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Unexpectedly low affinity of aromatic disulfides for π-stacking interactions of the arene–polyfluoroarene type

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Abstract

1,2,3,4,5-Pentafluorodiphenyl disulfide (**1**) was synthesized from C_6F_5SCl and $C_6H_5SSiMe_3$ in quantitative yield. The homo-crystals of disulfide **1** and co-crystals of 1,1′,2,2′,3,3′,4,4′,5,5′-decafluorodiphenyl disulfide (**2**) with naphthalene (stoichiometry 1:2, complex **4**) and diphenyl disulfide (**3**) with octafluoronaphthalene (stoichiometry 2:1, complex **5**) were prepared followed by XRD characterization. In the crystal lattice of **1**, face-to-face and face-to-edge Ph_H/Ph_F orientations of neighboring rings were observed together with face-to-edge Ph_F/Ph_F orientations. For the face-to-face Ph_H/Ph_F orientation, the large offset of Ph_H and Ph_F groups excludes their π-stacking interaction which is very non-typical of the field. The crystal lattice of **4** reveals standard π-stacking interactions of the arene–polyfluoroarene type. While in the lattice of **4** each Ph_F ring interacts alternating with naphthalenes, in **5** two disulfides **3** are bridged by one octafluoronaphthalene with only one of the Ph_H rings of each disulfide interacting with the polyfluoroarene π-system. The large offset of neighboring molecules excludes however their π-stacking interactions in complex **5**. An attempt to prepare **2**/**3** co-crystals failed.

Keywords: Stacking interactions; Supramolecular synthons; Self-assembled monolayers; Crystal engineering; X-ray structures

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1. Introduction

Non-bonding interactions are effective tools for controlling molecular conformations and packing structures in a crystal [1]. Especially, π-stacking interactions between hydrocarbon and fluorocarbon aromatic groups are recognized to be one of the most general supramolecular synthons (for recent publications, see [2–10] and references therein) important for both fundamental and applied chemistry. In particular, these Ar_H/Ar_F interactions are successfully used in the design and synthesis of various advanced functional materials (see representative references given in [2,10b]).

A large variety of geometrically both matched and mismatched molecular complexes was prepared from aromatic and polyfluoroaromatic compounds including variously functionalized derivatives ([2,4,6,7,10] and references therein). In particular, much attention has been paid to co-crystals of octafluoronaphthalene and C_6H_5–X–C_6H_5 compounds (X = – [4], –CH=CH– [2], –N=N– [2], –C≡C– [6,7]) along with homo-crystals of C_6F_5–X–C_6H_5 derivatives (X = – [9], –CH=CH– [8], –CH=N– [3], –C≡C– [5,8]). According to our knowledge related complexes and individual compounds with X = –S–S– have never been investigated in this context.

Compounds of the C_6F_5–S–S–C_6H_5 type can be precursors in the preparation of self-assembled monolayers (SAMs) of aromatic thiolates on gold surfaces [11]. The aromatic and aliphatic thiolate SAMs are promising components for nanoscience and nanotechnology [11]. Although these SAMs exhibit a high degree of structural order (i.e. true 2D translational order), some properties are not well-controlled. Various defects (for example, conformational arrangements) disturb their ideally single-crystalline packing and affect their properties [11]. In particular, aromatic thiolates with short backbones do not form well-oriented SAMs and it is necessary

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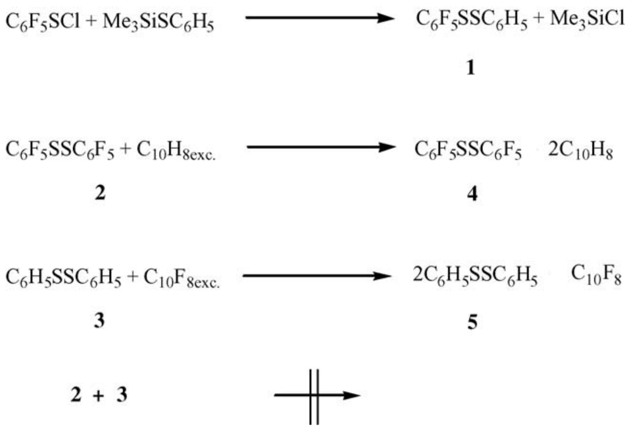
to use at least terphenyl derivatives in preparing practically interesting thioaromatic SAMs with high degree of molecular orientation [12].

The aim of this work is a preliminary estimation of the prospects of π-stacking interactions of the Ar_H/Ar_F type in controlling the structural order of aromatic disulfides since a similar ordering might be adopted by thiolate SAMs. For this purpose $C_6H_5SSC_6H_5/C_{10}F_8$ and $C_6F_5SSC_6F_5/C_{10}H_8$ co-crystals and $C_6F_5SSC_6H_5$ homo-crystals were prepared followed by XRD characterization. An attempt to prepare $C_6H_5SSC_6H_5/C_6F_5SSC_6F_5$ co-crystals failed.

