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Cooperative intermolecular S—Cl⋯O and F⋯F associations in the crystal packing of α,ω -di(sulfonyl chloride) perfluoroalkanes, $\text{ClSO}_2(\text{CF}_2)_n\text{SO}_2\text{Cl}$, where $n = 4, 6$

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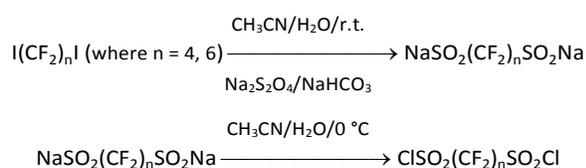
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Single-crystal, X-ray crystallographic studies of $\text{ClSO}_2(\text{CF}_2)_4\text{SO}_2\text{Cl}$ and $\text{ClSO}_2(\text{CF}_2)_6\text{SO}_2\text{Cl}$ reveal the first examples of S—Cl⋯O halogen bonding complemented by short F⋯F contacts between neighbouring chains that result in stabilized crystals. These compounds allow the study of intermolecular associations involving halogens where hydrogen bonding cannot be operative.

The title compounds have often been prepared via the deiodo-sulfination reaction of α,ω -diiodoperfluoroalkanes¹⁻⁴ as intermediates (see Scheme 1 below and ESI, Scheme S1) in the preparation of the corresponding di(sulfonyl fluorides) for use in applications such as energy conversion devices,⁵⁻¹³ resists,¹⁴ photo acid generators,¹⁵ N-F electrophilic fluorination reagents,¹⁶ room-temperature ionic liquids,¹⁷ etc. More recently Umemoto and Saito have reported an alternate preparation of the title compounds beginning with α,ω -dibromoperfluoroalkanes instead.¹⁸ Although α,ω -diiodoperfluoroalkanes have been co-crystallized with other molecules,^{18,19} their solid-state structures as individual molecules have not been reported. Furthermore, even though the title compounds have been well characterized spectroscopically (ESI, Figures S2-S5),^{2,3} they have not been characterized structurally.



Scheme 1 Simplified preparative sequence of the title compounds.

We were able to obtain diffraction quality crystals for the present study by dissolving the compounds in chloroform and allowing those solutions to evaporate slowly in a refrigerator

at 4 °C. Since α,ω -di(sulfonyl chloride) perfluoropropane is a liquid with a bp of 85–86 °C at 160 Torr,^{3,4} the corresponding perfluorobutane and –hexane must have sufficient intermolecular forces to be solids with melting points of 45–46 °C and 67–69 °C,³ respectively. Interestingly, we found that these forces were being driven by close-contact distances between the oxygen and chlorine atoms as well as fluorine atoms in neighbouring molecules. To our knowledge, the combination of S(O)⋯Cl and F⋯F intermolecular contacts within a single crystalline motif has not been studied, while the field of halogen bonding is becoming increasingly important²⁰⁻²⁴ and the number of examples of F⋯F intermolecular contacts is every increasing.²⁵⁻²⁷ Some of the closest examples that we could find to what will be reported herein are the examples of C—Br⋯O,²⁸ C=O⋯Br,²⁹ and H₂O⋯X₂ (where X = Cl, Br)³⁰ halogen bonding reported by Metrangolo, Resnati, and coworkers; Xiong, et al.; and Ripmeester and co-workers, respectively. More pertinent are the recent computational results on σ -hole bond tunability in the series YO₂X₂:NH₃ and YO₂X₂:H₂O (where X = F, Cl, Br and Y = S, Se) by Esrafilii and Mohammadian-Sabet.³¹ For example, they calculated a S—Cl⋯O contact distance of 2.91 Å between sulfonyl chloride and water.³¹

The structures of the α,ω -di(sulfonyl chloride) perfluoroalkanes, $\text{ClSO}_2(\text{CF}_2)_n\text{SO}_2\text{Cl}$ where $n = 4$ (**C4**) and 6 (**C6**), present an interesting canvas to study the forces involved in the long-range packing of molecules, since these compounds are solely reliant on halogen interactions. Colourless plate-like crystals were obtained, and their structures determined by single crystal X-ray diffraction (ESI). Details of the structure refinements are summarized in Table S1 (ESI). The two compounds presented here exhibit similar crystal structures, and both crystallize in the monoclinic space group $P2_1/c$ with similar packing arrangements. In both structures the asymmetric unit consists of half of the molecule, and the full molecule is generated by inversion symmetry (Fig. S1).

