Crystal Engineering with Symmetrical Threefold Acceptor-Substituted Triaminobenzenes

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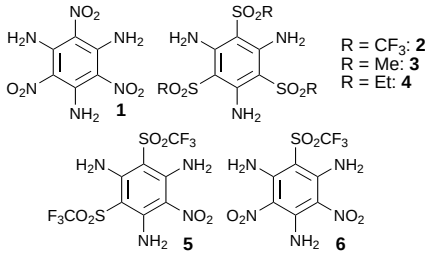
Dedicated to Professor Dr. Reinhard W. Hoffmann on the occasion of his 65th birthday

Abstract: The syntheses of threefold acceptor-substituted 1,3,5-triaminobenzene derivatives **2** – **6** and their crystal structure analyses are described. As acceptors, nitro, trifluoromethylsulfone, and alkylsulfone groups are employed. The combination of hydrogen bonding, arene ··· arene and F ··· F contacts leads to remarkably similar solid-state layer structures for sterically quite dissimilar molecules.

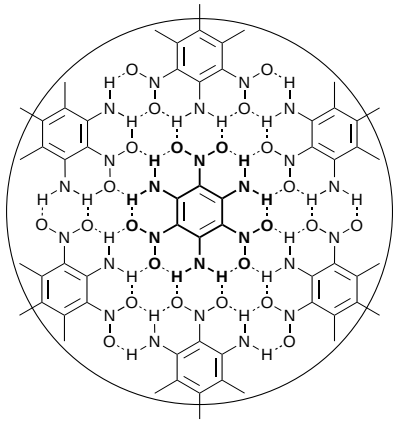
Keywords: arenes · crystal engineering · electrostatic interactions

Introduction

The use of organic molecules in materials science depends crucially on the superstructures that are formed from them. To a zeroth-order approximation, individuality of molecules is conserved in a material, and an observed bulk effect arises from the vectorial summation of molecular properties. The mutual orientation of the molecules therefore decides whether a promising molecular property can be translated into a useful bulk property. Molecular crystals offer a highly constrained and precisely defined environment that guarantees the highest degree of order observed in bulk structures. By the same token, their structure is in many cases easily elucidated. These advantages are countered by the difficulty of predicting these structures. Despite the numerous crystal structures now readily available in databases,[1] and despite great progress in their computation,[2, 3] little is known about how to specifically design crystal structures at will[4–6]—or, more specifically, how to predict a crystal structure on the basis of a known molecular constitution alone. It is not even possible to predict, except in the trivial case of pure enantiomers, whether a molecule will adopt a centrosymmetric space group or not.[7–9] The latter question, for example, is of crucial importance to second-order nonlinear optics.[10–14] The objective of this work is to design layer structures. We have recently shown that symmetrical trinitrotriaminobenzene (**1**, Scheme 1) exists in two polymorphs, one of which is noncentrosymmetric (space group $P3_1$) and almost ideally suited for use in nonlinear optics.[15, 16] In both polymorphs, graphitelike layer structures of approximate trigonal symmetry are found that arise from strong intra- and intermolecular hydrogen bonding (Scheme 2). In the centrosymmetric structure the layers are stacked antiparallel, whereas in the other they are stacked parallel, but with small displacements relative to each other.



Scheme 1.



Scheme 2.

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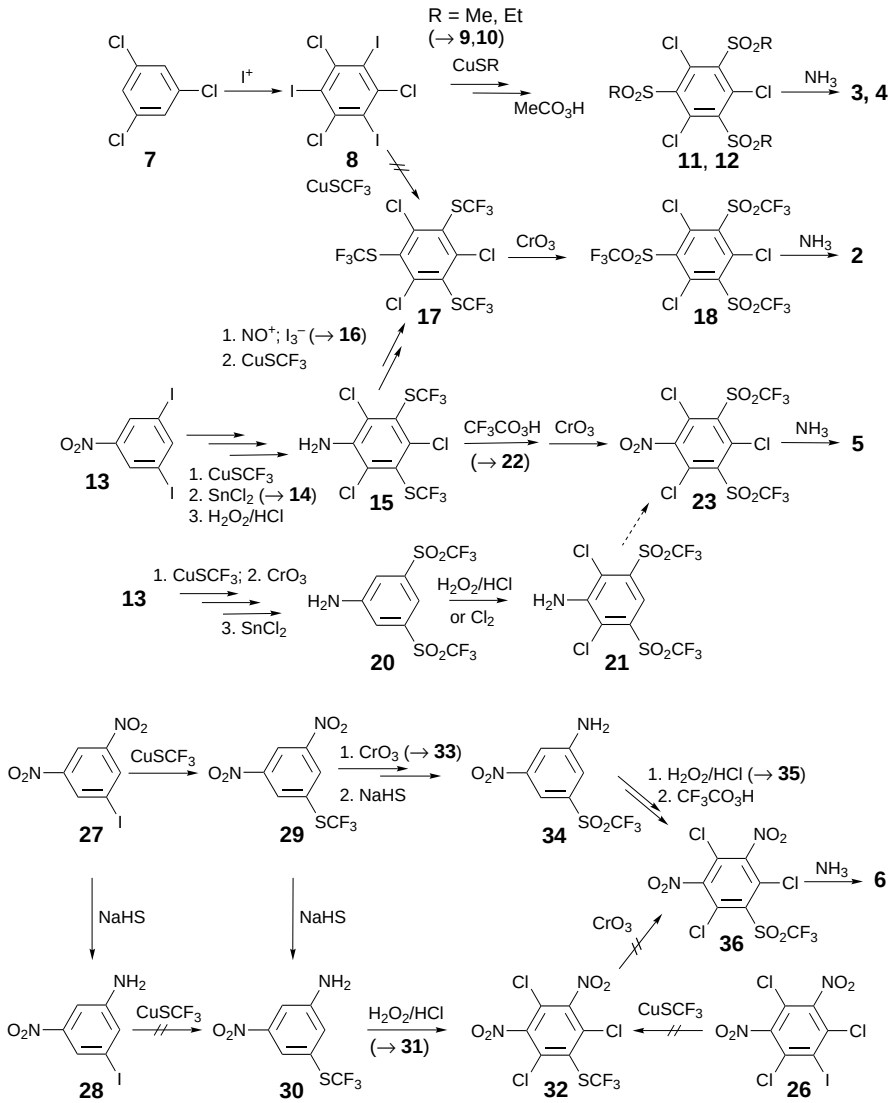
This situation is reminiscent of the stacking disorder found in graphite. We reasoned that the intralayer interactions in **1** are quite strong in comparison to the interlayer interactions. How tolerant is the formation of layer structures with respect to molecular asymmetry? Is it possible to identify molecular architectures that allow prediction of crystal structures? Can the factors that determine these structures be identified? To answer these questions, we tried to keep the directional capabilities of hydrogen bonding[17–22] and studied analogues of **1** where the nitro groups were replaced with sulfonyl (**2**–**4**) acceptors. We also analyzed the mixed derivatives **5** and **6** (Scheme 1). While it may be expected that the exchange of the trigonal nitrogen present in a nitro group with a tetrahedral sulfur would lead to a drastic change in the conformational and/or crystallographic behavior, we show here that, surprisingly, this is not the case.



Scheme 3. Synthesis of **2**–**6** by nucleophilic aromatic substitution of **18**, **11**, **12**, **23**, and **36**.