2. Results and discussion

2.1. Preparations

In this work, 1,2,3,4,5-pentafluorodiphenyl disulfide (**1**) [13] was synthesized from C_6F_5SCl and $C_6H_5SSiMe_3$ in quantitative yield, similar to the reported preparation of non-symmetric disulfides from ArSCl and $Ar'SSnBu_3$ [14]. Previously, **1** was obtained by heating of a 1:1 mixture of the symmetric disulfides $C_6F_5SSC_6F_5$ (**2**) and $C_6H_5SSC_6H_5$ (**3**) [15]:



$$\underset{}{C_6F_5SCl + Me_3SiSC_6H_5} \longrightarrow \underset{\mathbf{1}}{C_6F_5SSC_6H_5} + Me_3SiCl$$

$$\underset{\mathbf{2}}{C_6F_5SSC_6F_5} + C_{10}H_{8exc.} \longrightarrow \underset{\mathbf{4}}{C_6F_5SSC_6F_5 \quad 2C_{10}H_8}$$

$$\underset{\mathbf{3}}{C_6H_5SSC_6H_5} + C_{10}F_{8exc.} \longrightarrow \underset{\mathbf{5}}{2C_6H_5SSC_6H_5 \quad C_{10}F_8}$$

$$\mathbf{2} + \mathbf{3} \nrightarrow$$

Low-temperature crystallization of **1** (mp 22 °C) from hexane gave crystals which were not suitable for XRD. High-quality single crystals of **1** were prepared by crystallization from its melt.

An attempt to prepare co-crystals of disulfides **2** and **3** by low-temperature crystallization of their 1:1 mixture from hexane failed, only individual **2** and **3** were identified in the solid phase. On the other hand, co-crystals of **2** with naphthalene (molar ratio 1:2, complex **4**) and **3** with octafluoronaphthalene (molar ratio 2:1, complex **5**) were obtained by

Table 1
Crystal data and structure refinement for **1**, **4** and **5**

	Compound		
	1	**4**	**5**
Empirical formula	$C_{12}H_5F_5S_2$	$C_{32}H_{16}F_{10}S_2$	$C_{34}H_{20}F_8S_4$
Formula weight	308.28	654.57	708.74
Temperature (K)	173 (2)	243 (2)	173 (2)
Wavelength (pm)	71.073	71.073	71.073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pna*2$_1$	*P*2$_1$/*c*	*P*2$_1$/*c*
Unit cell dimensions			
a (pm)	1097.0 (2)	724.00 (7)	1669.7 (5)
b (pm)	1278.20 (10)	2997.8 (3)	587.20 (10)
c (pm)	860.80 (10)	1328.95 (12)	1568.2 (3)
β (°)	90	104.164 (7)	95.93 (2)
Volume (nm^3)	1.2070 (3)	2.7967 (4)	1.5293 (6)
Z	4	4	2
Density (calculated) (Mg m^{-3})	1.696	1.555	1.539
Absorption coefficient (mm^{-1})	0.485	0.280	0.385
F(0 0 0)	616	1320	720
Crystal size (mm^3)	0.8 × 0.4 × 0.4	1.0 × 0.3 × 0.2	0.80 × 0.60 × 0.30
θ range for data collection (°)	2.85–27.50	2.08–25.00	2.61–27.50
Index range	$-14 \leq h \leq 14, -16 \leq k \leq 16, -11 \leq l \leq 1$	$-8 \leq h \leq 8, -35 \leq k \leq 0, -15 \leq l \leq 15$	$-21 \leq h \leq 21, -7 \leq k \leq 1, -20 \leq l \leq 1$
Reflections collected	6368	6826	4706
Independent reflections	1709 [*R*(int) = 0.0400]	4897 [*R*(int) = 0.0466]	3518 [*R*(int) = 0.0428]
Completeness to θ° (%)	99.8	99.4	99.8
Absorption correction	None	Integration	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1709/1/174	4897/0/397	3518/0/247
Goodness-of-fit on F^2	1.066	1.046	1.032
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0248, w*R*2 = 0.0673	*R*1 = 0.0563, w*R*2 = 0.1520	*R*1 = 0.0483, w*R*2 = 0.1243
R indices (all data)	*R*1 = 0.0266, w*R*2 = 0.0687	*R*1 = 0.0866, w*R*2 = 0.1747	*R*1 = 0.0574, w*R*2 = 0.1327
Extinction coefficient	0.0071 (19)	0.0000	0.0153 (19)
Largest diff. peak and hole (e Å^3)	0.209 and −0.244	0.360 and −0.310	0.614 and −0.589

Table 2
Selected bond lengths (pm), bond and torsion angles (°) for disulfides **1**–**3** and for the disulfides **2** and **3** in the complexes **4** and **5** (for atom numbering, see Figs. 1, 3, 4)

