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2,5-Bis[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfanyl]-1,3,4-thiadiazole

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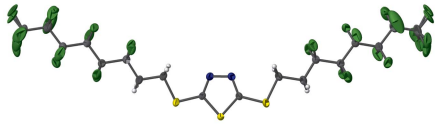
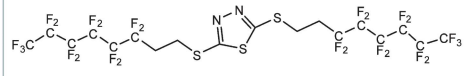
The title compound, $C_{18}H_8F_{26}N_2S_3$, was obtained by double *S*-perfluorohexylethylation of dipotassium 1,3,4-thiadiazole-2,5-dithiolate in methanol. The molecule exhibits twofold rotational symmetry, with the S atom lying on the rotation axis. The fluorocarbon chains adopt helical conformations and the F atoms of the two terminal C atoms are disordered over two sets of sites. No directional intermolecular interactions occur in the crystal.

3D view



Chemical scheme



Structure description

The widespread use of polyfluoroalkyl compounds (Buck *et al.*, 2012), *e.g.* as fire-fighting foams, raise questions about their impact on health. As a result of toxicological concerns, commercial production has shifted toward short-chain alternatives and new functional replacement substances (Buck, 2015). The oxidation chemistry of R_F-segmented sulfur compounds (Brace, 2000), in particular the biotransformation of surfactants in the environment, is of highest relevance. Thus, the degradation of a 6:2 (perfluorohexylethyl) telomer thioether, comparable to the title compound, to sulfonate by aerobic biological oxidation is noteworthy (Harding-Marjanovic *et al.*, 2015). A related tridecafluorooctylthiol-derived crystal structure has been reported (Hibbert *et al.*, 2001). The 1,3,4-thiadiazole system is widely employed as spacer in ligands for organometallic polymers (Wang *et al.*, 2008).

The asymmetric unit of the title compound contains one half-molecule which is completed by a twofold rotation axis through the S1 atom and the midpoint of the N1—N1^{i} bond (Fig. 1). The fluoroalkyl chains adopt a typical helical conformation (Fournier *et al.*, 2010). Positional disorder of the terminal F atoms of the fluoro tail was observed with occupancies of 0.55 and 0.45. The central 1,3,4-thiadiazole heterocycle matches in all respects the one in the known structure of 1,3,4-thiadiazole-2,5-bis(thioacetic acid)

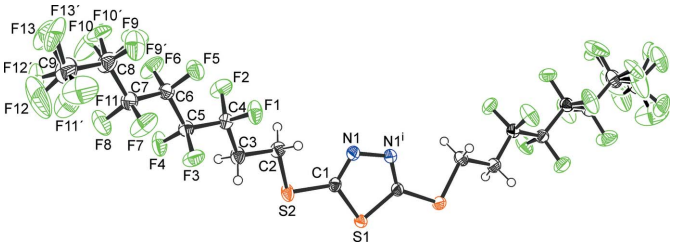


Figure 1
The molecular structure of the title compound, showing the atom labels and 50% probability displacement ellipsoids for non-H atoms. [Symmetry code: (i) $1-x, y, \frac{3}{2}-z$.]

(Mistry *et al.*, 2014). The molecular structure of the title compound is shown in Fig. 1. There are no significant directed intermolecular interactions. The packing of the molecules is displayed in Fig. 2.

Synthesis and crystallization

Dipotassium 1,3,4-thiadiazole-2,5-dithiolate (2.00 g, 8.83 mmol) and 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide (8.53 g, 18.00 mmol) were refluxed in MeOH (20 ml) for 24 h. After cooling to room temperature, precipitation of the product was completed by addition of H_2O (200 ml) and storage at 4° C for 2 h. The product was filtered off, washed with H_2O (60 ml) and vacuum-dried for 24 h to yield 6.30 g (85%) of a white powder, mp. 68° C. Single crystals were obtained by slow cooling of a hot solution in MeOH.

^{1}H NMR (300 MHz, MeOH-d_4): δ 3.58–3.48 (*m*, 4H), 2.75 (*tt*, J = 17.2, 7.6 Hz, 4H) ppm IR (neat): ν 2948, 1445, 1435, 1385, 1364, 1314, 1296, 1239, 1183, 1138, 1085, 1074, 1043, 957, 913, 898, 817, 770, 743, 727, 709, 691, 636, 566, 527, 408 cm^{-1}. FAB–MS: *m*/*z* 842.9482 (calculated 842.9507 for $C_{18}H_9F_{26}N_2S_3^+$ $[M+H]^+$).