We observe segregation of the fluorine-rich and SO₂Cl-rich

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regions of the molecules in the packing structures of **C4** and **C6** (Fig. 1). This suggests a preference for the SO₂Cl groups to interact with one another, while the fluorinated chains cross-link by complementary F...F interactions (Table 1). In both structures, the sulfonyl chloride groups on the ends of the molecules interact with those of neighbouring molecules through Cl...O interactions (Fig. 1). In **C4** one interaction, Cl1...O2, exists at a distance of 3.227(7) Å. In **C6** two such intermolecular interactions occur, Cl1...O2 at 3.214(5) Å and Cl1...O1 at 3.236(5) Å. In **C4**, each sulfonyl chloride group connects to two neighbouring molecules, while in **C6** each sulfonyl chloride group connects to three neighbouring molecules through these interactions. This results in three-dimensional connectivity in both **C4** and **C6**, though the framework is perhaps reinforced in **C6** by the additional intermolecular contact. All of these intermolecular interactions are shorter than the sum of the van der Waals radii,³²⁻³⁴ suggesting that some attractive interactions occur between the sulfonyl chloride groups. It is interesting to note that, compared to the Cl1...O1 interaction of 3.236(5) Å in **C6**, the Cl1...O1 interaction in **C4** occurs at a longer distance of 3.412(7) Å, which is greater than the sum of the van der Waals radii. The S-Cl...O and S-O...Cl angles are such that the Cl1...O2 interactions are probably best viewed as quasi-Type I/II interactions.³⁵ However, the symmetrical angles involving the Cl1...O1 interaction in **C6** reflect a Type I interaction.³⁵

A search of the Cambridge Structural Database for the -CSO₂Cl...O motif results in ten hits, of which, six involve intermolecular Cl...O contacts between SO₂Cl groups occurring at distances shorter than the sum of the van der Waals radii (ranging from 2.990 Å to 3.231 Å). In these six structures, the SO₂Cl group is directly attached to cyclic or cyclic aromatic

Table 1 Intermolecular contacts in **C4** and **C6**.

	Interaction	Distance (Å)	Angle (°)	Type
C4	F1...F1	2.705(10)	C1-F1...F1 = 154.9(5)	Type I
	Cl1...O2	3.227(7)	S1-Cl1...O2 = 160.4(2) S1-O2...Cl1 = 136.3(5)	Quasi-Type I/II
C6	F3...F1	2.880(5)	C1-F1...F3 = 149.8(4) C2-F3...F1 = 144.9(4)	Type I
	F1...F5	2.745(6)	C1-F1...F5 = 152.7(4) C3-F5...F1 = 152.4(4)	Type I
	Cl1...O1	3.236(5)	S1-Cl1...O1 = 113.48(12) S1-O1...Cl1 = 121.5(3)	Type 1
	Cl1...O2	3.214(5)	S1-Cl1...O2 = 154.33(14) S1-O2...Cl1 = 130.4(3)	Quasi-Type I/II

systems, and none involve alkyl chains or perfluoroalkyl systems. Given the dearth of structural characterization of alkyl and perfluoroalkyl sulfonyl chlorides, comparisons of the Cl...O interactions in the title compounds must be made to such aromatic sulfonyl chlorides. The most pertinent comparison may be to the structure of 1,4-di(sulfonyl chloride)-2,3,5,6-tetrafluorobenzene, which has two SO₂Cl groups in a *para*-arrangement on a tetrafluorobenzene backbone.³⁶ This structure features Cl...O contacts of 3.174 Å between one SO₂Cl group of a central molecule with those of two neighbouring molecules. The structure also has numerous short contacts from Cl...F, O...F, F...F, and O...π interactions. In this structure, the fluorinated aromatic backbone is not especially segregated from the SO₂Cl end-caps of neighbouring molecules in the packing arrangement, enabling a larger variety of interactions. When other substituents such as NO₂,³⁷ Cl,³⁸ N₃,³⁹ or CH₃⁴⁰ are opposite the sulfonyl chloride on a normal benzene ring, the sulfonyl chloride groups of neighbouring molecules do not interact with one another. In 4-chlorobenzenesulfonyl chloride, the SO₂Cl end interacts with the pi system and has hydrogen bonding interactions with