	S1S2	S1C1	S2C7	S1S2C7	S2S1C1	C1S1S2C7	S1S2C7C8	S2S1C1C6
1	204.4 (1)	176.7 (2)	178.9 (2)	106.20 (9)	102.32 (8)	81.45 (1)	27.2 (2)	72.8 (2)
2	205.9 (4)	177.0 (7)	–	–	101.3 (3)	73.62 (1)	73.21 (2)	76.37 (2)
2 in **4**	206.6 (1)	176.4 (3)						
		177.5 (4)	–	103.9 (1)	104.7 (1)	−107.15 (17)	−100.1 (3)	−91.3 (3)
3	203.0 (5)	–	180.0 (11)	104.95 (5)	106.19 (4)	84.18 (5)	163.12 (8)	179.4 (8)
3 in **5**	203.4 (1)	–	178.1 (2)	104.76 (7)	105.22 (7)	−85.38 (9)	−174.4 (2)	−170.7 (1)

this technique. The stoichiometry of complex **5** is rather remarkable since the molar ratio of the starting materials used in the preparation was 2:1 in favor of $C_{10}F_8$.

In contrast to **2** and **3**, the corresponding diselenides do not produce complexes with $C_{10}H_8$ and $C_{10}F_8$, respectively, under conditions of crystallization from hexane. It should also be noted that **3** and $C_6H_5SeSeC_6H_5$ do not produce complexes with C_6F_6 under conditions of crystallization from the latter.

2.2. Structural investigations

In Table 1 details of the crystal structure determinations and structure refinements of compound **1** and the complexes **4** and **5** are given. Table 2 shows selected bond lengths, bond and torsion angles for **1** (for atom numbering, see Fig. 1), for the disulfides **2** and **3** in complexes **4** and **5** together with the relevant data for individual **2** and **3**.

2.2.1. Solid state interactions

The main purpose of the present paper is the investigation of non-bonding interactions between arene and perfluoroarene groups in the solid state, with special emphasis on the π-stacking interactions. **1** crystallizes in the polar space group $Pna2_1$ with one molecule in the asymmetric unit. In the homocrystals of **1** (Fig. 2) face-to-face and face-to-edge Ph_H/Ph_F orientations were observed together with face-to-edge Ph_F/Ph_F orientations. For the face-to-face Ph_H/Ph_F orientation, the interplanar separation (C5···C10 contact, Fig. 2) is only 339.8 pm. However the large offset of Ph_H and Ph_F groups excludes their π-stacking interactions. This is very non-typical of the field since, based on many examples, it is accepted that arene and polyfluoroarene moieties are always involved in π-stacking interactions when present in the same crystal lattice ([2–10] and references therein). Several factors might contribute to this unusual packing. The intermolecular F···F contact of 279.5 pm, which is in the range of the sum of the van der Waals radii, might prevent the π-stacking in **1**, the observed edge-to-face contact F5···C2 (300.2 pm), and the weak H···F contacts in the range 260–300 pm (indicated in Fig. 2) might stabilize the packing of **1**.

4 crystallizes in the space group $P2_1/c$ with one molecule of **2** and two molecules of $C_{10}H_8$ in the asymmetric unit. These molecules are combined to π-stacks along the *a* axis and each Ph_F ring interacts alternating with two naphthalene molecules

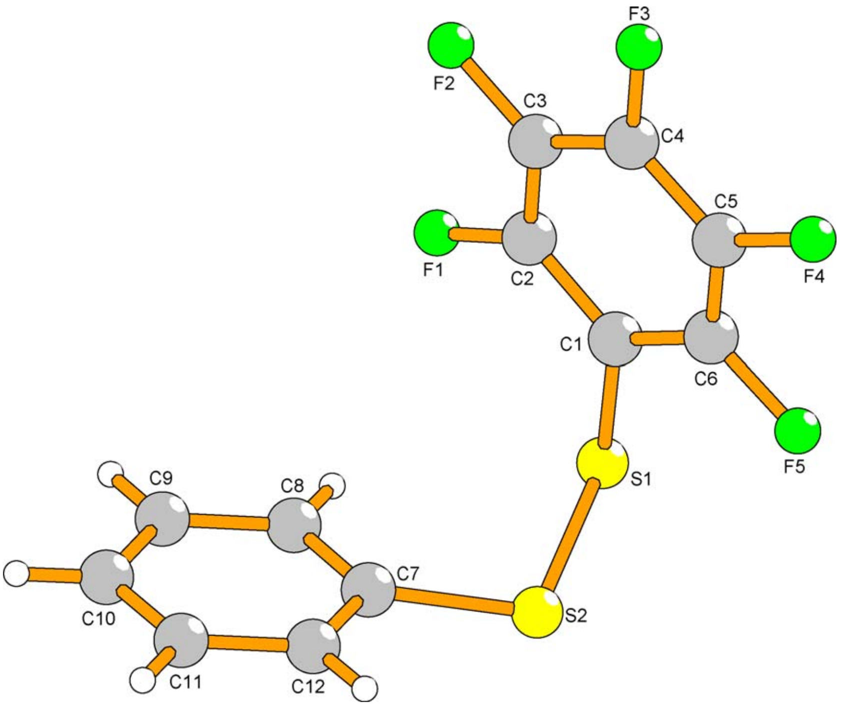


Fig. 1. The molecular structure of disulfide 1. For selected bond lengths, bond and torsion angles of **1**, see Table 2.

