarbonate, in the presence of water and of a phase transfer catalyst as depicted in scheme 2. Results obtained for n=8, m=2 are summarized in table I. It appears that a large excess of sodium carbonate is necessary in order to achieve a good conversion. Some amounts of disulfide have been observed, though strongly limitated when working under nitrogen. This method has been applied to various perfluoroalkyl alkyl iodides, working with two equivalents of sodium thiocarbonate. Satisfactory yields in trithiocarbonates obtained in the pure state have been observed (Table II).

TABLE I Synthesis of the symmetrical di-terminally perfluorinated alkyl trithiocarbonate [$F(CF_2)_8(CH_2)_2S]_2CS$, from the corresponding iodide and sodium thiocarbonate, under phase transfer conditions

starting iodide RI $F(CF_2)_8(CH_2)_2I$ equiv.	*Na_2CS_3 equiv.*	*Recovered fluorinated compounds after 7h*	*unreacted iodide RI*	*disulfide RSSR*	*trithio carbonate $(RS)_2CS$*
			Molar percentage		
2	1	77%	50	10	40
2	1	77% under nitrogen	62	2	36
2	2	78% under nitrogen	20	10	70

TABLE II Yields of symmetrical di-terminally perfluorinated alkyl trithiocarbonates [$F(CF_2)_n(CH_2)_mS]_2CS$ (n=4,6,8 m=2 and n=6,8 m=11) from the corresponding iodides and sodium thiocarbonate (2 eq), under phase transfer conditions

Starting compounds	*Recovered fluorinated compounds after 7 h*	*RX*	*RSSR*	*$(RS)_2CS$*	*Yield in $(RS)_2CS$ isolated after purification*
		Molar percentage			
$F(CF_2)_4(CH_2)_2I$	88%	5	10	85	40%
$F(CF_2)_6(CH_2)_2I$	85%	10	15	75	43%
$F(CF_2)_8(CH_2)_2I$	78%	20	10	70	53%
$F(CF_2)_6(CH_2)_{11}I$	54%	16	15	70	38%
$F(CF_2)_8(CH_2)_{11}I$	54%	15	15	70	38%



SCHEME 1 Synthesis of 11-perfluoroalkylundecanols, n = 6,8

$$3\,F(CF_2)_n(CH_2)_{11}OH + 3/2\,I_2 + P \xrightarrow{5\text{ h, }140\,^{\circ}C} 3\,F(CF_2)_n(CH_2)_{11}I + H_3PO_3 \quad (1)$$

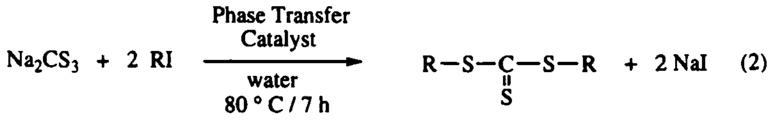
SCHEME 2 Synthesis of 1-iodo-11-perfluoroalkylundecanes, n= 6,8

EXPERIMENTAL

General information: 1-iodo-2-perfluoroalkylethanes, 1-iodoperfluoroalkanes, undecyl-10-en-1-ol were supplied by Elf-ATOCHEM and used without any further purification. Azo-bis-iso-butyronitrile (AIBN), toluene, hexane, KF, tributyltin hydride, sodium thiocarbonate (40 % in water), tributylhexadecylphosphoniumbromide (Aldrich), red phosphorus (Fluka) and iodine (Prolabo) were used as received. *Measurements and instruments*: ^{1}H-NMR, ^{19}F-NMR and ^{13}C-NMR spectra were obtained in $CDCl_3$, using a Bruker AC-250 spectrometer operating at 250.13 MHz for ^{1}H, at 235.36 MHz for ^{19}F, and a Bruker DRX 400 operating at 400,13 MHz for ^{13}C. Chemical shifts δ are given in ppm, using as internal standards $Si(Me)_3$ for ^{1}H-NMR and ^{13}C-NMR, CCl_3F for ^{19}F-NMR, H_3PO_4 for ^{31}P-NMR. Mass spectra were obtained from the Jeol JMS D100 apparatus. Fusion points were obtained from DSC (differential scanning calorimetry) Mettler TA 4000.

