Inclusion Complexes of the Bicyclic Aryl-Substituted Sulfur-Nitrogen Compounds Ar−CN_5S_3 with Fluorocarbon and Hydrocarbon Aromatics

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Inclusion compounds with a stoichiometry of 2:1 were prepared from 7-Ar-1λ^4,3λ^4,5λ^4-trithia-2,4,6,8,9-pentaazabicyclo[3.3.1]nona-1(9),2,3,5,7-pentaenes Ar–CN_5S_3 and hexafluorobenzene (Ar = C_6H_5, 4-$CH_3C_6H_4$, 4-$C_6H_5C_6H_4$ and 2,6-$F_2C_6H_3$) and toluene (Ar = C_6F_5), by crystallization of the bicycles from the corresponding aromatics. Similar to the pure host compounds, the bicycles in the inclusion compounds form centrosymmetric dimers. The packing of the dimers in the pure host compounds is dominated by the interaction of the substituents at the aryl groups, and in the inclusion compounds by the interaction of the host and guest. The parallel-displaced arrangement of the aromatic rings of the host and guest is typical of non-covalent π-stacking interactions of the arene-polyfluroarene type. The inability of benzene (in contrast to hexafluorobenzene) to form an inclusion compound with the title bicycle (Ar = C_6H_5) indicates that inclusion is driven by π-stacking interactions of the arene-polyfluoroarene type. Crystallization of the title bicycle (Ar = C_6H_5) from a 1:1 molar mixture of benzene and hexafluorobenzene gave the same inclusion compound as the crystallization from pure hexafluorobenzene. This can be considered as molecular recognition based on π-stacking interactions. The compounds prepared provide the first example of aromatic units bearing extremely sterically demanding polyheteroatom bicyclic substituents involved in non-covalent arene-polyfluoroarene π-stacking interactions. Attempts to prepare inclusion compounds with octafluoronaphthalene and decafluorobiphenyl, as well as co-crystals of *para*-tolyl- and pentafluorophenyl-substituted bicycles, failed. The origin of the 2:1 stoichiometry and the lack of inclusion in the case of $C_{12}F_{10}$ and $C_{10}F_8$ are discussed.

Introduction

Non-covalent interactions[1] between aromatic groups,[2−5] including those between hydrocarbon and fluorocarbon counterparts featuring π-stacked arrangement (refs.[5−7] and references cited therein), are recognized to be one of the most general supramolecular motifs. The arene-polyfluoroarene π-stacking interactions are important not only in fundamental research but also in the design and synthesis of advanced functional materials (for example, nematic[8] and discotic[9] liquid crystals, J aggregates,[10] photochromic crystals,[11] etc.).

Recently, we described 1:1 molecular complexes between octafluoronaphthalene and acyclic (Ar−N=S=N−Ar, Ar−N=S=N−$SiMe_3$) and heterocyclic (7-methyl-2,1-benzisothiazole) sulfur-nitrogen compounds featuring π-stacking interactions of the arene-polyfluoroarene type.[6,7] It follows from the results obtained that geometrical matching of the components of the complexes can be considered a less significant structural requirement.

In the context of crystal engineering, it is of obvious interest to investigate how broad the molecular diversity of aryl-substituted sulfur-nitrogen compounds involved in the arene-polyfluoroarene π-stacking interactions can be, with special emphasis on derivatives with enlarged spatial demand.

The present work deals with the preparation and X-ray structural characterization of the molecular complexes of the aryl-substituted sulfur-nitrogen derivatives Ar−CN_5S_3 (7-aryl-1λ^4,3λ^4,5λ^4-trithia-2,4,6,8,9-pentaazabicyclo[3.3.1]-nona-1(9),2,3,5,7-pentaenes) with aromatic compounds in both the fluorocarbon and hydrocarbon series.

Results and Discussion

The target complexes of the Ar−CN_5S_3 derivatives **1**−**4** (Ar = C_6H_5, 4-$CH_3C_6H_4$, 4-$C_6H_5C_6H_4$ and 2,6-$F_2C_6H_3$, respectively) with hexafluorobenzene were prepared (Scheme 1) as single crystals suitable for X-ray crystallography by crystallization of the compounds **1**−**4** from hexa-