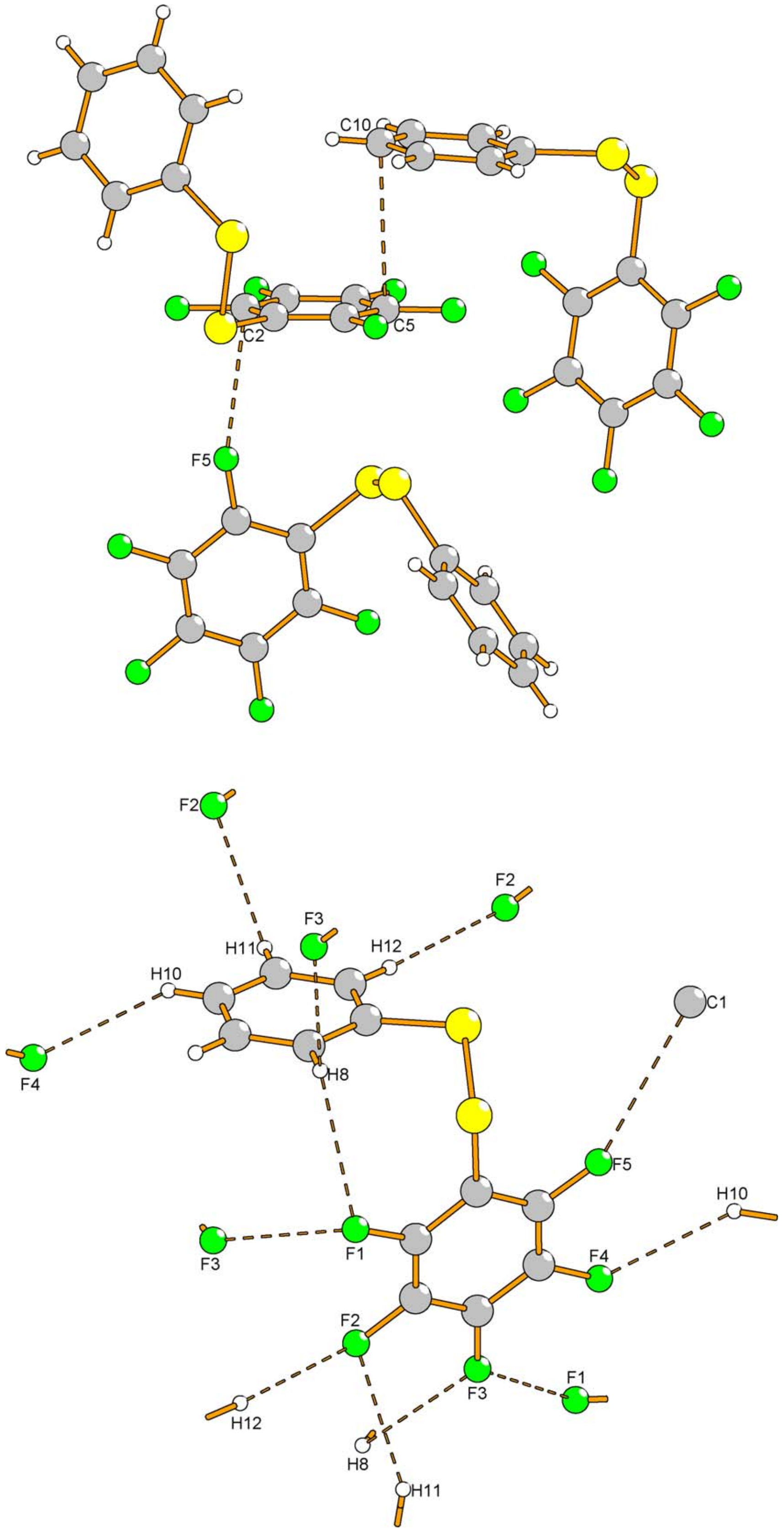


Fig. 2. Orientations of neighboring molecules (above), and H···F and F···F interactions (below) in disulfide **1**.

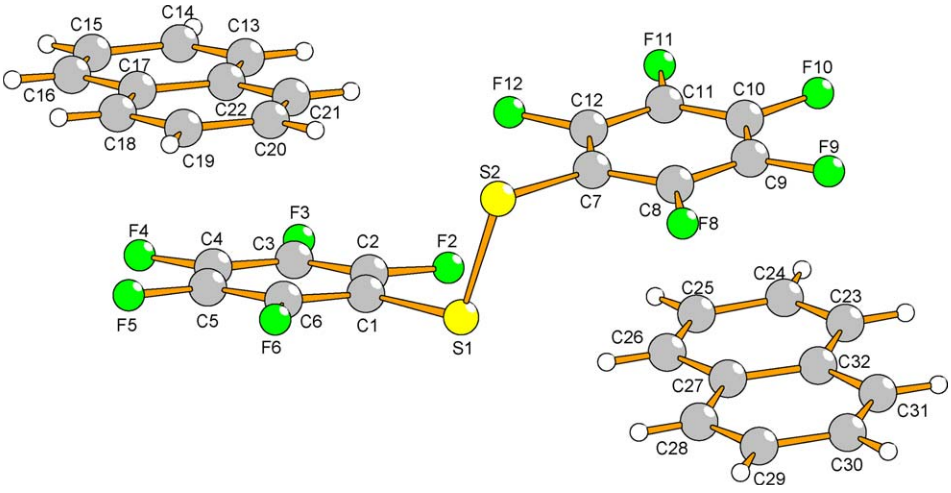


Fig. 3. The structure of complex **4**. For selected bond lengths, bond and torsion angles of the disulfide **2**, see Table 2.

