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Electronic Supporting Information (ESI)

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Cooperative intermolecular S—Cl···O and F···F associations in the crystal packing of α,ω-di(sulfonyl chloride) perfluoroalkanes, $ClSO_2(CF_2)_nSO_2Cl$, where n = 4, 6

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EXPERIMENTAL

Materials

The following reagents were purchased and used as received: 1,1,2,2,3,3,4,4-octafluoro-1,4-diiodobutane [I(CF_2)$_4$I)] and 1,1,2,2,3,3,4,4,5,5,6,6-decafluoro-1,6-diiodohexane [I(CF_2)$_6$I] – SynQuest, NaS_2O_4 and $NaHCO_3$ – Sigma-Aldrich, acetonitrile – Mallinckrodt Baker, chloroform – Alfa Aesar, and deuterochlorform ($CDCl_3$, NMR solvent) – Cambridge Isotope Laboratories, Inc.

Instrumentation

NMR spectroscopic data were collected on a multinuclear JOEL ECX-300 Spectrometer. The frequency for ^{19}F NMR spectroscopy is 282.78 MHz. Multiplicities are as follows: s (singlet), t (triplet). The internal standard of ^{19}F NMR spectroscopy is CF_3Cl (0.00 ppm). Single crystal X-ray data were collected using a Bruker D8 Venture and Rigaku AFC-8 instruments. The D8 Venture instrument was equipped with an Oxford Cryosystems low temperature device, enabling data collection at 100 K (for **C6**), while the Rigaku system afforded only room temperature data collection (for **C4**). Diffraction quality crystals were grown by dissolving the compounds in chloroform and allowing those solutions to evaporate slowly in a refrigerator at 4 °C. The structures were solved and refined by using full-matrix least-squares on F^2 method with Bruker SHELXTL-2014 Software Package.

Synthesis of $NaSO_2(CF_2)_4SO_2Na$

To a 500-mL, three-necked flask equipped with a magnetic stir bar, 100 mL acetonitrile, 150 mL DI water, 34.8 g (0.2 mol) $Na_2S_2O_4$ and 33.6 g (0.4 mol) $NaHCO_3$ were added and mixed. An amount of 45.4 g (0.1 mol) I(CF_2)$_4$I was added drop-wise to the above mixture at 40-45 °C with stirring. ^{19}F NMR spectra were taken on the reaction mixture to ensure the completion of the reaction.

<u>^{19}F NMR chemical shifts:</u>

$NaSO_2CF_2^aCF_2^bCF_2^bCF_2^aSO_2Na$: $\delta_a = -122.56$ ppm (s), $\delta_b = -130.05$ ppm (s).

*Synthesis of $ClSO_2(CF_2)_4SO_2Cl$ (**C4**)*

Enough water was added to the above reaction mixture to fully dissolve all the salts. A condenser cooled to -50 to -60 °C was placed on one of the three necks of the reaction flask. The reaction mixture was cooled to ice temperature, and chlorine gas was passed through the mixture with stirring. The bulk solution turned bright yellow, and a white solid precipitated. The chlorine gas was stopped when no more white solid was observed to be precipitating. The white solid was filtered out and dissolved in dichloromethane. The dichloromethane solution was washed with water two times, and the bottom layer was separated and dried over Na_2SO_4. The solvent was then evaporated, giving the white solid as the desired product. The yield was 79%.

<u>^{19}F NMR chemical shifts:</u>

$ClSO_2CF_2^aCF_2^bCF_2^bCF_2^aSO_2Cl$: $\delta_a = -104.21$ ppm (t, $^3J_{FF} = 16.8$ Hz), $\delta_b = -118.8$ ppm (t, $^3J_{FF} = 16.8$ Hz).