Synthesis of 11-perfluoroalkylundecanols $F(CF_2)_n(CH_2)_{11}OH$. General procedure

1-iodoperfluoroalkanes (0.1 mole), undecyl-10-en-1-ol (0.12 mole) and azo-bis-iso-butyronitrile (1 %, 0.0012 mole AIBN), choosen as initiator[21]



$$\mathrm{Na_2CS_3} + 2\,\mathrm{RI} \xrightarrow[\text{water} \quad 80\,^\circ\mathrm{C}/7\,\mathrm{h}]{\text{Phase Transfer Catalyst}} \mathrm{R{-}S{-}\underset{\overset{\|}{S}}{C}{-}S{-}R} + 2\,\mathrm{NaI} \qquad (2)$$

R : $F(CF_2)_n(CH_2)_m$ (n=4,6,8 m = 2 and n=6,8 m=11).
PTC : tributylhexadecylphophoniumbromid.

SCHEME 3 Synthesis of di-terminally perfluorinated alkyl trithiocarbonates

were placed under a nitrogen atmosphere in a 250-ml bi-necked flask equipped with a reflux condenser. The reaction mixture was stirred for 4 h at 80°C. 11-perfluoroalkyl-10-iodoundecan-1-ol, $F(CF_2)_nCH_2CHI(CH_2)_9OH$, was not isolated but directly reduced by tri-*n*-butyltin hydride. At room temperature, AIBN (10%, 0.1 mole) was dissolved in 10 ml of toluene and added under a purge of nitrogen to the reaction mixture, followed by a dropwise addition of tributyltin hydride[22] (0.2 mole) through a septum. The mixture was heated for 18 h at 80°C under stirring. At room temperature, toluene was vacuum evaporated under reduced pressure, then the mixture was recovered by extraction with diethylether, washed with saturated aqueous NaCl three times. The ethereal layer was dried with sodium sulfate and filtered. The required amount of KF was dispersed in the ethereal solution and kept 8 h under stirring, in order to transform the excess of tri-n-butyltin iodide into tributyltin fluoride, insoluble in diethylether, thus permitting its efficient removal[23]. The solution appeared as a milky-white suspension which was filtered. The filtrate was vacuum evaporated. The residue was purified by crystallization in heptane to give the 11-perfluoroalkylundecanols, $F(CF_2)_n(CH_2)_{11}OH$, in the pure state. *17,17,17,16,16,15,15,14,14,13,13,12,12-tridecafluoroheptadecanol* $F(CF_2)_6(CH_2)_{11}OH$, white solid, yield 70% relative to the starting perfluorohexyl iodide. Mp: 51.1°C. ^{1}H-NMR: δ 1.29 (m, 15 H, $(CH_2)_7$ and s, 1H, OH); 1.56 (m, 4H, CH_2CH_2OH and $CH_2CH_2CF_2$); 2.05 (m, 2H, CH_2CF_2); 3.64 (t, 2H, J=6.6 Hz, CH_2OH). ^{19}F-NMR: δ – 126.7 (m, 2F, CF_2CF_3); – 125.43 (m, 2F, $CF_2CF_2CF_3$); – 123.45 (m, 2F, $CF_2(CF_2)_2CH_2$); – 122.51 (m, 2F, $CF_2CF_2CH_2$); – 114.99 (m, 2F, CF_2CH_2); – 81.32 (m, 3F, CF_3). MS (FAB +, matrix NBA) (*m/z*): 491 (40) $(M+H)^+$; 473 (5) $(M+H-H_2O)^+$. 19,19,19,18,18,17,17,16,16,15,15,14,14,13,13,12,12-heptadecafluorononadecanol $F(CF_2)_8(CH_2)_{11}OH$, white solid, yield 60% relative to the starting perfluorooctyl iodide. ^{1}H-NMR: as for the preceding compound. Mp: 77.2°C. ^{19}F-NMR: δ – 126.62 (m, 2F, CF_2CF_3); - 124.06 (m, 2F, $CF_2CF_2CF_3$); – 123.24 (m, 2F, $CF_2(CF_2)_4CH_2$); – 122.37 (m, 6F, $(CF_2)_3CF_2CH_2$);-114.99 (m, 2F, CF_2CH_2); – 81.26 (m, 3F, CF_3). MS (FAB +, matrix NBA) (m/z): 591 (40) $(M+H)^+$; 573 (5) $(M + H - H_2O)^+$.