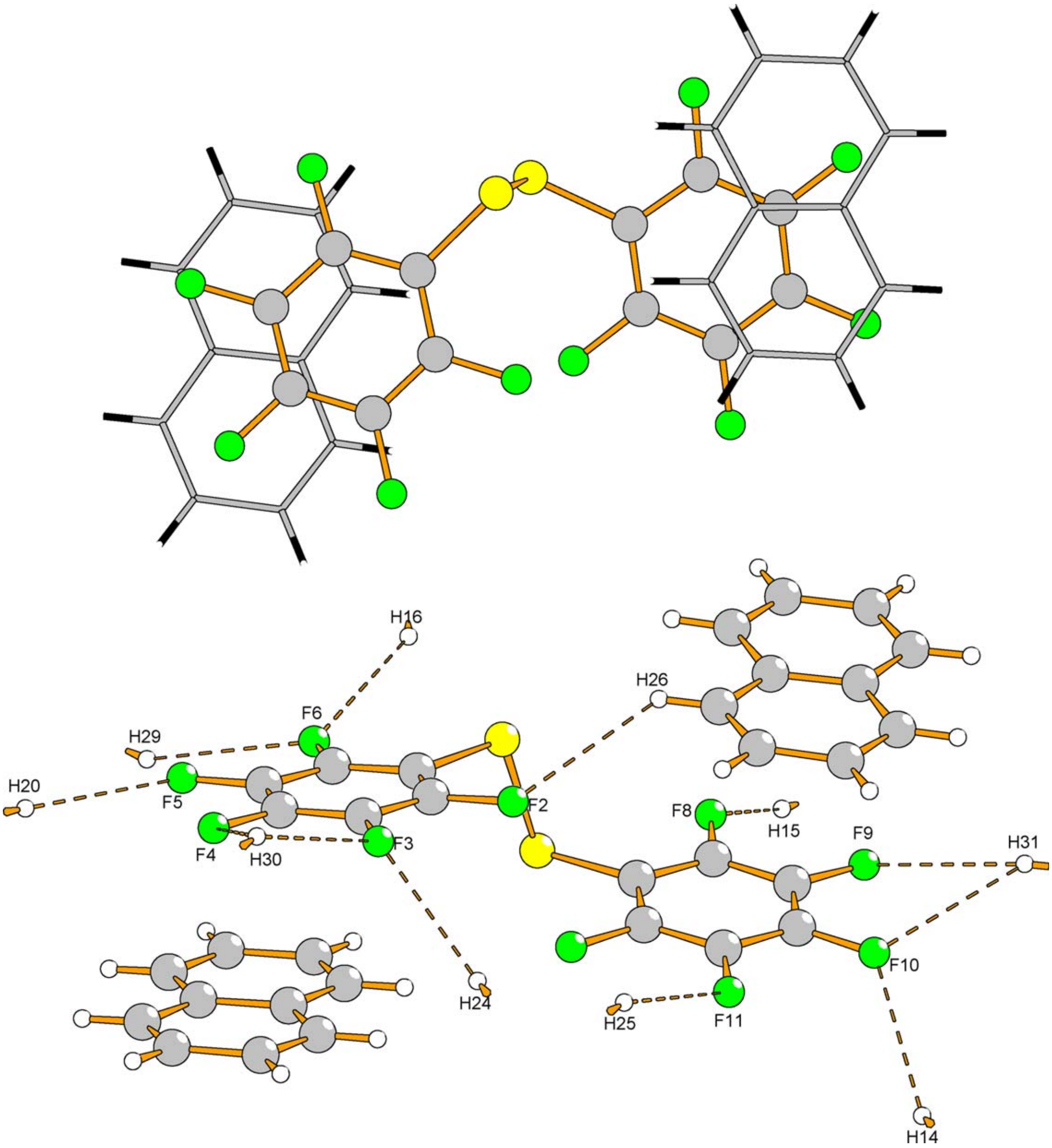


Fig. 4. $Ar_F\cdots Ar$ overlap (above) and $H\cdots F$ and $F\cdots F$ contacts (below) in complex **4**.