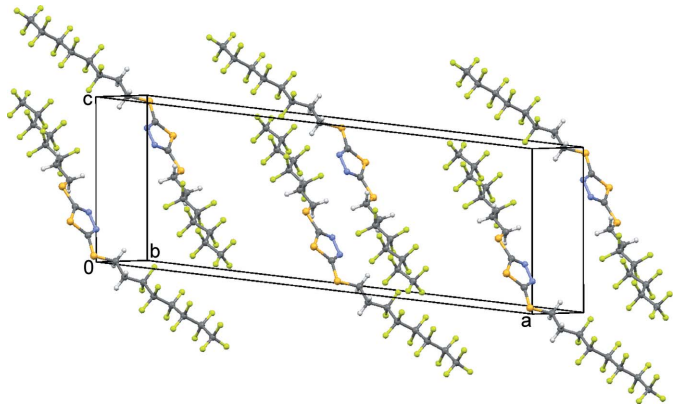


Figure 2
The unit cell of the title compound, viewed perpendicular to the *ac* plane.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_8F_{26}N_2S_3$
M_r	842.44
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	176
a, *b*, *c* (Å)	41.014 (11), 5.7338 (15), 11.880 (3)
β (°)	94.442 (8)
V (Å^3)	2785.4 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.46
Crystal size (mm)	0.16 × 0.12 × 0.05
Data collection	
Diffractometer	Bruker D8 QUEST PHOTON 100
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.844, 0.914
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26073, 2448, 2213
R_{int}	0.045
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.594
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.099, 1.10
No. of reflections	2448
No. of parameters	268
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.45, −0.25

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *XT* in *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

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full crystallographic data

IUCrData (2017). **2**, x170110 [https://doi.org/10.1107/S2414314617001109]

2,5-Bis[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfanyl]-1,3,4-thiadiazole

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2,5-Bis[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfanyl]-1,3,4-thiadiazole

Crystal data

$C_{18}H_8F_{26}N_2S_3$
M_r = 842.44
Monoclinic, $C2/c$
a = 41.014 (11) Å
b = 5.7338 (15) Å
c = 11.880 (3) Å
β = 94.442 (8)°
V = 2785.4 (13) Å^3
Z = 4
$F(000)$ = 1648
D_x = 2.009 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9946 reflections
θ = 3.0–25.3°
μ = 0.46 mm^{-1}
T = 176 K
Prism, colourless
0.16 × 0.12 × 0.05 mm

Data collection

Bruker D8 QUEST PHOTON 100 diffractometer
Radiation source: Incoatec Microfocus
Multi layered optics monochromator
Detector resolution: 10.4 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2012)
T_{min} = 0.844, T_{max} = 0.914
26073 measured reflections
2448 independent reflections
2213 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 25.0°, θ_{min} = 3.0°
h = −48→48
k = −6→6
l = −14→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.099
S = 1.10
2448 reflections
268 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 5.7325P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0025 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Positional disorder around ratio 1:1 of fluorine atoms at the end of the C8F13-unit (F9-F13:F9A-F13A).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.5000	1.00393 (13)	0.7500	0.0257 (2)	
S2	0.53603 (2)	0.85182 (11)	0.55112 (5)	0.0335 (2)	
N1	0.50855 (5)	0.5709 (3)	0.70144 (15)	0.0275 (4)	
C1	0.51458 (5)	0.7812 (4)	0.66790 (17)	0.0230 (5)	
C2	0.55301 (5)	0.5683 (4)	0.52066 (19)	0.0283 (5)	
H2A	0.5636	0.4978	0.5903	0.034*	
H2B	0.5356	0.4619	0.4894	0.034*	
C3	0.57815 (6)	0.6099 (4)	0.4343 (2)	0.0321 (5)	
H3A	0.5670	0.6765	0.3646	0.039*	
H3B	0.5945	0.7248	0.4650	0.039*	
C4	0.59534 (5)	0.3881 (4)	0.40543 (18)	0.0253 (5)	
C5	0.62393 (5)	0.4299 (4)	0.33031 (19)	0.0269 (5)	
C6	0.63965 (5)	0.2116 (4)	0.28023 (19)	0.0285 (5)	
C7	0.67203 (6)	0.2533 (4)	0.2252 (2)	0.0324 (5)	
C8	0.68717 (6)	0.0386 (5)	0.1714 (2)	0.0426 (7)	
C9	0.71765 (7)	0.0801 (7)	0.1079 (3)	0.0549 (8)	
F1	0.60748 (4)	0.2780 (3)	0.50030 (12)	0.0435 (4)	
F2	0.57418 (3)	0.2354 (3)	0.35119 (14)	0.0485 (4)	
F3	0.64731 (3)	0.5471 (3)	0.39435 (14)	0.0452 (4)	
F4	0.61347 (4)	0.5721 (3)	0.24509 (13)	0.0509 (5)	
F5	0.64402 (4)	0.0478 (3)	0.35936 (13)	0.0468 (4)	
F6	0.61772 (3)	0.1280 (3)	0.19835 (14)	0.0530 (5)	
F7	0.69446 (4)	0.3290 (3)	0.30676 (16)	0.0614 (5)	
F8	0.66726 (4)	0.4198 (3)	0.14744 (16)	0.0605 (5)	
F9	0.6973 (3)	−0.1100 (18)	0.2579 (8)	0.065 (3)	0.55
F10	0.6653 (2)	−0.0771 (12)	0.1052 (10)	0.0508 (16)	0.55
F11	0.7399 (4)	0.197 (3)	0.1638 (13)	0.100 (5)	0.55
F12	0.70735 (19)	0.1862 (16)	0.0105 (6)	0.0701 (19)	0.55
F13	0.7295 (3)	−0.140 (2)	0.0725 (10)	0.064 (2)	0.55
F9A	0.6907 (3)	−0.1311 (19)	0.2408 (11)	0.073 (4)	0.45
F10A	0.6647 (4)	−0.011 (2)	0.0816 (14)	0.118 (6)	0.45
F11A	0.7417 (5)	0.128 (4)	0.1932 (19)	0.103 (7)	0.45
F12A	0.7178 (3)	0.267 (2)	0.0470 (10)	0.123 (5)	0.45
F13A	0.7288 (4)	−0.072 (3)	0.0679 (16)	0.099 (5)	0.45