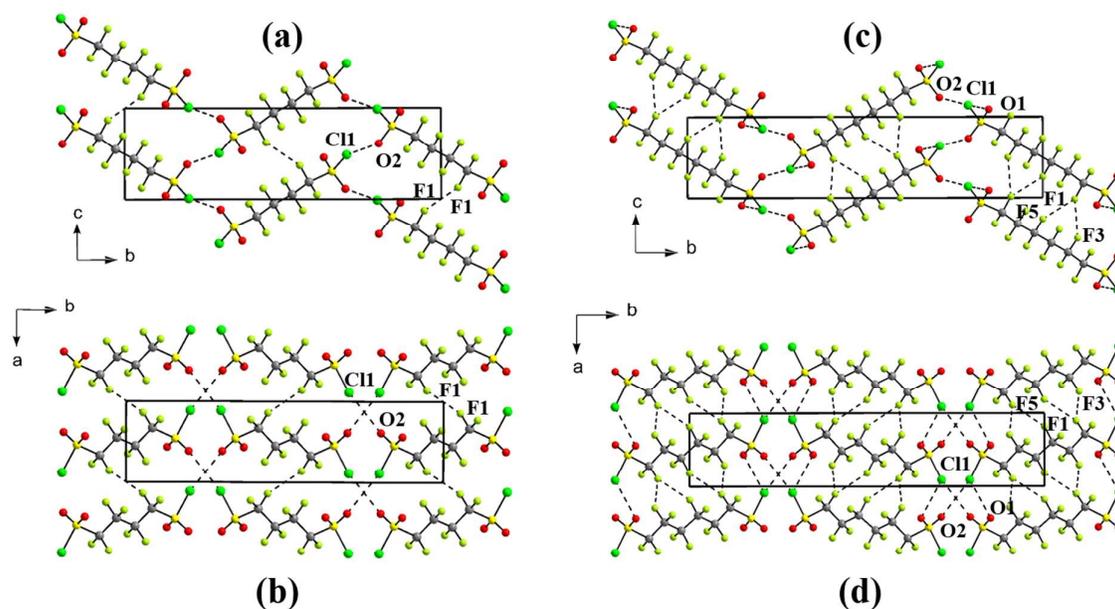


Fig. 1 Packing arrangements and short intermolecular contacts in the structures of **C4** and **C6**. (a) **C4** along [100], (b) **C4** along [001], (c) **C6** along [100], (d) **C6** along [001]. Note, the Cl...O interactions in (c) that appear to be intramolecular within the SO₂Cl group are instead intermolecular, occurring between the Cl and O atoms of neighbouring molecules along the a-axis (see (d)).

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neighbouring benzene rings. In 4-nitrobenzenesulfonyl chloride, the SO₂Cl end interacts with the NO₂ end of a neighbouring molecule, again with additional hydrogen bonding interactions to benzene. In 4-azidobenzenesulfonyl chloride, the SO₂Cl group has a Cl...N interaction with the end of the azide substituent on a neighbouring molecule. And, in 4-methylbenzenesulfonyl chloride, the chlorine atom interacts with the pi system of a neighbouring aromatic ring, while the oxygen atoms have weak hydrogen bonding arrangements with neighbouring rings. In the case of the highly decorated 2,4,6-tris(chlorosulfonyl)aniline structure,⁴¹ the SO₂Cl groups interact extensively with one another. In that structure, Cl...O interactions of 3.059–3.222 Å as well as N-H...O and O...π intermolecular contacts exist.

The molecules of **C4** and **C6** are further tethered through short intermolecular F...F contacts between the fluorocarbon chains. In **C4**, one such contact exists, F1...F1 at 2.705(10) Å, bridging the first and fourth CF₂ units (which are symmetry equivalent) of neighbouring molecules along [101]. The longer fluorocarbon chain of **C6** provides a greater region of fluorine-fluorine overlap, and neighbouring molecules of **C6** are crosslinked by a total of four short F...F contacts – two each of F1...F3 at 2.880(5) Å and F1...F5 at 2.745(6) Å. The F1...F5 contact is the equivalent contact between the first and fourth CF₂ groups of **C4**, and the F1...F3 contact may be viewed as the “extra” contact enabled by the longer **C6** chain. As a comparison, in the structure of n-perfluorohexane,⁴² one F...F contact of 2.919 Å exists between CF₂ groups of neighbouring chains, and a pair of CF₃...CF₂ contacts of 2.923 Å exist that form a dimer between one end of a molecule and its neighbour. Examining the C-F bond lengths in **C6** (ESI, Table S2), we observe that the C1-F1 (1.336(8) Å) and C3-F5 (1.352(8) Å) bonds are slightly elongated compared to the C1-F2 (1.319(8) Å) and C3-F6 (1.332(8) Å) bonds where the fluorine atoms are not involved in intermolecular F...F contacts. This may serve as additional indirect evidence of intermolecular attraction through the F1...F5 contact. The F...F contacts all appear to be Type I arrangements, having C-F...F angles of 154.9(5)° in **C4** and ranging from 144.9(4)° to 152.7(4)° in **C6**.^{25–27}