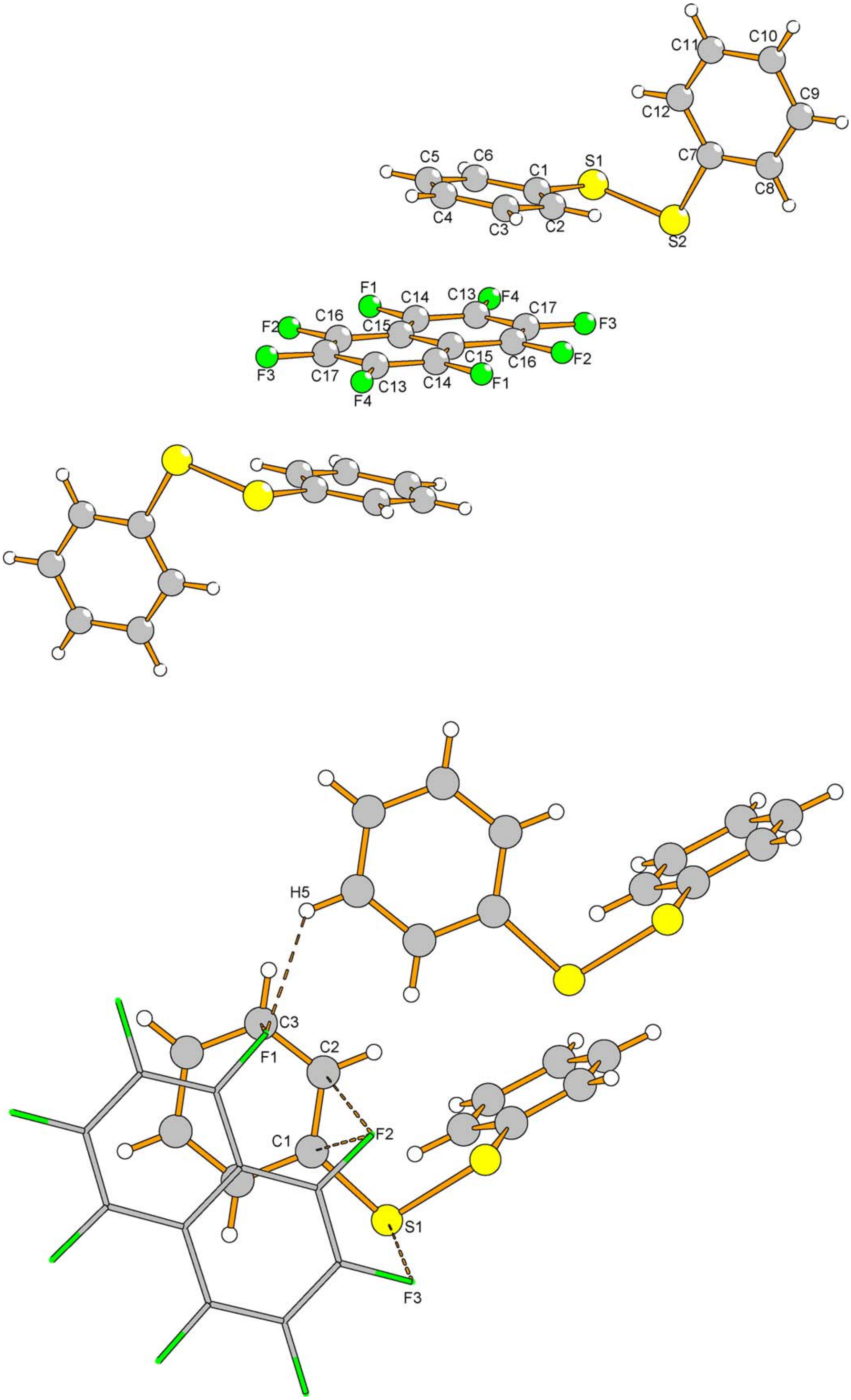


Fig. 5. The structure of (above), and C–H· · ·π, C· · ·F, and S· · ·F interactions in (below), complex **5**. For selected bond lengths, bond and torsion angles of the disulfide **3**, see Table 2.