Results and Discussion

1. Syntheses: Compounds **2**–**6** were made by nucleophilic aromatic substitution of the corresponding trichloro triacceptor compounds (**18**, **11**, **12**, **23**, **36**, of which **23** had been prepared by others before;[23] Scheme 3). Synthesis of the alkylsulfone precursors **11** and **12** proved straightforward: the key step is the threefold Ullmann reaction[24] of **8** with the corresponding Cu^{I} thiolate (modified by the addition of α,α-bipyridyl), followed by standard oxidation with peracetic acid formed in situ. Trichlorotriiodobenzene **8** was prepared by use of a known[25] oxidative iodination method. Unfortunately, due to redox processes, reaction with $CuSCF_3$ gives a very low yield of impure product under these conditions, so synthesis of **18** was attempted by two routes starting from **13**.[26] The route via **20** was not successful, because chlorination of this deactivated and sterically encumbered substrate only gave the dichlorinated product **21**. Triple chlorination, however, is easy with the less deactivated **14**.[23]

Four routes had to be tried for the synthesis of **36**. It turns out that reaction with $CuSCF_3$ is unsuccessful both at the hexa-substituted stage and when an amino functionality is present. In addition, oxidation of the sulfide to the sulfone as the final step proved capricious. The successful route relies on the introduction of the sulfone functionality at an early stage and oxidation of an amino to a nitro group with concentrated trifluoroperacetic acid. Thus, **27** is converted by a clean reaction with $CuSCF_3$ and subsequent Cr^{VI} oxidation to **33**. One nitro group has then to be reduced to activate the ring for the chlorination. While partial reduction of *sym*-trinitrobenzene with ammonium sulfide is possible in moderate yield,[27] the formation of Meisenheimer complexes and their respective follow-up reactions compete with reduction. A trifluoromethylsulfone favors their formation even at lower *p*H with respect to a nitro group.[28–30] The *p*H of the reaction mixture had therefore to be kept as low as possible, and a solution of NaHS[31] was employed to produce **34** in moderate yield. Chlorination and oxidation then gave **36**.

2. Crystal structures

2.1 Molecular parameters: Due to the substitution with three donors and three acceptors, π-electron density is shifted from the benzene core to the substituents and the π system can adopt several multipolar resonance structures (Figure 1).[32]

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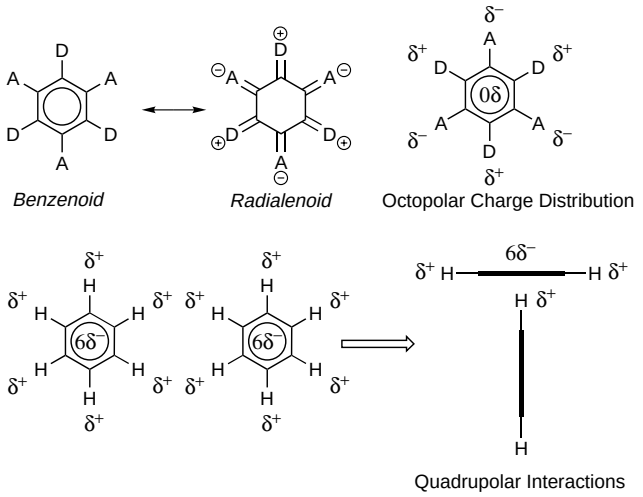
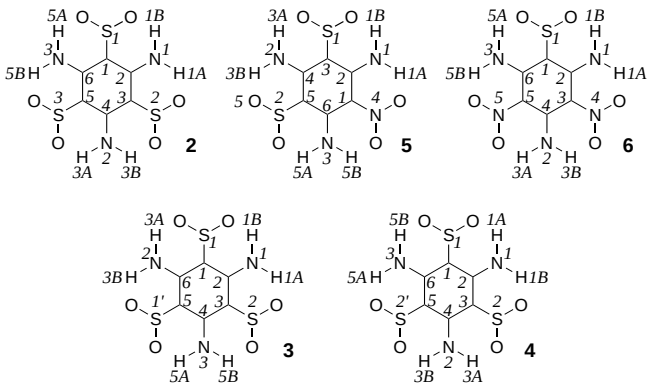


Figure 1. Charge distribution in symmetrical threefold donor–acceptor substituted benzenes, and preferred stacking of quadrupolar benzene derivatives.

Structures with highly nonplanar rings result in the case of *N*-substituted derivatives, but six intramolecular hydrogen bonds planarize the ring.[33] These are also present in **2**–**6** to oxygen atoms of both types of acceptor groups (Table 1). The intramolecular hydrogen bonding to a sulfonyl oxygen is weaker than to a nitro oxygen atom: the distances H···O(S) and (H)N···O(S) are larger than the corresponding distances H···O(N) and (H)N···O(N). This can be ascribed to the longer C–S bond and the tetrahedral environment of sulfur.

The C–C bond length alternation in **2**–**6** is insignificant, but the average endocyclic C–C bonds are elongated and the exocyclic C–N and C–S bonds shortened (Table 1) as the comparison with the following reference values[34] reveals: substituted $C_{ar}-C_{ar}$: 1.397, $C_{ar}-N_{sp2}H_2$: 1.355, $C_{ar}-NO_2$: 1.468, $C_{ar}-SO_2C$: 1.763 Å. The effects are less pronounced in **3** and **4**; this is in accordance with the weaker electron-withdrawing character of alkylsulfones.[35] Nevertheless, the radialene form assumes considerable weight in the description of all of the π

Table 1. Selected structural features of **2**–**6**.[a]



	2	**3**	**4**	**5**	**6**
bond lengths [Å]					
C1–C2	1.443(3)	1.426(2)	1.427(3)	1.447(3)	1.435(7)
C2–C3	1.434(5)	1.424(2)	1.417(3)	1.433(4)	1.444(7)
C3–C4	1.436(5)	1.424(2)	1.427(3)	1.430(4)	1.444(7)
C4–C5	1.442(3)	1.426(2)	1.427(3)	1.432(3)	1.446(7)
C5–C6	1.431(5)	1.422(2)	1.417(3)	1.435(4)	1.448(7)
C6–C1	1.435(4)	1.422(2)	1.427(3)	1.437(4)	1.444(7)
average C(ar)–C(ar)	1.437	1.424	1.424	1.436	1.444
average C(ar)–NH	1.322	1.348	1.340	1.322	1.322
average C(ar)–NO	–	–	–	1.419	1.413
average C(ar)–S	1.727	1.757	1.763	1.733	1.746
Σ|tors. ∢| [°][b]	29.2	32.2	10.0	30.3	15.3
hydrogen bonds					
intramolecular					
range H···O	1.90(3)–2.03(3)	1.95(2)–2.05(2)	1.88(2)–2.02(2)	1.81(3)–1.97(3)	1.80(6)–1.88(8)
range N···O	2.648(4)–2.664(3)	2.672(2)–2.709(2)	2.621(2)–2.718(3)	2.503(4)–2.667(3)	2.503(7)–2.657(7)
intermolecular[c]					
range H···O	2.54(4)–2.62(3)	2.58(2)	2.63(2)	2.48(3)–2.65(3)	2.32(8)–2.42(5)
N1···O	3.199(3)	2.991(2)	2.968(3)	3.017(3)	–
N1···O	3.194(4)	–	–	3.088(3)	–
N2···O	3.190(4)	–	–	–	3.020(6)
N2···O	3.173(3)	–	–	–	2.984(6)
N3···O	3.194(3)	2.991(2)	2.968(3)	3.112(3)	2.971(6)
N3···O	3.187(3)	–	–	3.167(3)	3.015(6)

[a] Numbering as defined in accompanying scheme; does not always coincide with numbering in X-ray file due to different molecular structure and site symmetry. [b] Sum of absolute torsional angles within the six-membered ring (measure of puckering). [c] All contacts for H···O ≤ 2.7, and O···N ≤ 3.2 Å.