Synthesis of 1-iodo-11-perfluoalkylundecanes $F(CF_2)_n(CH_2)_{11}I$ (with n = 6, 8, 10). General procedure

The 1-iodo-11-perfluoalkylundecanes $F(CF_2)_n(CH_2)_{11}I$ were obtained from the corresponding alcohols as follows: the alcohol (2.10^{-2} mole), red phosphorus (8.10^{-3}at.) and iodine (2.10^{-2} at.) were introduced in a 250-ml Erlenmeyer flask equipped with a reflux condenser and a magnetic stirrer, and heated at 140°C for 5 h. The reaction mixture was cooled to room temperature and the solid product treated three times with diethylether (3×125-mL). The combined ether extracts were filtered and washed with saturated aqueous NaCl three times. The ethereal solution was dried over sodium sulfate and freed from solvent on a rotary evaporator. Iodides $F(CF_2)_n(CH_2)_{11}I$ were obtained in 95% yield relative to the sarting alcohols, as white solids. *17,17,17,16,16,15,15,14,14,13,13,12,12,tridecafluoro-1-iodoheptadecane*, $F(CF_2)_6(CH_2)_{11}I$, white solid. Mp: 22.1°C. ^{1}H-NMR: δ 1.35 (m, 14H, $(CH_2)_7$); 1.6 (m, 2H, $CH_2CH_2CF_2$); 1.8 (m, 2H, CH_2CH_2I); 2.2 (m, 2H, CH_2CF_2); 3.2 (t, 2H, J=7 Hz, CH_2I). ^{19}F-NMR: δ – 126.7 (m, 2F, CF_2CF_3); – 124.5 (m, 2F, $CF_2CF_2CF_3$); – 123.5 (m, 2F, $CF_2(CF_2)_2CH_2$); – 122.30 (m, 2F, $CF_2CF_2CH_2$); – 115 (m, 2F, CF_2CH_2); – 81.6 (m, 3F, CF_3). MS (EI; 70 eV; 72.2°C) (m/z): 599 (1) $(M-H)^+$; 473 (2.5) $(C_6F_{13}(CH_2)_{11})^+$; 417 (13) $(C_6F_{13}(CH_2)_7)^+$; 389 (13) $(C_6F_{13}(CH_2)_5)^+$; 375 (4) ($C_6F_{13}(CH_2)_4)^+$; 155 (13) $(C_{11}H_{22} + H)^+$; 55 (100) $(C_4H_7)^+$. *19,19,19,18,18,17,17,16,16,15,15,14,14,13,13,12,12,heptadecafluoro-1-iodononadecane*, $F(CF_2)_8(CH_2)_{11}I$, white solid. ^{1}H-NMR: as for the preceding compound. Mp: 42.8°C. ^{19}F-NMR: δ – 126.62 (m, 2F, CF_2CF_3); – 124.06 (m, 2F, $CF_2CF_2CF_3$); – 123.24 (m, 2F, $CF_2(CF_2)_4CH_2$); – 122.37 (m, 6F, $(CF_2)_3CF_2CH_2$); – 115 (m, 2F, CF_2CH_2); – 81.26 (m, 3F, CF_3). MS (EI; 70 eV; 69.8°C) (m/z): 699 (0.5) $(M-H)^+$; 573 (1) $(C_8F_{17}(CH_2)_{11})^+$; 517 (2.6) $(C_8F_{17}(CH_2)_7)^+$; 489 (4) $(C_8F_{17}(CH_2)_5)^+$; 475 (1) $(C_8F_{17}(CH_2)_4)^+$; 155 (8) $(C_{11}H_{22} + 1)^+$; 55 (100) $(C_4H_7)^+$.