Synthesis of $NaSO_2(CF_2)_6SO_2Na$

To a 250-mL, three-necked flask, 20 mL acetonitrile, 40 mL DI water, 7.4 g (0.036 mol) $Na_2S_2O_4$, and 4.54 g (0.054 mol) NaHCO3 were added and mixed with stirring at 45 °C. An amount of 5.0 g (0.01 mol) $I(CF_2)_6I$ was dissolved in 15 mL of acetonitrile, and the solution was added to the above mixture drop-wise over 30 min. ^{19}F NMR spectra were taken on the reaction mixture to ensure the completion of the reaction.

^{19}F NMR chemical shifts:

$NaSO_2CF_2{}^aCF_2{}^bCF_2{}^cCF_2{}^cCF_2{}^bCF_2{}^aSO_2Na$: δ_a = -121.96 ppm (bm), δ_b = -122.29 ppm (m), δ_c = -130.09 ppm (m).

*Synthesis of $ClSO_2(CF_2)_6SO_2Cl$ (**C6**)*

Enough water was added to the above reaction mixture to fully dissolve all the salts. A condenser cooled to -50 to -60 °C was placed on one of the three necks. The reaction bulk was cooled to ice temperature, and chlorine gas was passed through the mixture with stirring. The bulk solution turned bright yellow, and a white solid was precipitated. The chlorine gas was stopped when no more white solid was observed to be precipitating. The white solid was filtered out and dissolved in dichloromethane. The dichloromethane solution was washed with water twice, and the bottom layer was separated and dried through Na_2SO_4. The solvent was then evaporated, giving the white solid as the desired product. The yield was 65%.

^{19}F NMR chemical shifts:

$ClSO_2CF_2{}^aCF_2{}^bCF_2{}^cCF_2{}^cCF_2{}^bCF_2{}^aSO_2Cl$: δ_a = -104.72 ppm (s), δ_b = -119.48 ppm (s), δ_c = -121.60 ppm (s).

*Crystal Structure Solution of **C4***

A single crystal of **C4** was mounted on a glass fiber using epoxy glue and centered in the X-ray beam of a Rigaku AFC8 diffractometer. Data were collected at room temperature using omega scans, with Mo Kα radiation from a glass sealed tube and a Mercury CCD detector. Data were processed, scaled and corrected for absorption effects using the CrystalClear software package.[4] Space group determination in $P2_1/c$ was made based on the systematic absences (XPREP), and the structure was solved by direct methods (SHELXS) and subsequently refined on F^2 using full matrix least squares techniques (SHELXL).[5] All atoms were refined anisotropically (we note that the resulting probability ellipsoids (Figure S1 below) are shown at 30% probability levels for aesthetic consistency with the 70% probability ellipsoids of **C6**, where a low temperature data collection was possible). The plate-like nature of the crystals lends itself to considerable twinning, making it difficult to obtain a sample with suitable diffracting strength that did not have some contributions from additional twin domains. Despite our best efforts, we suspect that the data quality was somewhat affected by the presence of twin domains that could not be reliably distinguished during data processing.

*Crystal Structure Solution of **C6***

A single crystal of **C6** was mounted on a low background cryogenic loop using paratone oil and immediately quenched to 100 K and centered in the X-ray beam. Data were collected at 100 K using phi and omega scans, with Mo Kα radiation from an Incoatec microfocus source and a Photon 100 CMOS detector. Instrument control, data processing, scaling, and absorption correction were performed through the Bruker Apex3 software package (SAINT and SADABS subroutines).[6] Space group determination in $P2_1/c$ was made based on the systematic absences (XPREP), and the structure was solved by intrinsic phasing (SHELXT) and subsequently refined on F^2 using full matrix least squares techniques (SHELXL).[5] All atoms were refined anisotropically.