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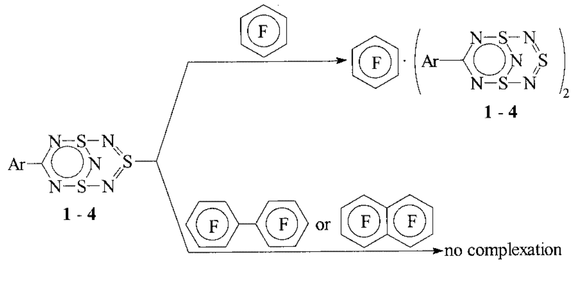
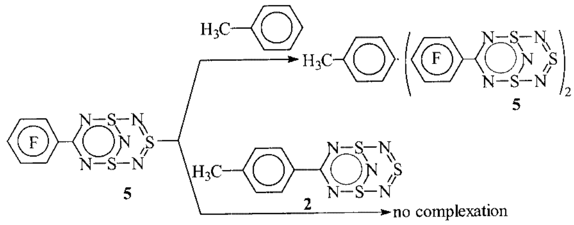
fluorobenzene. All attempts to prepare similar complexes of decafluorobiphenyl and octafluoronaphthalene by co-crystallization of the components from organic solvents (cf. ref.[6]), including *n*-hexane, $CHCl_3$, THF and MeCN, failed.



Ar = C_6H_5 (**1**), 4-$H_3CC_6H_4$ (**2**), 4-$C_6H_5C_6H_4$ (**3**), 2,6-$F_2C_6H_3$ (**4**)

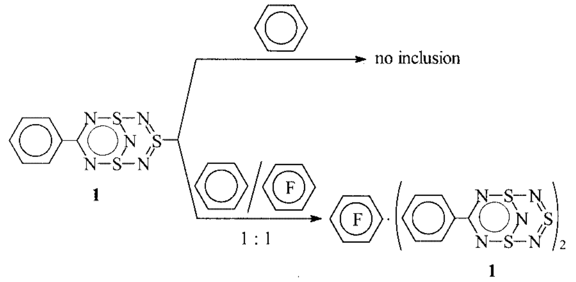
Scheme 1. The circle in the dithiatriazine cycle of the bicycles means delocalization, not aromaticity

Single crystals, suitable for X-ray diffraction, of the complex of $C_6F_5-CN_5S_3$ (**5**) with toluene were obtained (Scheme 2) by low-temperature co-crystallization of the components from *n*-hexane. An attempt to co-crystallize compound **5** with compound **2** (which can be considered a toluene derivative) from THF was unsuccessful.



Scheme 2

According to the results from X-ray crystallography, all complexes of the $Ar-CN_5S_3$ derivatives with aromatic compounds prepared (both fluorocarbon and hydrocarbon) possess a 2:1 stoichiometry rather than the usual 1:1 stoichiometry (refs.[5–14] and references cited therein), despite the fact that the corresponding aromatics were used in the preparation as solvents, i.e. in a large molar excess. The detailed analysis of their crystal packing (see below) confirms the inclusion nature of the co-crystals. It was found that benzene, in contrast to hexafluorobenzene, under the same conditions, does not form an inclusion compound with **1**. This indicates directly the critical importance of the π-stacking interactions of the arene-polyfluoroarene type for the discussed inclusion compounds. Significantly, crystallization of compound **1** from a 1:1 molar mixture of benzene and hexafluorobenzene leads to the same $C_6F_6\cdot(\mathbf{1})_2$ inclusion compound as the crystallization from pure hexafluorobenzene. This can be considered as molecular recognition based on π-stacking interactions (Scheme 3).



Scheme 3

Table 1 presents the crystal data and details of the structure refinements for the compounds $C_6F_6\cdot(\mathbf{1})_2$, $C_6F_6\cdot(\mathbf{2})_2$, $C_6F_6\cdot(\mathbf{3})_2$, $C_6F_6\cdot(\mathbf{4})_2$ and $CH_3C_6H_5\cdot(\mathbf{5})_2$. For comparison, the structures of the pure host compounds **1** and **4** are given in Figure 1 and Figure 2, Figure 3–5 present the crystal packing of the inclusion compounds. The interactions of the π-systems in the crystals of $C_6F_6\cdot(\mathbf{1})_2$ and $CH_3C_6H_5\cdot(\mathbf{5})_2$ are shown in Figure 6 and Figure 7. Relevant bond lengths and bond angles are listed only for $C_6F_6\cdot(\mathbf{3})_2$ and $CH_3C_6H_5\cdot(\mathbf{5})_2$, because the structures of the parent host compounds 4-$C_6H_5C_6H_4-CN_5S_3$ (**3**) and $C_6F_5-CN_5S_3$ (**5**) are not reported in the literature. Compared to the pure host compounds **1**, **2**, and **4** the geometries of the aryl-substituted bicycles remain nearly unchanged in the inclusion compounds.