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0308 (4)	0.0205 (4)	0.0274 (4)	0.000	0.0116 (3)	0.000
S2	0.0405 (4)	0.0308 (3)	0.0316 (3)	0.0128 (3)	0.0189 (3)	0.0087 (2)
N1	0.0332 (10)	0.0249 (10)	0.0254 (9)	0.0026 (8)	0.0083 (8)	−0.0001 (8)
C1	0.0228 (10)	0.0251 (11)	0.0215 (11)	0.0042 (9)	0.0036 (8)	0.0003 (9)
C2	0.0244 (11)	0.0299 (12)	0.0313 (12)	0.0049 (9)	0.0065 (9)	−0.0025 (10)

C3	0.0338 (12)	0.0332 (13)	0.0308 (12)	0.0104 (10)	0.0112 (10)	0.0036 (10)
C4	0.0232 (11)	0.0289 (12)	0.0235 (11)	0.0013 (9)	0.0008 (9)	0.0005 (9)
C5	0.0263 (11)	0.0274 (12)	0.0273 (11)	0.0041 (9)	0.0037 (9)	0.0026 (10)
C6	0.0284 (12)	0.0280 (12)	0.0298 (12)	0.0004 (10)	0.0060 (9)	−0.0009 (10)
C7	0.0269 (12)	0.0351 (13)	0.0361 (13)	0.0011 (10)	0.0084 (10)	−0.0009 (11)
C8	0.0363 (14)	0.0461 (17)	0.0465 (16)	0.0037 (12)	0.0115 (12)	−0.0092 (14)
C9	0.0382 (17)	0.065 (2)	0.064 (2)	0.0098 (16)	0.0215 (15)	−0.0073 (19)
F1	0.0452 (8)	0.0535 (9)	0.0337 (8)	0.0231 (7)	0.0148 (6)	0.0159 (7)
F2	0.0269 (7)	0.0560 (10)	0.0642 (10)	−0.0092 (7)	0.0126 (7)	−0.0264 (8)
F3	0.0337 (8)	0.0439 (9)	0.0597 (10)	−0.0106 (7)	0.0146 (7)	−0.0245 (8)
F4	0.0621 (10)	0.0533 (10)	0.0404 (9)	0.0282 (8)	0.0241 (7)	0.0215 (8)
F5	0.0585 (10)	0.0325 (8)	0.0531 (9)	0.0164 (7)	0.0279 (8)	0.0139 (7)
F6	0.0294 (8)	0.0730 (12)	0.0569 (10)	−0.0064 (7)	0.0040 (7)	−0.0358 (9)
F7	0.0266 (8)	0.0831 (13)	0.0747 (12)	−0.0072 (8)	0.0049 (8)	−0.0444 (10)
F8	0.0641 (11)	0.0496 (10)	0.0729 (12)	0.0147 (9)	0.0373 (9)	0.0276 (9)
F9	0.067 (4)	0.079 (7)	0.051 (3)	0.046 (4)	0.016 (3)	0.027 (3)
F10	0.034 (3)	0.047 (2)	0.072 (5)	−0.0019 (16)	0.008 (3)	−0.036 (2)
F11	0.041 (5)	0.152 (13)	0.111 (6)	−0.041 (7)	0.037 (4)	−0.076 (9)
F12	0.062 (4)	0.106 (5)	0.047 (2)	0.013 (3)	0.031 (2)	0.016 (3)
F13	0.053 (3)	0.058 (6)	0.083 (4)	0.021 (3)	0.028 (3)	−0.031 (3)
F9A	0.081 (7)	0.023 (3)	0.123 (9)	0.004 (4)	0.064 (6)	−0.009 (4)
F10A	0.062 (5)	0.202 (14)	0.086 (8)	0.017 (8)	−0.012 (4)	−0.092 (10)
F11A	0.033 (4)	0.102 (8)	0.177 (16)	0.005 (5)	0.025 (7)	−0.046 (8)
F12A	0.092 (8)	0.124 (9)	0.166 (13)	0.042 (6)	0.098 (8)	0.070 (8)
F13A	0.102 (6)	0.068 (9)	0.138 (8)	0.033 (5)	0.078 (6)	−0.027 (6)