Reaction Sequence 1

$$I(CF_2)_4I + 2\ Na_2S_2O_4 + 4\ NaHCO_3 \xrightarrow{H_2O/CH_3CN} NaO_2S(CF_2)_4SO_2Na + 2\ NaI + 2\ Na_2SO_3 + 4\ CO_2 + 2\ H_2O$$

Reaction Sequence 2

$$NaO_2S(CF_2)_4SO_2Na + 2\ Cl_2 \longrightarrow ClSO_2(CF_2)_4SO_2Cl + 2\ NaCl$$

$$NaI + 3\ Cl_2 + 3\ H_2O \longrightarrow NaIO_3 + 6\ HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2\ HCl$$

Scheme S1. Detailed reaction scheme of the preparation of $ClSO_2(CF_2)_4SO_2Cl$.

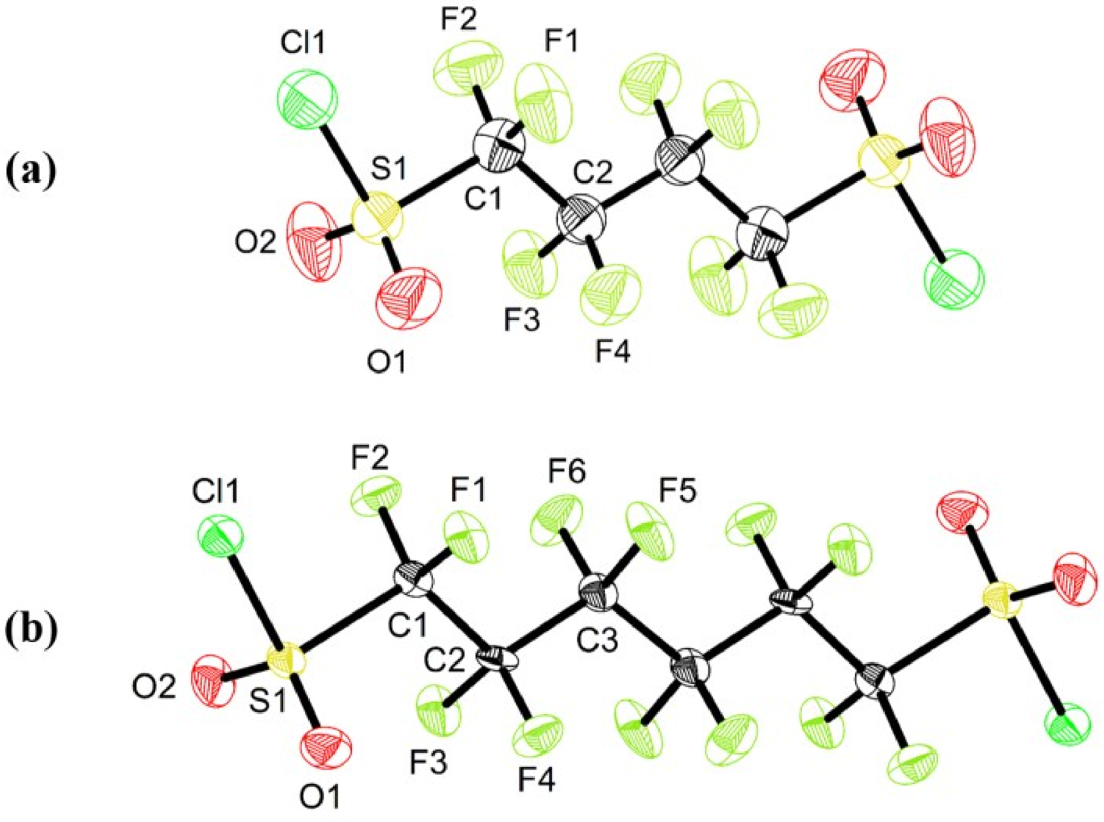

Figure S1. (a) Atomic structure of 1,1,2,2,3,3,4,4-octafluoro-1,4-butanedisulfonyl dichloride (**C4**) shown as 30% probability ellipsoids. (b) Atomic structure of 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-1,6-hexanedisulfonyl dichloride (**C6**) shown as 70% probability ellipsoids.