For compound **1** ($C_6H_5-CN_5S_3$)[15,16] and its derivatives $Ar-CN_5S_3$,[17] two dominant modes of molecular packing are known (for an in-depth discussion, see ref.[17]). They are described as "stacking" (the sulfur-nitrogen rings of neighboring molecules fit into one another like stacked crates; short N···C and N···S contacts are found), and "dimerization" (two molecules are arranged with their heterocyclic heads facing each other centrosymmetrically; only short S···N contacts are observed). Both packing patterns can be rationalized by Coulombic interactions between the CN_5S_3 units as shown by the mapped electrostatic potential.[17] Most of the $Ar-CN_5S_3$ bicycles including **1**, **2** and **4** form centrosymmetric dimers. The interaction between the dimers is influenced by the geometry of the monomers (e.g. Figure 1 and Figure 2) and the interaction of the substituents at the aryl groups.

Despite the differences in the packing of the individual host compounds, the crystal packing of the $C_6F_6\cdot Ar-CN_5S_3$ complexes and also of the inverse complex $CH_3C_6H_5\cdot Ar_F-CN_5S_3$, are very similar (Figure 3–5). A closer look shows that complex formation does not influence the geometry of the monomeric $Ar-CN_5S_3$ species, the formation of the dimer is also not affected, but the interaction between the dimers is dominated by π-stacking. Small differences in the π-stacking arise from the geometry and the charge distribution in the aryl substituents. π-Stacking H···F contacts (considered as supramolecular synthons)[18] seem to be important for the arrangement in the solid state (a representative example is given in Figure 3). The inclusion nature of the synthesized compounds ex-

Table 1. Crystal data and structure refinement for $C_6F_6\cdot(\mathbf{1})_2$, $C_6F_6\cdot(\mathbf{2})_2$, $C_6F_6\cdot(\mathbf{3})_2$, $C_6F_6\cdot(\mathbf{4})_2$ and $CH_3C_6H_5\cdot(\mathbf{5})_2$

Compound	$C_6F_6\cdot(\mathbf{1})_2$	$C_6F_6\cdot(\mathbf{2})_2$	$C_6F_6\cdot(\mathbf{3})_2$	$C_6F_6\cdot(\mathbf{4})_2$	$CH_3C_6H_5\cdot(\mathbf{5})_2$
Empirical formula	$C_7H_5N_5S_3\cdot0.5\ (C_6F_6)$	$C_8H_7N_5S_3\cdot0.5\ (C_6F_6)$	$C_{13}H_9N_5S_3\cdot0.5\ (C_6F_6)$	$C_6H_3F_2N_5S_3\cdot0.5\ (C_6F_6)$	$C_7F_5N_5S_3\cdot0.5\ (C_7H_8)$
Molecular mass	348.37	362.40	424.46	384.35	391.37
Temperature, K	173(2)	173(2)	173(2)	173(2)	173(2)
Wavelength, pm	71.073	71.073	71.073	71.073	71.073
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, pm	601.0(2)	600.90(12)	602.90(10)	760.90(10)	612.40(12)
b, pm	747.00(10)	750.80(15)	751.70(10)	879.1(2)	789.70(16)
c, pm	1462.9(2)	1561.1(3)	1939.9(3)	1127.1(2)	1520.0(3)
α (°)	87.400(10)	81.38(3)	85.010(10)	110.610(10)	92.44(3)
β (°)	87.49(2)	87.97(3)	84.080(10)	94.520(10)	90.94(3)
γ (°)	72.58(2)	74.26(3)	70.720(10)	103.790(10)	109.18(3)
Volume, nm^3	0.6257(2)	0.6702(2)	0.8241(2)	0.6743(2)	0.6933(2)
Z	2	2	2	2	2
$D_{calcd.}$, $Mg\cdot m^{-3}$	1.849	1.796	1.711	1.893	1.875
Absorption coefficient (mm^{-1})	0.629	0.591	0.495	0.614	0.599
Crystal size (mm^3)	0.90 × 0.50 × 0.10	0.50 × 0.40 × 0.10	0.60 × 0.40 × 0.10	0.60 × 0.50 × 0.50	0.40 × 0.40 × 0.30
θ range for data collection (°)	2.79−27.50	2.64−26.08	2.11−27.50	2.58−27.50	2.68−26.06
Reflections collected	3740	9442	4946	3771	9783
Independent reflections	2868 [R(int) = 0.0219]	2423 [R(int) = 0.0532]	3795 [R(int) = 0.0303]	3022 [R(int) = 0.0151]	2513 [R(int) = 0.0528]
Completeness to θ,% (θ,°)	99.8 (27.50)	91.0 (26.08)	99.9 (27.50)	97.6 (27.50)	91.3 (26.06)
Data/restrains/ parameters	2868/0/192	2423/0/202	3795/0/245	3022/0/210	2513/0/247
Goodness-of-fit on F^2	1.049	1.009	1.033	1.096	1.016
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0310$, $wR2 = 0.0822$	$R1 = 0.0361$, $wR2 = 0.0942$	$R1 = 0.0372$, $wR2 = 0.0906$	$R1 = 0.0311$, $wR2 = 0.0877$	$R1 = 0.322$, $wR2 = 0.0853$
R indices (all data)	$R1 = 0.0383$, $wR2 = 0.0865$	$R1 = 0.0472$, $wR2 = 0.0993$	$R1 = 0.0490$, $wR2 = 0.0965$	$R1 = 0.0322$, $wR2 = 0.0887$	$R1 = 0.0399$, $wR2 = 0.0888$
Largest diff. peak and hole, eA^{-3}	0.440, −0.320	0.497, −0.254	0.355, −0.364	0.363, −0.328	0.388, −0.255