Table 2. Structure determination summary of **2**–**6**.[a]

	2	**3**	**4**	**5**	**6**
empirical formula	$C_9H_6F_9N_3O_6S_3$	$C_9H_{15}N_3O_6S_3$	$C_{12}H_{21}N_3O_6S_3$	$C_8H_6F_6N_4S_2O_6$	$C_7H_6F_3N_5O_6S$
crystal size	$0.3 \times 0.20 \times 0.15$	$0.3 \times 0.25 \times 0.2$	$0.45 \times 0.40 \times 0.25$	$0.35 \times 0.3 \times 0.2$	$0.35 \times 0.27 \times 0.03$
habit	colorless prisms	light yellow prisms	yellow prisms	yellow prisms	yellow platelets
solvent	nitromethane	acetonitrile	toluene	toluene/acetone	dichloromethane
crystal system	triclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	*P*	*Pnma*	*Pnma*	$P2_1/c$	$C2/c$
a [Å]	9.453(1)	10.060(1)	10.818(3)	13.024(2)	30.345(15)
b [Å]	9.464(2)	16.549(2)	14.177(3)	9.368(1)	9.074(5)
c [Å]	11.080(1)	8.434(1)	11.461(3)	12.491(2)	8.409(4)
α [°]	81.35(1)	90	90	90	90
β [°]	86.76(1)	90	90	108.77(1)	97.55(3)
γ [°]	60.09(1)	90	90	90	90
V [Å^3]	849.2	1404.0(5)	1757.7(13)	1443.0(6)	2295(2)
Z	2	4	4	4	8
M_r	519	357	399	432	345
ρ_{calcd} [g cm^{-3}]	2.03	1.69	1.51	1.99	2.00
absorption correction	empirical	empirical	numerical	empirical	empirical
correction factor (max/min)	1.0/0.86	1.0/0.98	0.92/0.85	1.0/0.95	0.85/1.00
absorption coeff. [cm^{-1}]	5.48	5.36	4.36	4.63	3.71
F(000)	516	744	840	864	696
range of Θ [°]	2–26.5	2–28	2–28	2–28	2–25
collected reflns	3754	1730	2186	3605	2014
independent reflns	3507	1730	2186	3455	2014
observed reflns[b]	2363	1408	1305	2442	1066
hydrogen atoms refined[c]	all N–H	all H	all N–H	all N–H	all N–H
residual electron density [e Å^{-3}]	0.62/ − 0.17	0.29/ − 0.34	0.25/ − 0.39	0.32/ − 0.24	0.28/ − 0.40
parameters refined	296	134	150	259	223
R/R_w	0.040/0.054	0.032/0.042	0.039/0.046	0.039/0.055	0.055/0.137[d]
S value	2.35	2.02	1.83	2.21	1.01

[a] Four-circle diffractometers, room temperature, $Mo_{K\alpha}$ radiation. Programs for structure solution: **2:** SIR92, DIRDIF; **3:** SHELXS-86; **4:** SIR88 (14 reflections excluded from refinement); H51, H61, H62 on calculated positions. **5:** SIR88; **6:** SHELXL97. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications nos. CCDC-104511–104515. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). [b] $I \geq 2.5\Delta\sigma(I)$; for **6**: $I \geq 2.0\Delta\sigma(I)$. [c] Those hydrogen atom positions that were located on the electron density difference map and refined isotropically. [d] Weighted R factor based on F^2 instead of F for all measured reflections.

systems investigated. Likewise, the charge distribution has a strong octopole moment, but most likely a low quadrupole moment. For example, both benzene and hexafluorobenzene have strong quadrupole moments of opposite signs, but the small moment of 1,3,5-trifluorobenzene closely corresponds to the arithmetic mean of the two former moments.[36] The significance for crystal packing lies in the fact that packing an arrangement of planar π systems with *like* quadrupole moments is optimized in T-shape geometries (Figure 1). Thus the familiar herringbone patterns, but *not* layer structures, are observed as the characteristic motifs for the packing of aromatic hydrocarbons (although many exceptions are known) that are also favorable in solution.[37, 38] Such a counteracting force is not present in molecules with a low quadrupolar moment. Layer structures with π–π stacking only result from intermolecular complexes of planar π systems with *opposite* quadrupolar moments, like in the well-known benzene–hexafluorobenzene complex and similar structures.[36, 39–43] It should be noted that minimal intermolecular charge transfer occurs in these complexes.[36] The presence of an octopolar charge distribution (Figure 1) should also favor a layer structure formed from like molecules, as the absence of a quadrupolar moment does. As the interaction energy of octopoles is small, however, the purely electrostatic influence is not likely to be structure-determining.

2.2 Crystal packing: The structures of fluorinated sulfones will be discussed first. Sulfone **2**, in which all three nitro groups have been replaced, is—in contrast to the general observations with fluorinated sulfones—a poorly soluble compound, and can be induced to form crystals suitable for X-ray analysis only with difficulty (the results of the X-ray structure determination are given in Table 2). The crystals are easily cleaved. Only one crystal form suitable for X-ray analysis could be found. The structure in the solid state is strikingly similar to the one of **1**: intermolecular hydrogen bonds are present which guarantee the formation of layers (Figure 2). The latter are of approximate trigonal symmetry and stacked in parallel. As a consequence, the CF_3 groups of one molecule all point in one direction, a conformation not likely to be favored in solution simply on the basis of statistics. Two basic stacking arrangements of layers are compatible with this arrangement of layers in **2**, namely, one where the layers expose like sides to each other, and one where unlike sides are in contact. Sulfone **2** forms a structure reminiscent of a micelle: the layers are arranged in a centrosymmetric fashion, hence, like sides are in contact. Apparently, the contact F···π system is not favorable in **2**. A particular attractive interaction between the fluorine groups that point to each other cannot be rigorously excluded, but we note that the closest distance between them, 3.087(5) Å, is slightly larger than the sum of the van der Waals radii (a radius of

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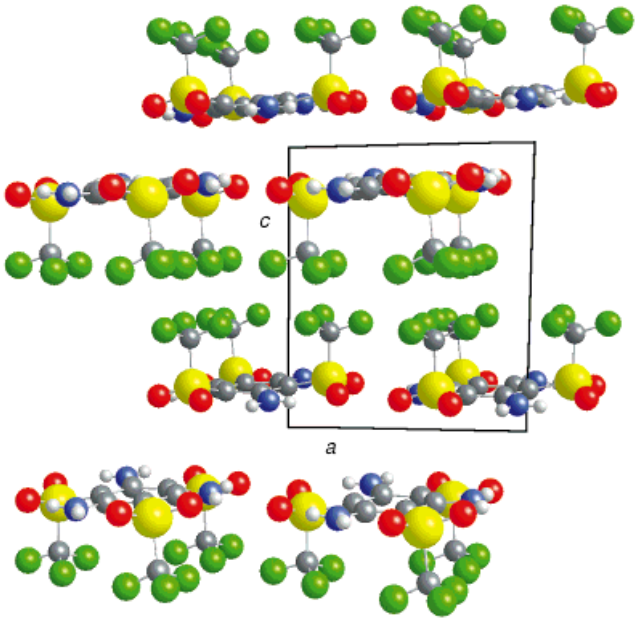

Figure 2. Packing diagram of **2**.

1.47 Å is generally assumed for Ar–F[44]). A recent statistical survey[45] of the 1995 release of CSD[1] has revealed 385 structures with a range of F···F contacts of 2.40–2.95 Å, and 1908 structures with 2.95–3.50 Å. Hence, the closest distance found here is rather on the long side.

If the structural motifs (layer structures through hydrogen-bonding and exposition of like sides resulting in π–π stacking) persisted, *planar* layer structures would no longer be expected with **5** and **6** because there would be a void in the F···F layer, especially in **6**. Space filling can be effected, however, if the layers are *tilted* with respect to each other. Accordingly, a modified layer structure is present in crystalline **5** (Figures 3 and 4; structure determination details in

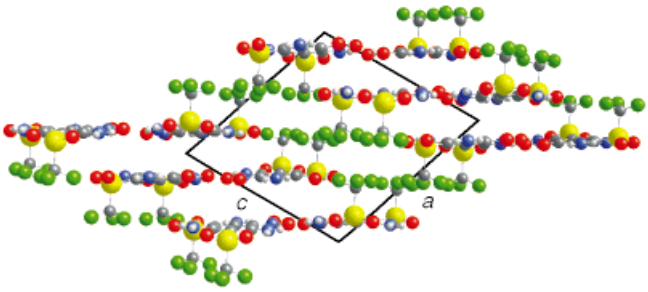

Figure 3. Packing diagram of **5**.