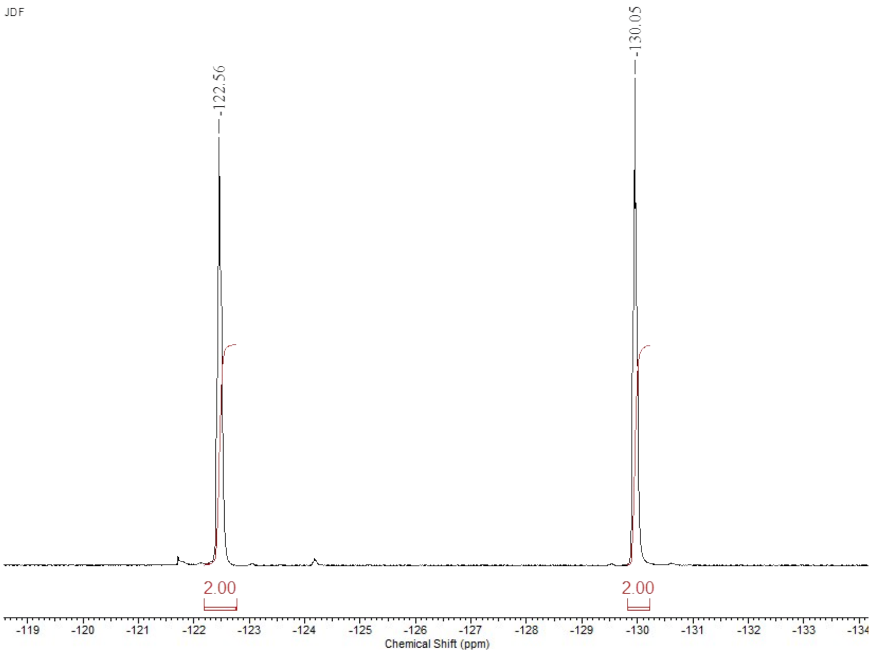

Figure S2. ^{19}F NMR spectrum of $NaSO_2(CF_2)_4SO_2Na$.

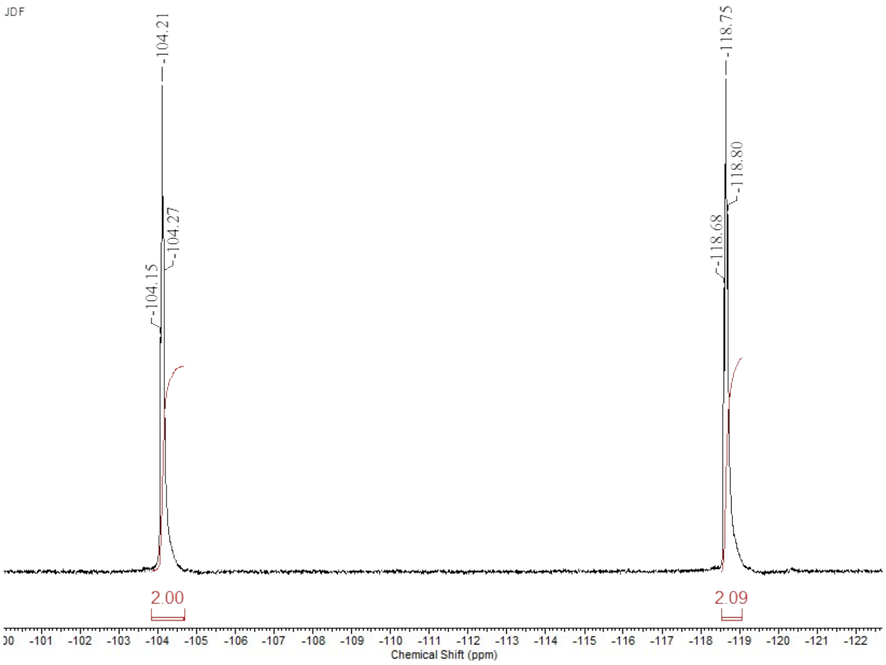

Figure S3. ^{19}F NMR spectrum of $ClSO_2(CF_2)_4SO_2Cl$ (**C4**).