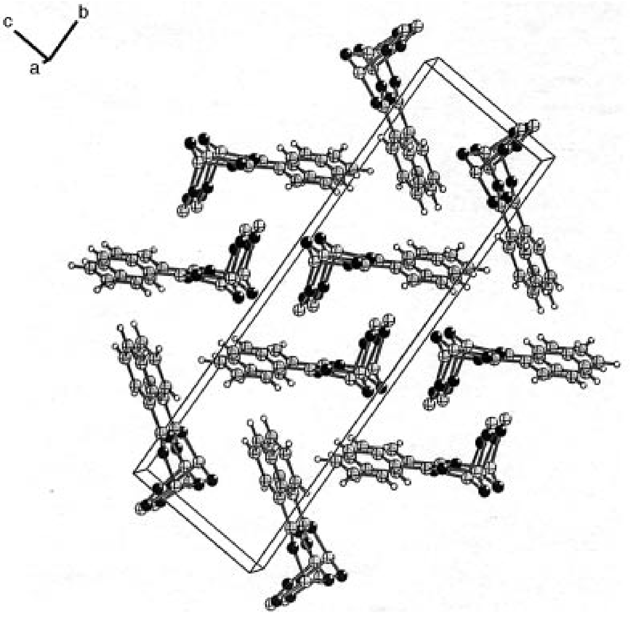


Figure 1. Crystal packing diagram of **1**[15,16]

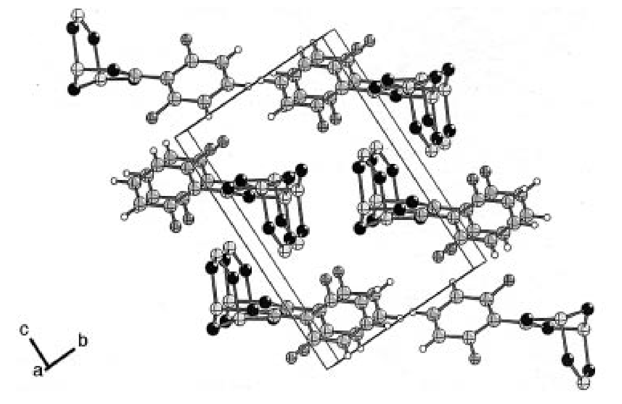


Figure 2. Crystal packing diagram of **4**[17]

plains the aforementioned unsuccessful co-crystallization with decafluorobiphenyl or octafluoronaphthalene since only the relatively small hexafluorobenzene and toluene molecules fit into the van der Waals holes in the co-crystals with **1−5**.

The 2:1 stoichiometry observed in the $(Ar{-}CN_5S_3)_2\cdot C_6F_6$ and $(Ar_F{-}CN_5S_3)_2\cdot C_6H_5CH_3$ compounds results from the non-equivalence of the two sides of the aryl ring planes in the bicycles. In the co-crystals, both the hexafluorobenzene and toluene groups interact with the side of the aryl ring of the $Ar{-}CN_5S_3$ species that is opposite to the N=S=N fragment (Figure 3−5). In the case of **3,** which possesses two non-equivalent aromatic rings, only the monosubstituted ring is involved in the inter-