Synthesis of di(perfluoroalkylalkyl)trithiocarbonates $[F(CF_2)_n(CH_2)_mS]_2C{=}S$ (with n = 4,6,8 m = 2 and n = 6,8 m = 11) from the corresponding iodides. General procedure

Perfluoroalkyl alkyl iodide (0.01 mole), sodium thiocarbonate (40% in water, 0.01 mole), tributylhexadecylphosphoniumbromid (5%, 5.10^{-4} mole) and 6 ml of water were placed under a nitrogen atmosphere in a 100 ml bi-necked flask equipped with a reflux condenser. The solution was heated for 6 h at 70°C under stirring. After cooling to room temperature, the mixture was extracted with 100 ml of carbon tetrachloride and washed with saturated hot aqueous NaCl three times. The organic layer was dried over anhydrous sodium sulfate, filtrated and then vaccum evaporated. The crude product was purified by one recrystallization in ethanol, thus permitting the efficient removal of residual tributylhexadecylphosphoniumbromide, followed by several recrystallizations in diethylether where traces of the starting iodide and the few per cent of disulfide formed are soluble. Trithiocarbonates were thus obtained in the pure state. In order to perform its identification the disulfide can be separated from the iodide by recrystallization in ethanol for m=11 and by column chromatography for m=2 (eluent: hexane).

Trithiocarbonates *di-6,6,6,5,5,4,4,3,3,nonafluorohexyltrithiocarbonate* $[F(CF_2)_4(CH_2)_2S]_2C{=}S$, yellow solid, yield 40 %. Mp: 44.9°C. ^{1}H-NMR: δ 2.5 (m, 4H, 2 CH_2CF_2); 3.55 (m, 4H, 2 CH_2S). ^{19}F-NMR : δ – 126.69 (m, 4F, 2 CF_2CF_3); – 124.97 (m, 4F, 2 $CF_2CF_2CH_2$); – 115,25 (m, 4F, 2 CF_2CH_2);-81.73 (t, 6F, 2 CF_3), ^{13}C-NMR: δ 27.69 (s, 2 CH_2S); 30,76 (m, 2 CH_2CF_2); 221,57 (s, C=S). MS (EI$^+$, 70 eV, 54.2°C) (*m/z*): 602 (2.5) $(M)^{+\cdot}$; 356 (15) $(C_4F_9CH_2CH_2SC(S)SH)^{+\cdot}$; 323 (57) $(M\text{-}S(CH_2)_2C_4F_9)^+$; 247 (2) $(C_4F_9CH_2CH_2)^+$; 77 (100) $(CS_2 + H)^+$. HRMS: cald for 602.9579 $(M+H)^+$. obsd for $C_{13}H_9F_{18}S_3$ 602.9632. *Anal.* Calc. for $C_{13}H_9F_{18}S_3$: C, 26.24; H, 1.51; S, 16.13; F, 55.27. Found: C, 25.92; H, 1.34; S, 15.96; F, 56.77. *di-8,8,8,7,7,6,6,5,5,4,4,3,3,tridecafluorooctyltrithiocarbonate* $[F(CF_2)_6(CH_2)_2S]_2C{=}S$, yellow solid, yield 43%. Mp: 70.8°C. ^{1}H-NMR: as for the preceding compound. ^{19}F-NMR: δ-126.71 (m, 4F, 2 CF_2CF_3); – 123.92 (m, 4F, 2 $CF_2CF_2CF_3$); – 123.44 (m, 4F, 2 $CF_2(CF_2)_2CH_2$);-122.43 (m, 4F, 2 $CF_2CF_2CH_2$); – 114.9 (m, 4F, 2 CF_2CH_2); – 81.34 (m, 6F, 2 CF_3), ^{13}C-NMR: δ 27.73 (s, 2 CH_2S); 30,85 (m, 2 CH_2CF_2); 221,55 (s, C=S). MS (EI+, 70 eV, 40.7°C) (m/z): 802 (2.5) $(M)^{+\cdot}$; 456 (24) $(C_6F_{13}CH_2CH_2SC(S)SH)^{+\cdot}$; 423 (100)