Table 2). Again, intermolecular hydrogen bonding is noticeable (Figure 4), but only the nitro groups and two of the amino groups are involved in it. The amino group in the position between the sulfonyl groups does not engage in *inter*molecular hydrogen bonding, nor does one of the sulfonyl groups. No indication of any F···H hydrogen bonding is detectable in accordance with recent statistical surveys;[46, 47] the closest distance amounts to 2.71(3) Å. Tilted layers, for the arrangement of arenes better described as ribbons, are formed where like sides are exposed as in the structure of **2**. The tilt angle

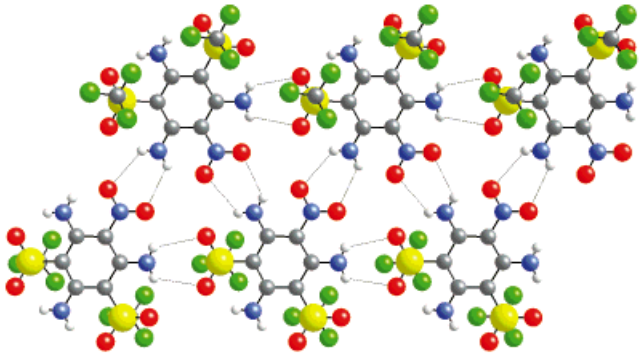

Figure 4. Intermolecular hydrogen bonding in layers of **5**.

between the least squares plane through the fluorine layer and the plane though the six-membered ring amounts to 27°. The ribbonlike packing pattern with its hydrogen-bonded inner side and its outer fluorine layer creates the impression of base-pairing in DNA (although, of course, no helical twist is present here), or a micellar structure where the hydrophobic fluorine layers are in contact and enclose a hydrophilic hydrogen-bonded arene layer. The overall features of this structure are reproduced in solid **6**, which shows a surprisingly similar arrangement of layers (Figures 5 and 6; closest F···F contact: 2.967 Å). At 53°, the inclination angle of the layers is

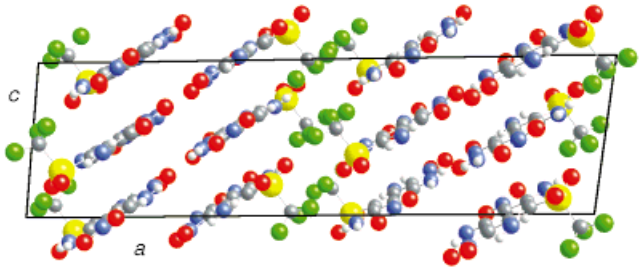

Figure 5. Packing diagram of **6**.

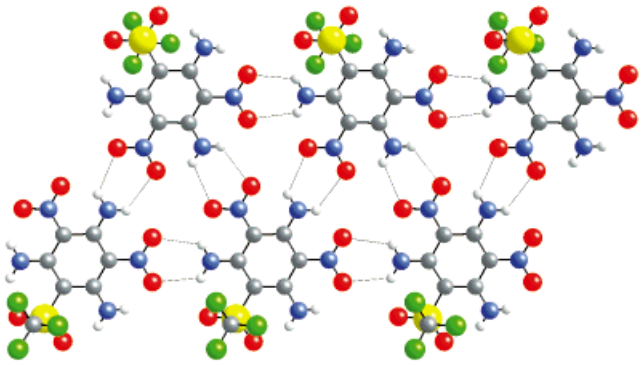

Figure 6. Intermolecular hydrogen bonding in layers of **6**.

close to double the value for **5** for reasons connected with space-filling: the fluorine layer is formed only by one instead of two CF_3 groups. Further hypothetical increase of the angle on exchange of the last sulfone with a nitro group to give **1** again yields a value of close to 90°—which corresponds to a parallel stacking of the benzene rings and thus to the planar layer structure which is indeed found for **1** (Figure 7).

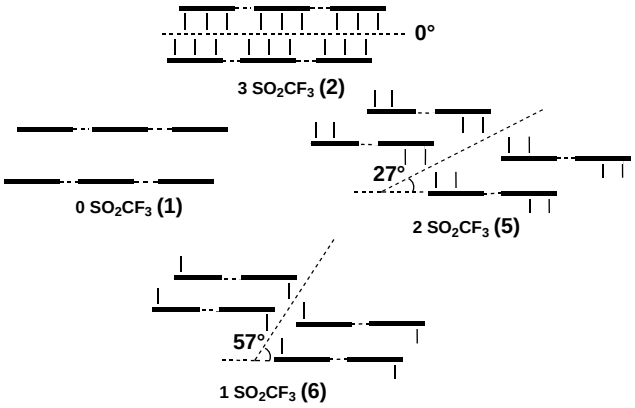

Figure 7. Inclination of planes through fluorine layers with respect to planes through six-membered rings in **1**, **2**, **5**, and **6**.

If the structures of **2**, **5**, and **6** are determined both by the attractive hydrogen bonding and the tendency for like sides of the molecule to be exposed, then exchange of CF_3 with CH_3 groups should lead to a drastic change in the observed crystal structure, although, on a purely geometric basis, this change is minor in comparison to the structural differences between **2**, **5**, and **6**. As shown in Figure 8, **3** does *not* form a layer structure (see also Table 2). The packing can be described as

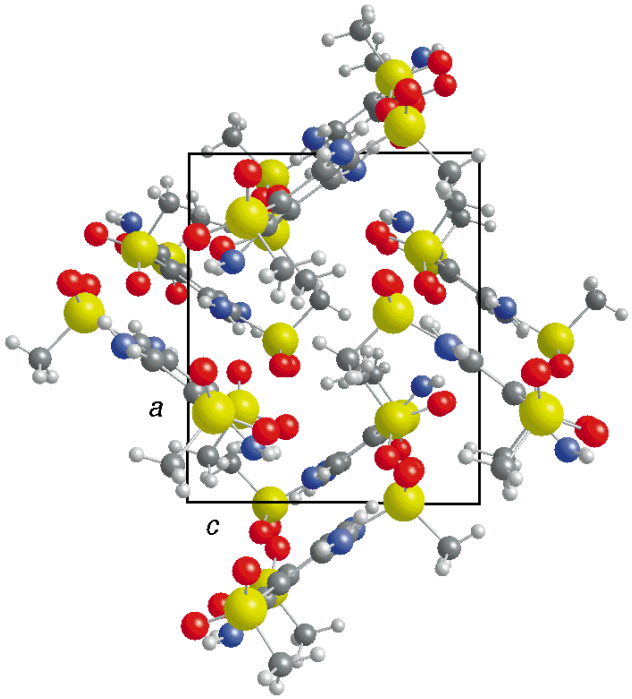

Figure 8. Packing diagram of **3**.

an arrangement of sandwich-type dimers that are oriented in an almost perpendicular fashion with respect to each other. There are two symmetry-related hydrogen bonding contacts between the two molecules in the dimeric unit. The total of four such interactions probably assists in its formation, even though with 113° the angle O-H-N is quite acute. In order to form these dimers effectively, the methyl groups have to point in one direction, a conformation not observed in solution by VT-NMR (see Experimental Section). If the methyl groups are replaced with bulkier ethyl groups, as in **4**, the conformation changes to the one favored in solution, where the alkyl chains point in both directions (Figure 9). VT-NMR shows

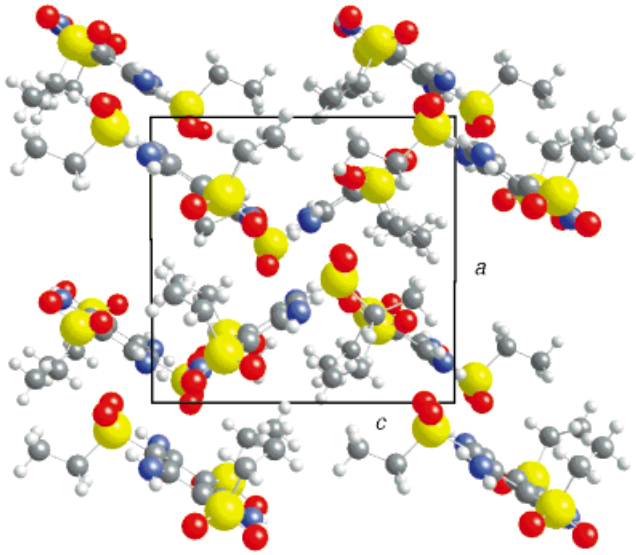

Figure 9. Packing diagram of **4**.

that this conformation is favored by at least 7.8 kJ mol^{-1} at 240 K. However, the structural features are preserved to some extent; it may therefore be concluded that this arrangement is particularly favorable. It should be noted, however, that the dimers slip apart and the hydrogen bonding, again with quite an acute angle O-H-N of 107° and with the distances on the verge of the accepted boundaries, now no longer occurs within the dimeric units, but between them.