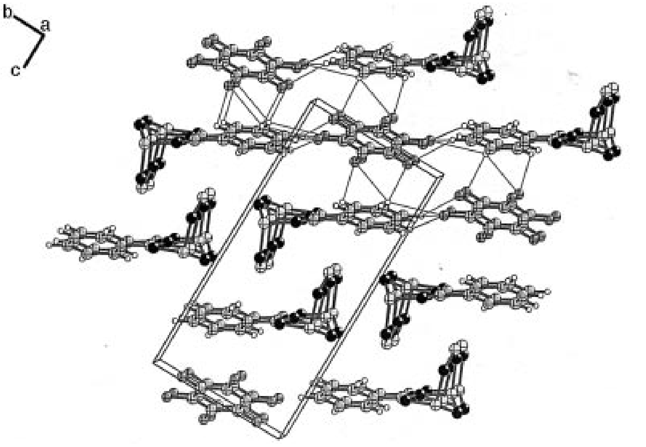


Figure 3. Crystal packing diagram of $C_6F_6\cdot(\mathbf{1})_2$ (molecular geometry of **1**[15,16])

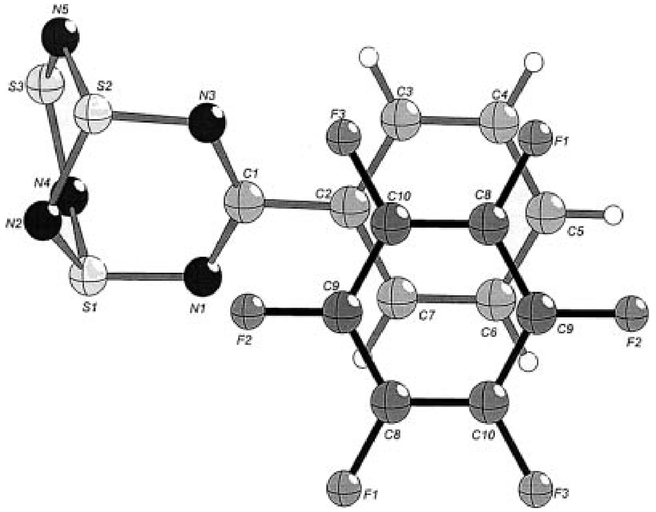


Figure 6. Arene-perfluoroarene overlap in $C_6F_6\cdot(\mathbf{1})_2$

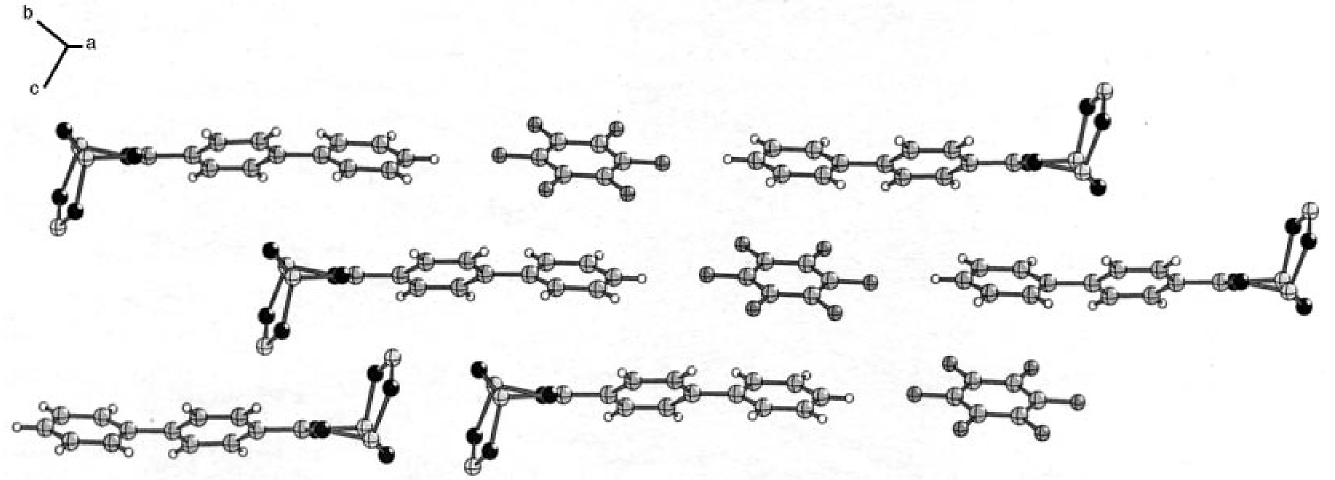


Figure 4. Crystal packing diagram of $C_6F_6\cdot(\mathbf{3})_2$; selected bond lengths (pm), bond and dihedral angles (°) of **3** (for atom numbering, see Figure 6): C(1)−N(1) 134.1(2), C(1)−N(3) 133.9(2), C(1)−C(2) 148.9(3), N(3)−S(2) 162.70(17), S(1)−N(1) 162.37(17), S(1)−N(2) 163.21(17), S(1)−N(4) 173.29(19), N(2)−S(2) 163.38(17), S(2)−N(5) 173.29(18), N(4)−S(3) 154.94(18), S(3)−N(5) 155.46(18); N(1)−C(1)−N(3) 130.06(18), N(3)−C(1)−C(2) 114.26(17), N(1)−C(1)−C(2) 115.67(17), C(1)−N(3)−S(2) 120.82(14), N(1)−S(1)−N(2) 108.63(9), N(1)−S(1)−N(4) 103.19(9), N(2)−S(1)−N(4) 106.05(9), S(1)−N(2)−S(2) 111.66(10), N(3)−S(2)−N(2) 110.06(9), N(3)−S(2)−N(5) 101.69(9), N(2)−S(2)−N(5) 105.57(9), C(1)−N(1)−S(1) 117.22(14), S(3)−N(4)−S(1) 122.55(11), N(4)−S(3)−N(5) 119.09(10), S(3)−N(5)−S(2) 117.76(10); *dihedral angle* between aromatic rings 39.7