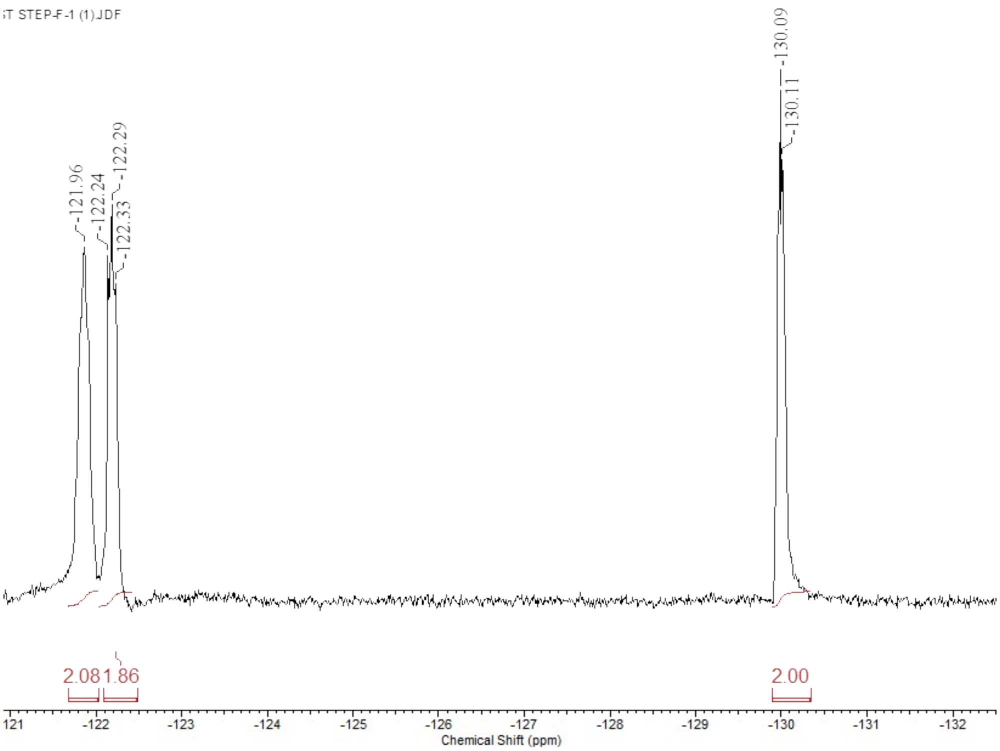

Figure S4. ^{19}F NMR of $NaSO_2(CF_2)_6SO_2Na$.