$(M-S(CH_2)_2C_6F_{13})^+$; 77 (44) $(CS_2 +H)^+$. *Anal.* Calc. for $C_{17}H_8F_{26}S_3$: C, 25.44; H, 1; S, 11.98; F, 61.56. Found: C, 25.5; H, 1.11; S, 12.18; F, 59.03. *di-10,10,10,9,9,8,8,7,7,6,6,5,5,4,4,3,3,heptadecafluorodecyltrithiocarbonate* $[F(CF_2)_8(CH_2)_2S]_2C{=}S$, yellow solid, yield 53%. Mp: 110°C. ^{1}H-NMR: as for the preceding compound. ^{19}F-NMR: δ – 126.69 (m, 4F, 2 CF_2CF_3); – 123.88 (m, 4F, 2 $CF_2CF_2CF_3$); – 123.28 (m, 4F, 2 $CF_2(CF_2)_4CH_2$); – 122.33 (m, 12F, 2 $(CF_2)_3CF_2CH_2$); – 114.92 (m, 4F, 2 CF_2CH_2); – 81.37 (m, 6F, 2 CF_3), ^{13}C-NMR: δ 27.58 (s, 2 CH_2S); 30,85 (m, 2 CH_2CF_2); 221,50 (s, C=S). MS (EI^+, 70 eV, 74°C) (*m/z*): 982 (2.5) $(M- HF)^+$.; 555 (2.5) $(C_8F_{17}CH_2CH_2SC(S)S)^+$; 523 (20) $(M-S(CH_2)_2C_8F_{17})^+$.; 77 (100) $(CS_2 +H)^+$. *di-17,17,17,16,16,15,15,14,14,13,13,12,12,tridecafluoroheptadecyltrithiocarbonate* $[F(CF_2)_6(CH_2)_{11}S]_2C{=}S$, yellow solid, yield 38%. Mp: 76.5°C. ^{1}H-NMR: δ 1.3 (m, 28H, 2 $(CH_2)_7$); 1.55 (m, 4H, 2 $CH_2CH_2CF_2$); 1.65 (m, 4H, 2 CH_2CH_2S); 1.95 (m, 4H, 2 CH_2CF_2); 3.28 (m, 4H, 2 CH_2S). ^{19}F-NMR: δ – 126.93 (m, 4F, 2 CF_2CF_3); – 124.3 (m, 4F, 2 $CF_2CF_2CF_3$);-123.53 (m, 4F, 2 $CF_2(CF_2)_2CH_2$); – 122.64 (m, 4F, 2 $CF_2CF_2CH_2$); – 115.21 (m, 4F, 2 CF_2CH_2);-81.65 (m, 6F, 2 CF_3), ^{13}C-NMR: δ 27.73 (s, 2 CH_2S); 31.54 (m, 2 CH_2CF_2); 224,58 (s, C=S). MS (EI, 70 eV, 176.4°C) (*m/z*): 1054 (0.3) $(M)^+$.; 1034 (0.35) $(M-HF)^+$.; 549 (10) $(C_6F_{13}(CH_2)_{11}SCS)^+$; 548 (38) $(C_6F_{13}(CH_2)_{11}SCS - H)^+$.; 57 (100) $(C_4H_9)^+$. *Anal.* Calc. for $C_{35}H_{44}F_{26}S_3$: C, 39.85; H, 4.2; S, 9; F, 46.82. Found: C, 39.62; H, 3.94; S, 9.14; F, 45.9. *di-19,19,19,18,18,17,17,16,16,15,15,14,14,13,13,12,12, heptadecafluorononadecyltrithiocarbonate* $[F(CF_2)_8(CH_2)_{11}S]_2C{=}S$, yellow solid, yield 38%. Mp: 98.2°C. ^{1}H-NMR: as for the preceding compound. ^{19}F-NMR: δ – 126.71 (m, 4F, 2 CF_2CF_3); – 123.92 (m, 4F, 2 $CF_2CF_2CF_3$); – 123.44 (m, 4F, 2 $CF_2(CF_2)_4CH_2$); – 122.43 (m, 12F, 2 $(CF_2)_3CF_2CH_2$); – 114.9 (m, 4F, 2 CF_2CH_2); – 81.34 (m, 6F, 2 CF_3), ^{13}C-NMR: δ 27.73 (s, 2 CH_2S); 30,85 (m, 2 CH_2CF_2); 224,6 (s, C=S). MS (EI, 70 eV, 201.1°C) (*m/z*): 1254 (0.5) $(M)^+$.; 1234 (0.4) $(M-HF)^+$.; 680 (5) $(C_6F_{13}(CH_2)_{11}SC(S)S - H)^+$.; 649 (28) $(C_6F_{13}(CH_2)_{11}SCS)^+$; 57 (100) $(C_4H_9)^+$.