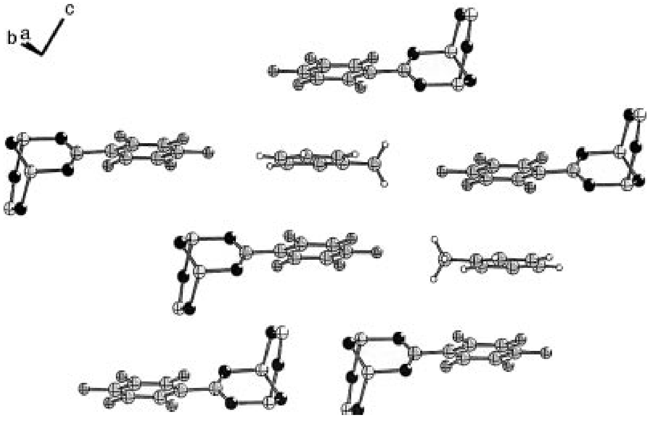


Figure 5. Crystal packing diagram of $CH_3C_6H_5\cdot(\mathbf{5})_2$

actions (Figure 4). All co-crystals demonstrate a parallel-displaced arrangement of the aromatics, i.e. face-to-face π-stacking of the aromatic rings of the bicycles with a ring of a second partner showing some offset of the interacting rings (Figure 6 and Figure 7). In $CH_3C_6H_5\cdot(\mathbf{5})_2$ the toluene molecules are highly disordered.

The dihedral angle between the planes of the cofacial hydrocarbon and fluorocarbon rings (the tilt) is 6.8, 8.6, 6.0, 12.7, and 5.8° for $C_6F_6\cdot(\mathbf{1})_2$, $C_6F_6\cdot(\mathbf{2})_2$, $C_6F_6\cdot(\mathbf{3})_2$, $C_6F_6\cdot(\mathbf{4})_2$ and $CH_3C_6H_5\cdot(\mathbf{5})_2$, respectively. The arene-polyfluoroarene separation within the stacks varies between 352.0−381.6 (366.4), 347.5−403.6 (373.9), 353.8−378.9 (366.4), 346.8−403.5 (374.6) and 360.1−389.6 (378.3) pm, respectively (in brackets: distance between the centers of the rings which is not equal to the separation due to the offset and tilt). For comparison, this separation is 377 pm[12] for the lowest-temperature phase of the benzene-hexafluoroben-