Geometric parameters (Å, º)

S1—C1^{i}	1.741 (2)	C6—F5	1.331 (3)
S1—C1	1.741 (2)	C6—F6	1.360 (3)
S2—C1	1.747 (2)	C6—C7	1.544 (3)
S2—C2	1.816 (2)	C7—F8	1.332 (3)
N1—C1	1.300 (3)	C7—F7	1.355 (3)
N1—N1^{i}	1.396 (4)	C7—C8	1.540 (4)
C2—C3	1.529 (3)	C8—F9A	1.277 (12)
C2—H2A	0.9900	C8—F10	1.325 (11)
C2—H2B	0.9900	C8—F9	1.374 (9)
C3—C4	1.506 (3)	C8—F10A	1.383 (16)
C3—H3A	0.9900	C8—C9	1.528 (4)
C3—H3B	0.9900	C9—F13A	1.108 (15)
C4—F1	1.353 (3)	C9—F11	1.275 (15)
C4—F2	1.360 (3)	C9—F12A	1.293 (12)
C4—C5	1.546 (3)	C9—F12	1.347 (10)
C5—F4	1.344 (3)	C9—F11A	1.38 (2)
C5—F3	1.355 (3)	C9—F13	1.429 (11)
C5—C6	1.548 (3)		
C1^{i}—S1—C1	85.62 (15)	F5—C6—C5	109.65 (18)

C1—S2—C2	100.09 (10)	F6—C6—C5	106.74 (18)
C1—N1—N1^{i}	111.92 (12)	C7—C6—C5	115.8 (2)
N1—C1—S1	115.27 (16)	F8—C7—F7	108.8 (2)
N1—C1—S2	125.32 (16)	F8—C7—C8	109.1 (2)
S1—C1—S2	119.41 (13)	F7—C7—C8	106.24 (19)
C3—C2—S2	106.43 (16)	F8—C7—C6	108.65 (19)
C3—C2—H2A	110.4	F7—C7—C6	107.77 (19)
S2—C2—H2A	110.4	C8—C7—C6	116.1 (2)
C3—C2—H2B	110.4	F10—C8—F9	106.6 (7)
S2—C2—H2B	110.4	F9A—C8—F10A	112.2 (9)
H2A—C2—H2B	108.6	F9A—C8—C9	112.5 (7)
C4—C3—C2	111.9 (2)	F10—C8—C9	109.2 (5)
C4—C3—H3A	109.2	F9—C8—C9	104.7 (6)
C2—C3—H3A	109.2	F10A—C8—C9	99.9 (7)
C4—C3—H3B	109.2	F9A—C8—C7	111.7 (6)
C2—C3—H3B	109.2	F10—C8—C7	111.7 (4)
H3A—C3—H3B	107.9	F9—C8—C7	107.1 (5)
F1—C4—F2	105.92 (19)	F10A—C8—C7	102.6 (6)
F1—C4—C3	110.69 (18)	C9—C8—C7	116.9 (3)
F2—C4—C3	111.02 (18)	F13A—C9—F12A	113.0 (12)
F1—C4—C5	107.84 (17)	F11—C9—F12	112.0 (10)
F2—C4—C5	108.12 (18)	F13A—C9—F11A	100.2 (12)
C3—C4—C5	112.95 (19)	F12A—C9—F11A	102.2 (11)
F4—C5—F3	107.01 (19)	F11—C9—F13	111.9 (8)
F4—C5—C4	108.44 (17)	F12—C9—F13	103.7 (6)
F3—C5—C4	106.73 (17)	F13A—C9—C8	118.0 (10)
F4—C5—C6	108.62 (18)	F11—C9—C8	113.8 (7)
F3—C5—C6	108.63 (17)	F12A—C9—C8	116.4 (5)
C4—C5—C6	116.98 (19)	F12—C9—C8	106.3 (4)
F5—C6—F6	107.6 (2)	F11A—C9—C8	103.5 (10)
F5—C6—C7	109.59 (19)	F13—C9—C8	108.5 (6)
F6—C6—C7	107.13 (19)		

Symmetry code: (i) $-x+1, y, -z+3/2$.