Disulfides *8,8,8,7,7,6,6,5,5,4,4,3,3-tridecafluorooctyloctyldisulfide* $[F(CF_2)_6(CH_2)_2S]_2$, white solid. Mp: 39,2°C. ^{1}H-NMR: δ2.9 (m, 4H, CH_2S); 2.5 (m, 4H, CH_2CF_2). ^{19}F-NMR: δ – 126.94 (m, 4F, 2 CF_2CF_3); – 124.55 (m, 4F, 2 $CF_2CF_2CF_3$); – 124 (m, 4F, 2 $CF_2(CF_2)_2CH_2$); – 122.6 (m, 4F, 2 $CF_2CF_2CH_2$); – 114.3 (m, 4F, 2 CF_2CH_2); – 81.64 (m, 6F, 2

CF_3). MS (EI, 70 eV, 47.1°C) (*m/z*): 758 (100) $(M)^+$; 739 (15) $(M\text{-}F)^+$; 425 (30) $(M\text{-}CH_2C_6F_{13})^+$. HRMS: cald for 757.9652 $(M)^+$. Obsd for $C_{16}H_8F_{26}S_2$: 757.9747. *10,10,10,9,9,8,8,7,7,6,6,5,5,4,4,3,3-heptadecafluorodecyldisulfide* $[F(CF_2)_8(CH_2)_2S]_2$ white solid. Mp: 76.4°C. ^1H-NMR: as for the preceding compound. ^{19}F-NMR: δ – 127.1 (m, 4F, 2 CF_2CF_3); – 124.37 (m, 4F, 2 $CF_2CF_2CF_3$); – 123.67 (m, 4F, 2 $CF_2(CF_2)_4CH_2$); – 122.83 (m, 12F, 2 $(CF_2)_3CF_2CH_2$); – 114.5 (m, 4F, 2 CF_2CH_2); – 81.61 (m, 6F, 2 CF_3). MS (EI, 70 eV, 71.1°C) (*m/z*) : 958 (74) $(M)^+$.; 939 (12.3) $(M\text{-}F)^+$; 525 (32.3) $(M - CH_2C_8F_{17})$+; 512 (22.3) $(C_8F_{17}CH_2CH_2S_2H)^+$.. HRMS: found 957.9525 $(M)^+$.. Obsd for $C_{20}H_8F_{32}S_2$: 957.9433. *17,17,17,16,16,15,15,14,14,13,13,12,12-tridecafluoroheptadecyldisulfide* $[F(CF_2)_6(CH_2)_{11}S]_2$, white solid. Mp: 50.4°C. ^1H-NMR: δ 1.3 (m, 28 H, 2 $(CH_2)_7$); 1.55 (m, 8H, 2 $CH_2CH_2CF_2$ and 2 CH_2CH_2S); 2 (m, 4H, 2 CH_2CF_2); 2.68 (t, 4H, J=7.3 Hz, 2 CH_2S). ^{19}F-NMR: δ – 126.7 (m, 4F, 2 CF_2CF_3); – 125.13 (m, 4F, 2 $CF_2CF_2CF_3$); – 123.45 (m, 4F, 2 $CF_2(CF_2)_2CH_2$); – 122.5 (m, 4F, 2 $CF_2CF_2CH_2$); – 114.9 (m, 4F, 2 CF_2CH_2); – 81.34 (m, 6F, 2 CF_3). MS (EI, 70 eV, 159°C) (m/z): 1010 (10) M^+.; 505 (29) $(M\text{-}S(CH_2)_{11}C_6F_{13})^+$; 503 (0.8) $(C_6F_{13}(CH_2)_{10}\text{-}CS)^+$; 57 (100) $(C_4H_9)^+$.

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