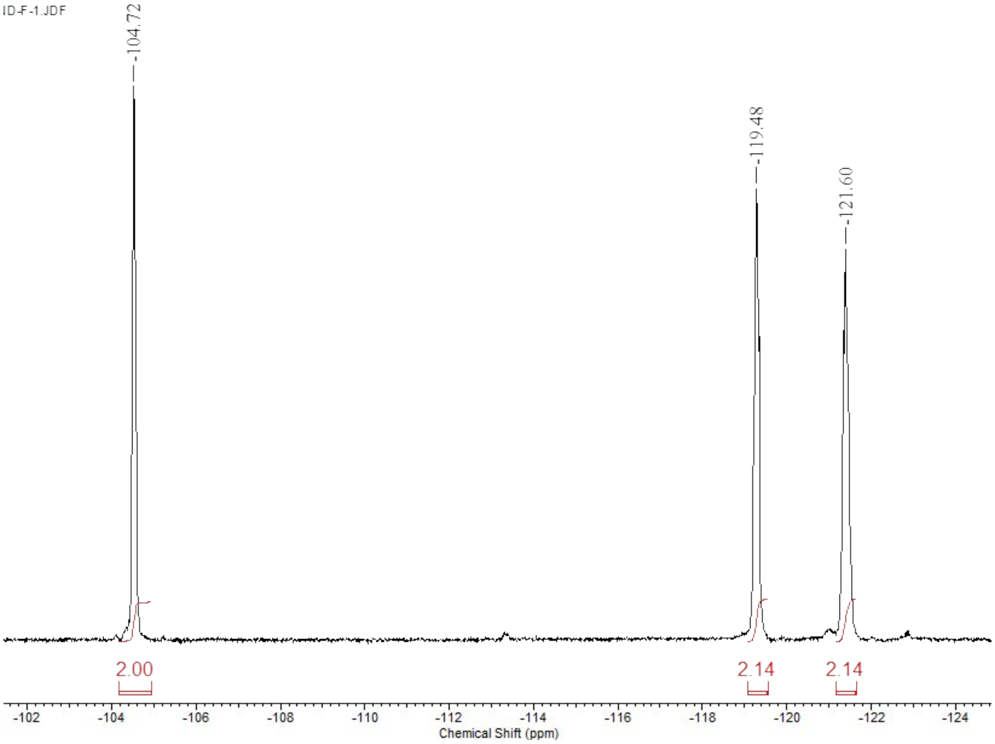

Figure S5. ^{19}F NMR spectrum of $ClSO_2(CF_2)_6SO_2Cl$ (**C6**).

Table S1. Crystallographic data of α,ω-di(sulfonyl chloride) perfluoroalkanes.

Compound	**C4**	**C6**
Empirical Formula	$C_4Cl_2F_8O_4S_2$	$C_6Cl_2F_{12}O_4S_2$
F. W. (g/mol)	399.06	499.08
Temperature (K)	299(2)	100(2)
Crystal System	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	5.4994(11)	5.3148(7)
b (Å)	19.724(4)	24.007(3)
c (Å)	6.2190(12)	5.8975(8)
β (°)	114.278(5)	111.669(3)
Volume (Å^3)	614.9(2)	699.29(16)
Z	2	2
D(calcd)(g/cm^3)	2.155	2.370
μ, mm^{-1}	0.978	0.926
F(000)	388	484
Crystal size (mm)	0.38 x 0.30 x 0.07	0.27 x 0.24 x 0.02
Reflns coll./ind./obs.	4905/1119/782	7587/1264/1159
No. of parameters	92	118
R indices (I>2σ(I))	R1 = 0.0892 wR2 = 0.1808	R1 = 0.0616 wR2 = 0.1578
Goodness of fit	1.175	1.141
Largest diff. peak/hole (e/Å^3)	0.442/-0.474	0.498/-0.637

Table S2. Selected Bond Lengths in **C4** and **C6**.

Crystal	Bond	Bond length Å
C4	C1-F1	1.316(8)
	C1-F2	1.319(1)
	S1=O1	1.415(7)
	S1=O2	1.404(1)
	S1-Cl1	1.991(3)
C6	C1-F1	1.336(7)
	C1-F2	1.319(1)
	C2-F3	1.331(7)
	C2-F4	1.336(9)
	C3-F5	1.352(7)
	C3-F6	1.332(1)
	S1=O1	1.417(7)
	S1=O2	1.419(5)
	S1-Cl1	2.000(2)

Table S3. Torsion angles in **C4**, **C6**, and n-perfluorohexane

Crystal	Atoms	Torsion, °
C4	C1-C2-C2-C1	180.0(6)
C6	C1-C2-C3-C3	-174.5(6)
	C2-C3-C3-C2	-180.0(6)
	C3-C3-C2-C1	174.4(6)
n-perfluorohexane	C1-C2-C3-C4	167.5(1)
	C2-C3-C4-C5	159.9(1)
	C3-C4-C5-C6	167.5(1)
$I(CF_2)_6I$	C1-C2-C3-C3	177.3(6)
	C2-C3-C3-C2	-180.0(5)
	C3-C3-C2-C1	-177.3(6)

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