Conclusion

We have shown that structures with planar or tilted layers are formed from 1,3,5-triaminobenzenes substituted with any combination of nitro or trifluoromethylsulfonyl groups. The arrangement is always centrosymmetric. These structures are satisfactorily explained as arising from a combination of intermolecular hydrogen bonding and the tendency of the fluorine substituents to segregate and to form layers (or ribbons). We suggest that the combination of these two effects should be a powerful control element in crystal engineering. This view is corroborated by the completely different structures observed when alkylsulfones are used as electron-attracting substituents.

Experimental Section

Melting points: hot-stage microscope or Büchi B-540. ^{1}H NMR recorded at 300.135 MHz and ^{13}C NMR at 75.469 MHz at RT, unless noted otherwise.

1,3,5-Triiodo-2,4,6-trichlorobenzene (**8**): A known iodination method was used.[25] Arene **8** has been claimed to form in 36% yield from reaction of trichlorobenzene (**7**) with $Py_2I^+BF_4^-$, but no characterization was given.[48] Powdered iodine (19.2 g, 75.1 mmol) was added to a vigorously stirred

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solution of periodic acid (5.8 g, 25 mmol) in conc sulfuric acid (180 mL). After 15 min, **7** (2.722 g, 15.00 mmol) was added to the dark solution, and the mixture stirred for 18 h at RT. It was poured onto ice, the precipitate was filtered, and washed with water, with a solution of bisulfite until the color disappeared, with methanol, and finally with ether. The residue (8.266 g, 98.6 %), nearly pure material, could be used directly in the next step. It could be recrystallized from dioxane to give colorless needles, m.p. 280.5–281.5 °C (6.615 g, 11.83 mmol, 78.9 %). ^{1}H NMR ($CDCl_3$): no signal; ^{13}C NMR (dioxane/$CDCl_3$, 50.3 MHz, 350 K): $\delta = 97.13, 144.95$; anal. calcd for $C_6Cl_3I_3$: (559.13) C 12.89, Cl + I 87.11, I 68.09; found: C 12.96, Cl + I 87.08, I 67.96.

1,3,5-Tris(methylthio)-2,4,6-trichlorobenzene (**9**): A mixture of **8** (5.048 g, 9.028 mmol), methylthiocopper (3.919 g, 35.42 mmol; prepared from methanethiol and copper(II) acetate) and α,α-dipyridyl (5.532 g, 35.42 mmol) in DMF (50 mL) was stirred at RT for 2.5 d. The mixture is then diluted with diethyl ether (300 mL) and is filtered. The precipitate was washed with the same solvent, and the combined extracts were washed three times with water, then satd brine, and were dried. Chromatography (silica, CCl_4) gave colorless prisms (2.042 g, 6.387 mmol, 70.7 %). An analytical sample was recrystallized from *n*-heptane, m.p. 114–114.5 °C. ^{1}H NMR ($CDCl_3$): $\delta = 2.43$ (s); ^{13}C NMR ($CDCl_3$): $\delta = 18.44$, 135.28, 146.73; anal. calcd for $C_9H_9Cl_3S_3$ (319.73): C 33.81, H 2.84, Cl 33.26, S 30.09; found: C 33.85, H 2.83, Cl 33.42, S 30.04.

1,3,5-Tris(ethylthio)-2,4,6-trichlorobenzene (**10**): A suspension of **8** (5.048 g, 9.028 mmol), copper ethylthiolate (4.416 g, 35.42 mmol; from freshly precipitated cuprous oxide and ethanethiol), and α,α'-bipyridyl (5.532 g, 35.42 mmol) in dry DMF (50 mL) was vigorously stirred for 4 d at RT. The mixture was diluted with diethyl ether (200 mL), and the red-brown copper complex filtered and washed with this solvent (200 mL). The filtrate was washed with water (4 × 300 mL) and brine, and dried (Na_2SO_4). The solvent was removed and the residue (4.007 g) chromatographed on silica gel eluting with CCl_4/light petroleum (1/1). Compound **10** was obtained as a colorless solid (2.160 g, 2.52 mmol, 66.1 %), m.p. 51–57 °C. An analytical sample was recrystallized from ethanol to give colorless prisms, m.p. 57.5–58 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.19$ (t, $J = 7.4$ Hz, 9 H), 2.93 (q, $J = 7.4$ Hz, 6 H); ^{13}C NMR ($CDCl_3$): $\delta = 14.52$, 29.66, 133.54, 147.93; anal. calcd for $C_{12}H_{15}Cl_3S_3$ (361.80): C 39.84, H 4.18, Cl 29.40, S 26.59; found: C 39.75, H 4.18, Cl 29.15, S 26.70. Reduction is a side reaction; 1,3-bis(ethylthio)-2,4,6-trichlorobenzene was isolated as a colorless oil in 12 % yield: ^{1}H NMR ($CDCl_3$): $\delta = 1.19$ (t, $J = 7.4$ Hz, 6 H), 2.91 (q, $J = 7.4$ Hz, 4 H), 7.52 (s, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 14.52$, 29.45, 128.78, 132.86, 141.35, 148.26.

The standard conditions to effect this Ullmann reaction (hot quinoline[49]) failed to produce any desired compound from **8**; the addition of bipyridyl (we would like to thank Prof. H.-J. Grützmacher for this suggestion) has been found to drastically increase the yield because the reaction can proceed at RT; otherwise, reductive removal of one iodine atom is observed to a considerable extent.

Reaction of **8** with $CuSCF_3$ failed to give the desired substitution product **17** in acceptable yields; about 5 % of an inseparable mixture of **17** and the corresponding reduction product bis(trifluoromethylthio)trichlorobenzene was isolated.

1,3,5-Tris(methylsulfonyl)-2,4,6-trichlorobenzene (**11**): To a stirred solution of the tristhioether **9** (1.610 g, 5.035 mmol) in glacial acetic acid (20 mL) at 100 °C, 30 % hydrogen peroxide (20 mL) was added dropwise. After being stirred for a further 2 h, the mixture was cooled, and the precipitate formed filtered and washed with water (1.608 g, 3.868 mmol, 76.8 %). An analytical sample was crystallized from nitromethane, colorless needles, decomp > 285 °C. The trisulfone is poorly soluble in most solvents; solutions of analytically pure samples in CD_3CN or DMSO decomposed appreciably. Impurities are not quoted in the following NMR data: ^{1}H NMR (CD_3CN): $\delta = 3.42$ (s); ^{13}C NMR ([D_6]DMSO): 45.34, 116.61, 128.91 (double intensity), 138.73 (double int), 167.99; anal. calcd for $C_9H_9Cl_3O_6S_3$ (415.72): C 26.00, H 2.18, Cl 25.58, S 23.14; found: C 26.28, H 2.24, Cl 25.78, S 23.31.