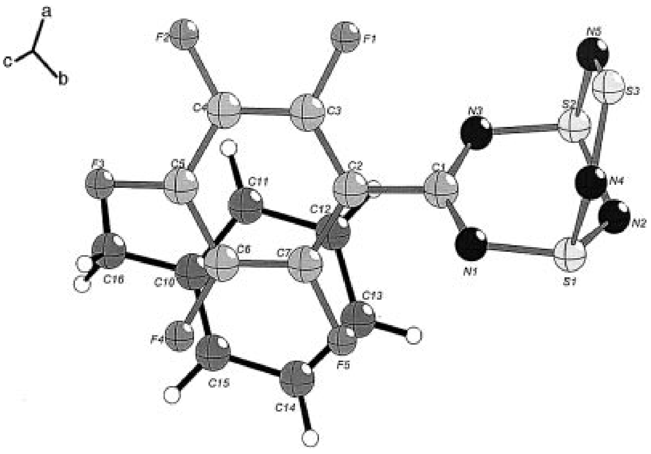


Figure 7. Arene-perfluoroarene overlap in $CH_3C_6H_5\cdot(\mathbf{5})_2$; selected bond lengths (pm) and bond angles (°) of **5**: C(1)−N(1) 133.0(3), C(1)−N(3) 133.5(3), C(1)−C(2) 149.3(3), N(1)−S(1) 163.80(18), S(1)−N(2) 162.8(2), S(1)−N(4) 173.27(18), N(2)−S(2) 163.46(17), S(2)−N(3) 162.2(2), S(2)−N(5) 173.91(18), N(4)−S(3) 155.16(18), S(3)−N(5) 154.84(19), av. C−F 134.0; N(1)−C(1)−N(3) 131.88(19), N(1)−C(1)−C(2) 114.46(18), N(3)−C(1)−C(2) 113.64(17), C(1)−N(1)−S(1) 118.93(15), N(2)−S(1)−N(1) 110.44(9), N(2)−S(1)−N(4) 105.46(9), N(1)−S(1)−N(4) 101.37(9), S(1)−N(2)−S(2) 112.33(10), N(3)−S(2)−N(2) 109.76(9), N(3)−S(2)−N(5) 103.07(10), N(2)−S(2)−N(5) 105.17(9), C(1)−N(3)−S(2) 118.78(14), S(3)−N(4)−S(1) 119.99(11), N(5)−S(3)−N(4) 119.36(9), S(3)−N(5)−S(2) 120.81(10).

zene co-crystals, and 333−354 pm for the naphthalene−octafluoronaphthalene co-crystals at room temperature[13] and 327−352 pm for the low-temperature structure.[14] Such a parallel-displaced arrangement is typical for this type of interaction since it diminishes the repulsive π-electron interactions, which are roughly proportional to the π-overlapping area. Thus, the compounds obtained possess all the typical characteristics of the stacking of six-membered aromatic rings in crystals.[19]

On the other hand, the stoichiometry of 2:1 arises from the stability of the packing motifs observed in the crystals of $Ar-CN_5S_3$ towards the incorporation of hexafluorobenzene or toluene molecules into their crystal lattices.

From this point of view, these compounds should be classified as inclusion compounds. It is well-known that the formation of inclusion compounds is possible even in the absence of attractive forces between host and guest. During crystal growth from solution, solvent molecules may be caught and held in intermolecular cavities as guests also through repulsive forces.[20] However, for the compounds discussed, inclusion is definitely driven by attractive[2,5] π-stacking interactions of the arene-polyfluoroarene type, as proved by the ability of the crystal lattice of compound **1** to recognize and discriminate benzene and hexafluorobenzene molecules.

It also follows from the data obtained that the molecular geometries of compounds **1**, **2** and **4** (known previously[15−17]) are practically not affected by the interaction with C_6F_6 (cf. similar observations were made for complexes of $C_{10}F_8$ [6]). In some cases (for example, compounds **3** and **5**), the co-crystals are much better suited for X-ray crystallography than crystals of the individual compounds of interest (including situations when one component is a liquid in its pure state; for example see refs.[6,7]); a methodology could be developed which uses these types of co-crystals for the structural characterization of aromatic compounds (including liquids) for which good quality single crystals are not available.

Conclusion

Inclusion compounds of aryl-substituted sulfur-nitrogen bicycles $Ar-CN_5S_3$ with fluorocarbon and hydrocarbon aromatics with 2:1 stoichiometry have been prepared for the first time. Their crystal structures demonstrate a parallel-displaced arrangement of the aromatic rings of the host and the guest typical of non-covalent π-stacking interactions of the arene-polyfluoroarene type. Thus, the compounds provide the first example of aromatic units bearing extremely sterically demanding polyheteroatom bicyclic substituents involved in non-covalent arene-polyfluoroarene π-stacking interactions. This confirms our earlier conclusion that the geometrical matching of the components of the complexes can be considered a less significant structural requirement and thus provides new and interesting prospects to crystal engineering based on the arene-polyfluoroarene π-stacking interactions. Molecular recognition and discrimination are also possible with the arene-polyfluoroarene π-stacking interactions in the $Ar-CN_5S_3$/arene/polyfluoroarene systems. Based on these findings, it seems possible that the π-stacking interactions of the arene-polyfluoroarene type might be used in solving some serious challenges of contemporary materials science. In particular, significant progress has been made during the last decade in the field of organic molecular magnets, especially those based on aryl-substituted thiazyl radicals such as 4-aryl-1,2,3,5-dithiadiazolyls, 1,2,3- and 1,3,2-benzodithiazolyls, including fluoro-containing derivatives. However, in the solid state, these radicals reveal a general tendency to form diamagnetic dimers by means of out-of-plane π*-π* interactions, leading to shortened intermolecular S···S and S···N contacts. The inhibition of the dimerization process is very important for further developments in the field.[21] One might try to overcome the dimerization process by utilizing π-stacking interactions of the arene-polyfluoroarene type in the solid state between aryl-substituted thiazyl radicals and suitable polyfluoroaromatics, and this can be a direction for further investigations in the field.