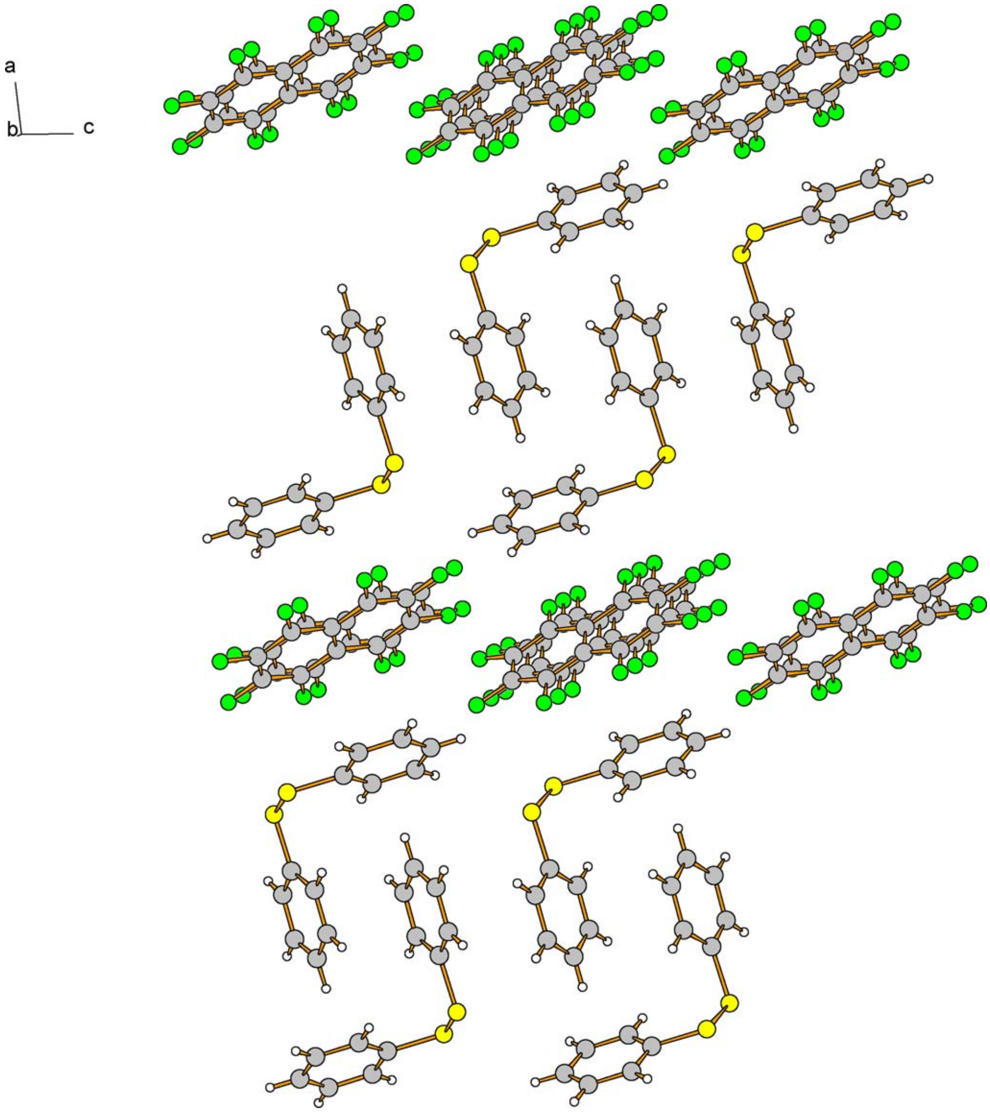


Fig. 6. View of the crystal packing of complex **5**.

(Fig. 3). The interplanar separation of 341–349 pm within the stacks is typical for arene–polyfluoroarene π-stacking interactions ([2–10] and references therein). The corresponding distances between the centers of the rings lie in the range of 362–393 pm revealing some offset of the interacting rings (Fig. 4), which is normal. H···F contacts between $C_{10}H_8$ and **2** within a **4** unit, which would be expected from Fig. 4, are much weaker (360 pm) than the interactions between different units. The H···F distances indicated in Fig. 4 are in the range of 260–300 pm.

5 crystallizes in the space group $P2_1/c$ with one molecule of **3** and 0.5 molecules of $C_{10}F_8$ in the asymmetric unit. In contrast to **4**, in complex **5** two disulfides **3** are linked by only one octafluoronaphthalene, and only one Ph_H group of **3** is involved in non-bonding interactions with $C_{10}F_8$, the second (not interacting) Ph_H group is disordered (Figs. 5 and 6). Fig. 5 shows the large offset between the planes of the interacting Ph_H groups of **3** and the $C_{10}F_8$ plane. Responsible for this offset might be weak H1···F5 (248.5 pm), F(Ar_F)···C(Ar) (350–365 pm), S1···F3 (338 pm) and C–H···π (Ar_F) interactions. The shortest F···F contacts between fluorines of $C_{10}F_8$ range from 287 to 296 pm. Many factors contribute to the reasons for complex **5** being another unexpected example of negligible π-stacking interactions between Ar_H and Ar_F groups.

2.2.2. Structural changes in aromatic disulfides on fluorination and complexation

The data in Table 2 for the mixed disulfide **1**, the fluorocarbon disulfide **2** [16] and the hydrocarbon disulfide **3** [17] in their homo-crystals show that **1** is combined from fragments of **2** and **3**. The SS distance in **1** (204.4 (1) pm) is intermediate between that of **2** (205.9 (4) pm) and **3** (203.0 (5) pm). The CS bonds in **2** are shorter than in **3**, a similar difference is found in **1** for S1C1 and S2C7. The angles at the sulfur centers in **2** (101.3°) are smaller than in **3** (106.2°), similar differences are found for the corresponding fragments in **1** (102.3° and 106.2°, respectively). The torsion angle C–S–S–C in **3** is equal to 84.2°, in **2** equal to 73.6°, in the mixed species **1** 81.45° is determined. According to a simple bonding model this torsion angle is a result of the interaction of the 3p lone pairs at the two sulfur centers which try to become orthogonal. For the H–S–S–H molecule an angle of 90.5° was calculated in this work at the MP2/6-31G* level of theory.