1,3,5-Tris(ethylsulfonyl)-2,4,6-trichlorobenzene (**12**): A solution of **10** (863 mg, 2.39 mmol) in glacial acetic acid (10 mL) was heated to 100 °C and treated dropwise with 30 % hydrogen peroxide (10 mL, 88 mmol). After 15 min, a colorless precipitate began to form, and heating was continued for 2 h. After cooling, the suspension was filtered and the precipitate washed with water. **12** was obtained as small colorless prisms (983 mg, 2.15 mmol, 90.0 %), m.p. ca. 260–275 °C (decomp) which could be recrystallized from dioxane without improvement in purity or alteration of the decomposition point. ^{1}H NMR ([D_6]DMSO; decomposes slowly in this solvent): $\delta = 1.12$ (t, $J = 7.3$ Hz, 6 H), 1.26 (t, $J = 7.4$ Hz, 3 H), 3.40 (q, $J = 7.4$ Hz, 2 H), 3.49 (q, $J = 7.3$ Hz, 4 H); ^{13}C NMR ([D_6]DMSO): $\delta = 6.77$, 7.20 (double int), 50.16 (double int), 50.99, 114.17, 126.38 (double int), 140.07 (double int), 168.95; MS (EI): 456 (M^+ for $^{35}Cl_3$, 6.3 %; isotope cluster in accordance with proposed formula); anal. calcd for $C_{12}H_{15}Cl_3O_6S_3$ (457.80): C 31.48, H 3.30, Cl 23.23; S 21.01; found: C 31.59, H 3.42, Cl 23.07, S 20.80.

1,3,5-Tris(methylsulfonyl)-2,4,6-triaminobenzene (**3**): Under slight pressure, dry ammonia was bubbled through a solution of the trichloride **11** (0.800 g, 1.92 mmol) in dry DMSO (10 mL). A yellow color developed, and the mixture was kept tightly closed overnight. It was diluted with water and neutralized with dil HCl, then extracted with dichloromethane. The organic layers are washed with water and satd brine, and dried to give a faintly yellow powder (673 mg, 1.88 mmol, 97.9 %) which is further purified by chromatography (silica, CH_2Cl_2/2 % MeOH); from toluene: large, light yellow plates, decomp > 280 °C. ^{1}H NMR ([D_6]DMSO): $\delta = 3.23$ (s, 9 H), 7.73 (br s, 6 H); ^{13}C NMR ([D_6]DMSO): $\delta = 42.86$, 93.41, 152.35. The molecule has C_s symmetry on the NMR time scale at 220 K and below (one methyl group up, two down). The ^{1}H NMR shows the intramolecular hydrogen bonds to be frozen because the three expected singlets of equal intensities in the N–*H* region are found: ^{1}H NMR (240 K, [D_6]acetone): $\delta = 3.25$ (s, 6 H), 3.29 (s, 3 H), 7.90 (s, 2 H), 7.94 (s, 2 H), 8.03 (s, 2 H); anal. calcd for $C_9H_{15}N_3O_6S_3$ (357.43): C 30.24, H 4.23, N 11.76, S 26.91; found: C 30.27, H 4.27, N 11.88, S 26.68.

1,3,5-Tris(ethylsulfonyl)-2,4,6-triaminobenzene (**4**): Dry ammonia was bubbled through a suspension of the sulfone **12** (326 mg, 0.712 mmol) in dry DMSO (15 mL); the vessel was held at an overpressure of 0.5 bar. The mixture turned yellow, and the sulfone dissolved. The mixture was allowed to stand overnight; dil HCl was then added and the mixture extracted with dichloromethane (3 × 15 mL). The combined organic layers were washed with water (3 ×) and brine, and dried (Na_2SO_4). The solvent was evaporated and the residue (284 mg) chromatographed over silica gel (200 g) eluting with diethyl ether. Compound **4** was isolated as colorless prisms (201 mg, 0.503 mmol, 70.7 %), m.p. 176.5–178 °C (from *n*-heptane/toluene). ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (t, $J = 7.4$ Hz, 9 H), 3.23 (q, $J = 7.3$ Hz, 6 H), 7.89 (br s, 6 H); ^{13}C NMR ($CDCl_3$): $\delta = 6.94$, 49.31, 91.18, 154.04. The molecule has C_s symmetry on the NMR time scale at 240 K and below (one ethyl group up, two down). The ^{1}H NMR shows the intramolecular hydrogen bonds to be frozen because the three expected singlets of equal intensities are found in the N–*H* region. A small additional singlet in this region integrating for 0.1 H may be ascribed to the presence of the C_3 symmetric conformer where all N–*H* are isochronous. This conformer would then be present in roughly 2 %: ^{1}H NMR (500 MHz, 240 K, CD_2Cl_2): $\delta = 1.24$ (t, $J = 7.2$ Hz, 9 H), 3.19 (m, 8 H), 7.76 (s, 2 H), 7.82 (s, 0.1 H), 7.88 (s, 2 H), 7.93 (s, 2 H); ^{13}C NMR (125 MHz, 240 K, CD_2Cl_2): $\delta = 7.17$, 48.98 and 49.06 (int 1:2), 90.11 and 90.33 (int 1:2), 153.53 and 154.55 (int 2:1); anal. calcd for $C_{12}H_{21}N_3O_6S_3$ (399.51): C 36.08, H 5.30, N 10.52, S 24.08; found: C 36.23, H 5.27, N 10.54, S 24.11.

3,5-Bis(trifluoromethylsulfonyl)-2,6-dichloroaniline (**21**): A solution of the aniline **20**[26, 50] (418 mg, 1.17 mmol) in acetic acid (10 mL) and 15 % HCl (2 mL) was saturated with chlorine gas at RT. After 30 min, colorless needles separate; the solution is saturated with chlorine gas again after 3 h. After standing overnight, the solution is extracted with dichloromethane to give almost pure (TLC) **21** (502 mg, quant) containing only small amounts of the trichlorination product as judged by MS. Conducting the reaction at reflux temperature with continuous saturation with chlorine only decreased the yield of **21**; only small amounts of trichlorinated product were formed. Faintly yellow, large prisms, m.p. 163.5–164 °C (slow evaporation from CH_2Cl_2), ref. [23] m.p. 157–158 °C. ^{1}H NMR ([D_6]acetone, 500 MHz): $\delta = 6.82$ (br s, 2 H), 8.11 (s, 1 H); ^{13}C NMR ([D_6]DMSO, 125 MHz): $\delta = 120.63$ (q, $J = 326.4$ Hz), 124.71 (CH), 126.87, 130.13 (q, $J = 2.0$ Hz), 148.62; MS (EI): M^+: 431 (0.8), 430 (1.2), 429 (11.5), 428 (5.5), 427 (45.7), 426 (8.2), 425 (53.5); intensities in accordance with composition $C_8H_3Cl_2F_6NO_4S_2$.

1,3,5-Tris(trifluoromethylsulfonyl)-2,4,6-triaminobenzene (**2**): From **18** (260 mg, 0.450 mmol) and ammonia in dry dichloromethane. The precipitate was filtered after 3 d and washed with water. The residue was crystallized from nitromethane to give colorless small platelets with a pinkish tinge, m.p. 261.5–262.5 °C (55 mg, 0.11 mmol, 24 %). The analyti-

cally pure compound shows two signals in the ^{1}H NMR and also two signals for *C*–S, possibly indicating freezing in the conformation with C_s symmetry. ^{1}H NMR ([D$_6$]DMSO): $\delta = 8.33$ and 8.53 (br s; int 2.7:1); ^{13}C NMR ([D$_6$]DMSO): $\delta = 80.72$ (br), 80.94 (br), 120.28 (q, $J = 328.1$ Hz), 157.07 (br); anal. calcd for $C_9H_6F_9N_3O_6S_3$ (519.35): C 20.81, H 1.16, N 8.09, S 18.52; found: C 20.78, H 1.13, N 8.06, S 18.39.

1,3-Bis(trifluoromethylsulfonyl)-5-nitro-2,4,6-trichlorobenzene (**23**): From the nitroso compound **22** by oxidation with CrO_3.[23] Compound **22** in turn was obtained from **15** by reaction with trifluoroperacetic acid. We found the reaction **15** →**22** to proceed at -10 to -5 °C for 2 h, but only slowly at the reported temperature of -20 °C.[23] Prolonged reaction times at RT led to overoxidation. Data for **23**: m.p. 136–138 °C (lit. m.p.); ^{1}H NMR (CD$_3$CN) no signal; ^{13}C NMR (CD$_3$CN): $\delta = 120.78$ (q, $J = 327.5$ Hz), 127.29, 134.45 (q, $J = 2.9$ Hz), 139.77, 147.95, 152.88 (br).