Experimental Section

Materials and Methods: The bicycles **1−5** were prepared by published methods.[15,17,22] Their inclusion compounds with the corresponding aromatics were prepared in an argon atmosphere. The melting points were taken on a Gallencamp Melting Point Apparatus in sealed capillaries. For all complexes, melting is accompanied by decomposition with gas evolution.

Preparation of $C_6F_6\cdot(1)_2$, $C_6F_6\cdot(2)_2$, and $C_6F_6\cdot(3)_2$: Compounds **1−3** (0.5 mmol) were dissolved in 5 mL of boiling hexafluorobenzene.

The solution was filtered hot and gradually cooled in a thermostat to 20 °C. During the cooling, orange-yellow crystals formed which were separated by filtration.

Complex C_6F_6·(**1**)$_2$ formed transparent orange-yellow plates (0.15 g, 86%), m.p. 125−126 °C.

Complex C_6F_6·(**2**)$_2$ formed transparent orange-yellow elongated thin plates (0.15 g, 83%), m.p. 143−144 °C.

Complex C_6F_6·(**3**)$_2$ formed transparent orange-yellow needles (0.20 g, 94%), m.p. 149−150 °C.

Preparation of C_6F_6·(4)$_2$: Compound **4** (0.15 g, 0.5 mmol) was dissolved in 2 mL of hot hexafluorobenzene. At 20 °C, 2 mL of *n*-hexane was added to this solution forming a two-layered system. After 2 days, after the diffusion of solvents had ceased, the crystals formed were filtered. Complex C_6F_6·(**4**)$_2$ formed transparent orange prisms (0.12 g, 65%), m.p. 104−105 °C.

Preparation of $CH_3C_6H_5$·(5)$_2$: Compound **5** (0.17 g, 0.5 mmol) was dissolved in 2 mL of hot toluene. At 20 °C, 2 mL of *n*-hexane was added to this solution forming a two-layered system, which was placed into a cryostat at −30 °C. After 2 weeks, the crystals formed were filtered. Complex $CH_3C_6H_5$·(**5**)$_2$ formed large transparent orange-yellow needles (0.10 g, 50%) m.p. 123−124 °C.

Preparation of C_6F_6·(1)$_2$ from C_6H_6/C_6F_6: Compound **1** (0.13 g, 0.5 mmol) was dissolved in 3 mL of a 1:1 molar mixture of boiling benzene and hexafluorobenzene. The solution was filtered while still hot and gradually cooled in a thermostat to 30 °C (i.e. above the reported m.p. of the C_6H_6·C_6F_6 complex, 24 °C[23]). The crystals formed were filtered. The complex C_6F_6·(**1**)$_2$ (0.16 g, 92%) isolated by this procedure was identical (unit cell parameters, m.p.) to that obtained by crystallization of **1** from pure hexafluorobenzene.

The crystallization of **1** from benzene did not lead to an inclusion compound. Only **1** was recovered.

X-ray Crystallographic Study: The crystallographic data were collected on a Siemens P4 diffractometer [C_6F_6·(**1**)$_2$, C_6F_6·(**3**)$_2$, C_6F_6·(**4**)$_2$] or on a Stoe IPDS [C_6F_6·(**2**)$_2$, $CH_3C_6H_5$·(**5**)$_2$] using Mo-K_α (0.71073 Å) radiation with a graphite monochromator. Refinement was based on F^2; $R1 = ||F_o| - |F_c||/|F_o|$; $wR2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$. Programs used: SHELX-97[24] and DIAMOND.[25]

The single crystals of the inclusion compounds were prepared as described above. They were mounted on a thin glass fiber using KEL-F oil. The structures were solved by direct methods (SHELXS[24]). Subsequent least-squares refinements (SHELXL-97−2[24]) located the positions of the remaining atoms in the electron density maps. All non-H atoms were refined anisotropically.

CCDC-226030 [for C_6F_6·(**1**)$_2$], -226031 [for C_6F_6·(**2**)$_2$], -226032 [for C_6F_6·(**3**)$_2$], -226033 [for C_6F_6·(**4**)$_2$], and -226034 [for $CH_3C_6H_5$·(**5**)$_2$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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