The most remarkable difference between the non-fluorinated and the fluorinated species is observed for the torsion angles C–C–S–S. They enlarge from 10.5° (average) in **3** to 74.8° in **2**, with the aryl groups almost parallel to the SS bond to almost perpendicular. Compared to **3**, in **1** the Ph_H group deviates more from the SS plane (27.2°) whilst the angle to the Ph_F group slightly decreases in comparison with **2**.

In complex **5** the interaction of **3** with $C_{10}F_8$ has almost no influence on bond distances and bond and torsion angles.

In complex **4** the C–C–S–S torsion angles increase to almost perpendicular (88.4°), and for the C–S–S–C torsion angle a dramatic increase from 73.6° to 107.15° **4** is determined in going from homo-crystals **2** to co-crystals **4**, seemingly due to π-stacking interactions between **2** and $C_{10}H_8$.

3. Conclusions

Unexpectedly, aromatic disulfides revealed rather low affinity for π-stacking interactions of the arene–polyfluoroarene type. However, it follows from this work that the disulfides can be involved in these interactions under certain circumstances. As a result, Ar_H/Ar_F π-stacking interactions might have some prospects in improving structural order of thiolate SAMs. The design and synthesis of (fluoro) aromatic disulfides with enlarged propensity to the discussed interactions, in particular based on the approach used in this work for preparing **1**, might be a direction for further research.

4. Experimental

The ^1H and ^{19}F NMR spectra were measured with a Bruker AV-300 spectrometer at frequencies of 300.13 and 282.37 MHz, respectively, for solutions in $CDCl_3$, with TMS and C_6F_6 as standards. The high-resolution mass-spectra were recorded with a Finnigan MAT MS-8200 instrument. GC–MS measurements were performed with a Hewlett-Packard G1800A GCD device for solutions in CH_2Cl_2.

4.1. Compounds

Compounds $C_6F_5SSC_6F_5$ (**2**) [18], C_6F_5SCl [19], $C_6H_5SSi(CH_3)_3$ [20], and $C_6F_5SeSeC_6F_5$ [21] were prepared as described before. Compounds $C_{10}F_8$, $C_{10}H_8$, $C_6H_5SSC_6H_5$ and $C_6H_5SeSeC_6H_5$ were commercially available (Aldrich).

4.1.1. 1,2,3,4,5-Pentafluorodiphenyl disulfide (1)

At 20 °C and under argon, a solution of 0.94 g (0.004 mol) of C_6F_5SCl in 5 mL of Et_2O was added dropwise to a stirred solution of 0.73 g (0.004 mol) of $C_6H_5SSi(CH_3)_3$ in 5 mL of the same solvent. After 1 h, the solvent was distilled off under reduced pressure, the residue was dissolved in 2 mL of hexane and solution was placed into cryostat at −50 °C. At the same temperature the solvent was removed with syringe and the residual solid was dried under vacuum, first at −50 °C, then at ambient temperature. Compound **1** was obtained as white crystals, 1.17 g (95%), mp 21–22 °C (22 °C [15]). MS, *m/z*: 307.9755 (M^+, calculated for $C_{12}H_5F_5S_2$ 307.9753). NMR, δ: ^1H: 7.53–7.29 (5H); ^{19}F: 31.0 (2F), 11.8 (1F), 1.7 (2F). According to the GC–MS analysis, the purity of **1** was 96.6%.

Crystals of **1** obtained as described above were too small to be measured by XRD. The single crystals suitable to XRD were prepared as follows: a drop of liquid **1** was placed into Krytox oil (Du Pont), and the system was cooled by stream of the cold nitrogen. Under these conditions, **1** solidified into well-shaped big transparent crystals.

4.1.2. Complex of 1,1′,2,2′,3,3′,4,4′,5,5′-decafluorodiphenyl disulfide with naphthalene (4) and complex of diphenyl disulfide with octafluoronaphthalene (5)

A mixture of 0.40 g (0.001 mol) of $C_6F_5SSC_6F_5$ and 0.26 g (0.002 mol) of $C_{10}H_8$, or 0.22 g (0.001 mol) of $C_6H_5SSC_6H_5$ and 0.54 g (0.002 mol) of $C_{10}F_8$, was dissolved in 2 mL of boiling hexane and solution was gradually cooled to 20 °C. Complexes **4** and **5** were obtained as transparent colorless needles: **4**, 0.38 g (58%), mp 58–59 °C; **5**, 0.26 g (68%), mp 55–56 °C.

The composition and stoichiometry of the complexes were confirmed by GC–MS data.

4.2. Crystallographic analysis

The single crystal X-ray determinations (Table 1) were carried out on a Siemens P4 diffractometer using Mo Kα (71.073 pm) radiation. The crystals were mounted using KEL-F oil on a thin glass fiber. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data using SHELX-97 software [22]. The structures obtained were analyzed for shortened contacts between non-bonded atoms with the PLATON program [23].

Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 290029 (**1**), CCDC 290030 (**4**) and CCDC 290028 (**5**). Copies of data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033 or E-mail: deposit@ccdc.cam.ac.uk).

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