1,3-Bis(trifluoromethylsulfonyl)-5-nitro-2,4,6-triaminobenzene (**5**): Ammonia was bubbled through a solution of **23** (258 mg, 0.526 mmol) in dry CH_2Cl_2 (30 mL). After 1 d the precipitate was filtered over silica (acetone, $CHCl_3$) to give a yellow powder (232 mg, quant) which was recrystallized from toluene to give yellow prisms (122 mg), 243.5–244.5 °C. ^{1}H NMR ([D$_6$]DMSO): δ = ca. 8.4 and 9.0 (v br s; int ca. 1:2); ^{13}C NMR ([D$_6$]DMSO): $\delta = 79.73$ (br), 114.62, 120.33 (q, $J = 328.4$ Hz), 152.98, 156.10; anal. calcd for $C_8H_6F_6N_4O_6S_2$ (432.28): C 22.23, H 1.40, N 12.96; found: C 22.32, H 1.45, N 13.04.

2,4,6-Trichloro-3,5-dinitroaniline (**25**):[51] A solution of 3,5-dinitroaniline[52] (5.494 g, 30.60 mmol) in glacial acetic acid (130 mL) and conc HCl (85 mL) was treated at 10–16 °C with 30% H_2O_2 (43 mL, 0.42 mol); the cooling bath was removed, and the temperature was allowed to rise to 32 °C. Yellow crystals separated and were collected once the exothermic reaction had subsided (7.539 g, 26.32 mmol, 87.7%). Crystallization from toluene/*n*-heptane gave yellow prisms, m.p. 229.5–231.5 °C (lit. m.p. 230 °C[51] from EtOH). ^{1}H NMR ([D$_6$]DMSO): 7.24 (s); ^{13}C NMR ([D$_6$]DMSO): δ = 100.61, 110.48, 144.04, 146.64.

2,4,6-Trichloro-3,5-dinitroiodobenzene (**26**): A solution of the aniline **25** (3.000 g, 10.47 mmol) in hot glacial acetic acid (20 mL) was rapidly cooled while being stirred. The resulting fine suspension was added to nitrosylsulfuric acid [from 787 mg (11.4 mmol) $NaNO_2$ and conc sulfuric acid (25 mL)] at 5 °C. the mixture was stirred for 30 min at RT, and was then added to KI/I$_2$ (4 g each) in water (50 mL). The mixture was heated to boiling, then cooled, the excess iodine removed by bisulfite, the precipitate filtered and washed with water, satd bicarbonate, then water. It was then washed through with diethyl ether, and the solution dried (Na_2SO_4). Filtration over silica gel (CH_2Cl_2/PE = 1/1) gave colorless crystals (3.592 g, 9.040 mmol, 86.3%). An analytical sample had m.p. 192.5–194.5 °C (from *n*-heptane/toluene). ^{1}H NMR ($CDCl_3$): no signal; ^{13}C NMR ($CDCl_3$): δ = 106.53, 119.53, 134.31, 146.10 (br); anal. calcd for $C_6Cl_3IN_2O_4$ (399.51): C 18.14, H 0.00, N 7.05, Cl 26.77, I 31.94; found: C 18.27, H 0.00, N 7.10, Cl 26.96, I 32.20.

Reaction of **26** with $CuSCF_3$ in DMF did not give the substitution product **32**.

3,5-Dinitroiodobenzene (**27**):[53] M.p. 100.5–103 °C, then recrystallizing and melting at 104.5–105.5 °C (first from EtOH, then from *n*-heptane/toluene), lit. m.p.[53] 99–100 °C (EtOH). ^{1}H NMR ($CDCl_3$): $\delta = 8.86$ (d, $J = 2.0$ Hz, 2H), 8.98 (t, $J = 2.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 93.33$, 118.26, 137.59, 148.43.

3-iodo-5-nitroaniline (**28**): Obtained from **27** according to ref. [54], but with NaHS solution as described for **34**, 50% yield after recrystallization from EtOH, still impure, m.p. 131–137 °C (ref. [54]: yield 35% with m.p. 135.5–139 °C and 140–141 °C when pure). ^{1}H NMR ([D$_6$]acetone]: $\delta = 5.53$ (br s, 2H), 7.41 (dd, $J = 2.1$ and 3.2 Hz, 1H), 7.48 (t, $J = 3.1$ Hz, 1H), 7.65 (dd, J = 2.0 and 3.1 Hz, 1H). It did not give 3-nitro-5-trifluoromethylthioaniline on reaction with $CuSCF_3$.

3,5-Dinitrotrifluoromethylthiobenzene (**29**): From **27**[53] by reaction with $CuSCF_3$[55] in DMF (cf. ref. [56]). Purified by chromatography (silica gel, CCl_4/Et$_2$O = 98/2); yellowish oil, yield, 94%.

3-Nitro-5-trifluoromethylthioaniline (**30**): A solution of NaHS in water/MeOH (237 mL of a 0.464 M solution, 110 mmol) was added in a thin stream to a refluxing solution of the dinitrosulfide **29** (17.855 g, 66.581 mmol) in MeOH (200 mL). The solution turns orange, then brown. After the addition, reflux is continued for 30 min. After cooling, the solution is extracted with CH_2Cl_2 (13.97 g) and chromatographed (silica, CH_2Cl_2/PE = 1/1; 9.553 g). Recrystallizion from *n*-heptane gives yellow needles (9.142 g, 38.38 mmol, 57.6%), m.p. 117–121 °C. For analysis, a sample is recrystallized again from heptane and then sublimed (110 °C/0.1 Torr), m.p. ca. 90 °C, recrystallizing and then melting at 118.5–120 °C. ^{1}H NMR (CD_2Cl_2): 7.24 (prob. ddq, $J = 1.5$, 2.5 and 0.5 Hz), 7.58 (pseudo-t, $J = 2.2$ Hz), 7.79 (ddq, $J = 1.5$, 2.5 and 0.5 Hz); ^{13}C NMR (CD_2Cl_2): δ = 111.38, 119.61 (q, $J = 1.0$ Hz), 126.95 (q, $J = 2.5$ Hz), 127.12 (q, $J = 0.8$ Hz), 129.78 (q, $J = 308.4$ Hz), 148.95, 149.86 (br); anal. calcd for $C_7H_5F_3N_2O_2S$ (238.19): C 35.30, H 2.12, N 11.76, S 13.46; found: C 35.28, H 2.15, N 11.80, S 13.58.

2,4,6-Trichloro-3-nitro-5-trifluoromethylthioaniline (**31**): The aniline **30** (0.800 g, 3.36 mmol) is chlorinated (9.5 mL HCl, 15 mL AcOH, 4.8 mL 30% H_2O_2) as described for **25**. Crude yield, 1.084 g (3.17 mmol, 94%), yellow prisms from heptane (766 mg, 2.24 mmol, 66%) that contain a small amount of dichlorinated product, m.p. 92.5–99 °C. The mother liquor is chromatographed (PE/CH_2Cl_2 = 7/3) and crystallized again from heptane; yellow prisms, m.p. 99–101 °C. ^{1}H NMR ($CDCl_3$): 5.02 (br s); ^{13}C NMR ($CDCl_3$): $\delta = 113.79$, 120.47 (q, $J = 1.2$ Hz), 123.92 (q, $J = 2.3$ Hz), 128.38 (q, $J = 0.8$ Hz), 128.56 (q, $J = 312.2$ Hz), 141.38, 143.22 (?, br); anal. calcd for $C_7H_2Cl_3F_3N_2O_2S$ (341.53): C 24.62, H 0.59, N 8.20, Cl 31.14, S 9.39; found: C 24.61 H, 0.70, N 8.24, Cl 31.37, S 9.13.