Perhaps another consequence of the Cl...O and F...F interactions in **C4** and **C6** is their influence on the conformation of the fluorocarbon chains. The fluorine atoms of the fluorocarbon chains in **C4** and **C6** are arranged in an eclipsed fashion along the zigzag chain, similar to the hydrogen atoms of comparable aliphatic hydrocarbon chains (Fig. 2). This differs from the structure of n-perfluorohexane where a helical rotation of the CF₂ groups exists as the fluorocarbon chain propagates (ESI, Table S3).^{18,43–45} Additionally, the structure of n-perfluorohexane only possesses two short

intermolecular F...F contacts (2.919–2.923 Å), which occur as single F...F contacts between a central F₃C(CF₂)₄CF₃ molecule and two different neighbouring molecules. The more extensive crosslinking in **C6** described above occurs at shorter F...F distances and is concentrated between two neighbouring molecules rather than three. The I(CF₂)₆I molecules in the extensive series of co-crystals involving that perfluoroalkyl chain exhibit a variety of eclipsed and rotated arrangements, which may also be influenced by the co-crystallized molecules in those structures.^{18,46–57}

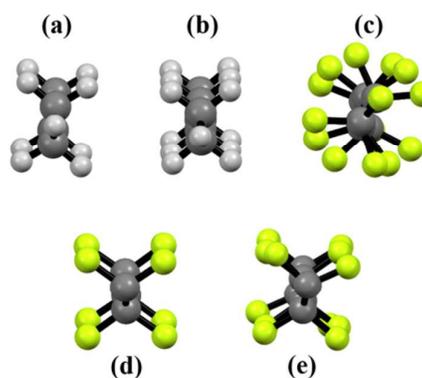


Fig. 2 Carbon chain propagation in (a) n-butane, (b) n-hexane, (c) n-perfluorohexane,⁴² (d) **C4** of the present study, and (e) **C6** of the present study.

The weak halogen interactions exhibited by these perfluorinated chains having sulfonyl chloride end-caps appear to have some significance in the formation of crystals, since the 4- and 6-membered α,ω -dihalo-perfluoroalkanes are always co-crystallized with other molecules. In the case of the title compounds, the three-dimensional intermolecular interactions of the SO₂Cl end-caps provide sufficient stabilization for crystallization, even as weak interactions. Thus, the use of sulfonyl chloride end-caps may be a useful approach for stabilizing molecules or structural fragments that would otherwise require additional co-crystallizing molecules in the lattice for stability. The packing diagrams of these molecules show that the molecules will align in a way that segregates fluorine rich regions and SO₂Cl-rich regions. This suggests that Cl...O interactions are meaningful long-range intermolecular contacts that occur readily between neighbouring sulfonyl chloride groups. Future work in preparing crystals and elucidating the structures of related compounds, particularly BrSO₂(CF₂)_nSO₂Br derivatives, which should give rise to even stronger halogen bonding interactions,³¹ additional ClSO₂(CF₂)_nSO₂Cl derivatives, where n = 2, 3, or an integer greater than 6; as well as

CISO₂(CF₂)_nO(CF₂)_nSO₂Cl with an oxygen atom spacer in the perfluoroalkyl chain, may provide additional insights into the role of such intermolecular forces influencing other structural features, such as alignment or helical rotation in perfluorinated alkyl chains.

Conflicts of interest

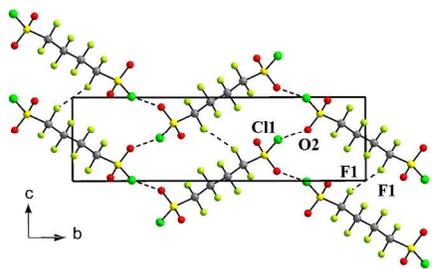
There are no conflicts to declare.

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Halogen bonding between neighboring sulfonyl chloride groups and short fluorine-fluorine contacts support crystal formation in the title compounds.