2,4,6-Trichloro-3,5-dinitrotrifluoromethylthiobenzene (**32**): **CAUTION! Concentrated hydrogen peroxide and trifluoroperacetic acid are powerful oxidants and may explode in contact with organic matter (dust particles, residues in sintered glass funnels) or metal salts! For the handling of these compounds, only glassware thoroughly cleaned with conc sulfuric acid and rinsed with distilled water should be used.** The aniline **31** was oxidized as described for **35** (see below) and chromatographed (PE/CH_2Cl_2 = 9/1). M.p. 86.5–87.5 °C (heptane); ^{1}H NMR ($CDCl_3$): no signal; ^{13}C NMR ($CDCl_3$): $\delta = 123.66$, 127.52 (q, $J = 2.4$ Hz), 128.02 (q, $J = 313.4$ Hz), 137.06 (q, $J = 0.8$ Hz), 147.83 (br); anal. calcd for $C_7Cl_3F_3N_2O_4S$ (371.51): C 22.63, H 0.00, N 7.54, S 8.63, Cl 28.63; found: C 22.60, H 0.00, N 7.63, S 8.84, Cl 28.41; MS (EI): 376 (3.1), 375 (2.2), 374 (35.0), 373 (7.9), 372 (100), 371 (8.0), 370 (85.8): M^+, intensities in accordance with proposed composition. The oxidation can be stopped at the nitroso stage, if the colorless precipitate that forms at -10 °C is collected after 150 min (yield, 62%); pure by TLC, m.p. 139–140 °C. 2,4,6-Trichloro-3-nitro-5-nitrosotrifluoromethylthiobenzene gives no signal in ^{1}H NMR, and a complex ^{13}C NMR (probably due to association). However, the MS (EI) is unequivocal: 360 (0.5), 359 (0.3), 358 (5.3), 357 (1.1), 356 (14.1), 355 (1.1), 354 (13.7). Both the nitroso compound and **32** only give water-soluble material on attempted oxidation with CrO_3 in TFAA/H_2SO_4 mixtures.

3,5-Dinitrotrifluoromethylsulfonylbenzene (**33**): By CrO_3 (2.5 g, 25 mmol) oxidation of the above thioether (2.326 g, 8.674 mmol) in TFAA/sulfuric acid mixture at RT, and purified by chromatography (silica gel, CH_2Cl_2). Colorless powder, m.p. 93–95 °C (2.216 g, 7.382 mmol, 85.1%). ^{1}H NMR ([D$_6$]acetone): $\delta = 9.20$ (dq, $J = 2.0$ and 0.5 Hz, 2H), 9.49 (t, $J = 2.0$ Hz, 1H); ^{13}C NMR ([D$_6$]acetone): $\delta = 120.44$ (q, $J = 325.4$ Hz), 127.38, 131.49 (q, $J = 0.8$ Hz), 134.99 (q, $J \approx 1.4$ Hz), 150.75. Compound **33** has been described in the literature, but no characterization was given.[57]

3-Nitro-5-trifluoromethylsulfonylaniline (**34**): To a boiling solution of the dinitrosulfone **33** (2.091 g, 6.966 mmol) in methanol (20 mL), a solution of NaHS (16 mL of a 0.70 M solution,[31] 11 mmol; pH 10–11) was added in one portion. The deep red color (Meisenheimer complex) changes within 30 min further reflux to a deep brown. The methanol is removed on a rotary evaporator, the mixture filtered, and the residue washed thoroughly with diethyl ether. The filtrate is washed with water, satd brine, and dried. Chromatography (silica, CH_2Cl_2) and crystallization from toluene/*n*-heptane gives orange-brown needles, m.p. 165–172 °C (395 mg, 1.46 mmol, 21.0%). For analysis, a sample was rechromatographed (silica, Et$_2$O) and crystallized again from *n*-heptane/toluene to give yellow needles, m.p. 171–172 °C. ^{1}H NMR ([D$_6$]acetone): 7.68 (ddq, $J = 1.7$, 2.3 and 0.6 Hz), 7.87 (ddq, $J = 1.6$, 2.1 and 0.5 Hz), 8.00 (pseudo-t, $J = 2.2$ Hz); ^{13}C NMR ([D$_6$]acetone): $\delta = 111.88$ (q, $J = 0.8$ Hz), 115.95, 120.12 (q, $J = 0.7$ Hz), 120.61 (q, $J = 325.3$ Hz), 133.74 (q, $J = 1.5$ Hz), 150.87, 152.69; anal. calcd for $C_7H_5F_3N_2O_4S$ (270.19): C 31.12, H 1.87, N 10.37, S 11.87; found: C 31.22, H 1.87, N 10.39, S 11.97.

2,4,6-Trichloro-3-nitro-5-trifluoromethylsulfonylaniline (**35**): To a stirred and cooled solution of the aniline **34** (500 mg, 1.85 mmol) in acetic acid (8 mL) and conc HCl (5 mL), 30% H_2O_2 (3 mL) was added. A precipitate

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formed. After 3.5 h, the mixture was heated briefly to reflux. After standing overnight, it was diluted with water and extracted with dichloromethane (3 ×). The extracts were washed with bicarbonate solution and dried. Chromatography (silica, $Et_2O/CH_2Cl_2/PE = 1/1/2$) and crystallization from *n*-heptane gave faintly yellow prisms; m.p. 137–138.5 °C (525 mg, 1.41 mmol, 76.0 %). ^{1}H NMR ([D$_6$]acetone): 6.73 (brs); ^{13}C NMR ([D$_6$]acetone): $\delta = 114.44$, 117.36, 120.71 (q, $J = 327.4$ Hz), 123.90, 128.10 (q, $J = 2.3$ Hz), 145.94, 150.36 (br); anal. calcd for $C_7H_2Cl_3F_3N_2O_4S$ (373.52): C 22.51, H 0.54, N 7.50, S 8.58, Cl 28.47; found: C 22.59, H 0.67, N 7.53, S 8.34, Cl 28.40; MS (EI): 378 (2.3), 377 (1.4), 376 (16.2), 375 (4.6), 374 (48.3), 373 (4.7), 372 (49.4): M^+, intensities in accordance with proposed formula.

2,4,6-Trichloro-3,5-dinitro-5-trifluoromethylsulfonylbenzene (**36**): **Caution! See warning above for the handling of conc peroxide!** ≈85 % hydrogen peroxide[58] (3 mL) was added in portions to trifluoroacetic anhydride (20 mL) with stirring at 0 °C. After several min, the biphasic mixture became homogeneous in an exothermic (*Caution!*) reaction. This reaction has to be awaited before the next portion is added. The aniline **35** (113 mg, 0.303 mmol) was added at 0 °C and slowly dissolved. A blue-greenish color was observed (probably nitroso compound) and a precipitate formed. The ice bath was removed after 4 h, and the mixture was stirred at RT overnight, whereupon the precipitate slowly dissolved to give a colorless solution. This was cooled again, and ice was added, whereupon a colorless precipitate was formed. After 30 min stirring, the almost pure **36** was filtered, washed with water, and dried (130 mg, 0.322 mmol, quant); m.p. 142–144.5 °C. For analysis, it was purified by sublimation (120 °C, 0.1 Torr); almost no residue was observed, m.p. 146–147 °C. ^{1}H NMR (CD_3CN): no signal; ^{13}C NMR (CD_3CN): $\delta = 120.56$ (q, $J = 326.9$ Hz), 128.34, 123.90, 131.27 (q, $J = 2.1$ Hz), 134.62, 150.56 (br); anal. calcd for $C_7Cl_3F_3N_2O_6$ (403.51): C 20.84, H 0.00, N 6.94, S 7.95, Cl 26.36; found: C 20.93, H 0.00, N 7.04, S 8.23, Cl 26.53; MS (EI): 408 (0.5), 407 (0.3), 406 (3.9), 405 (1.0), 404 (11.0), 403 (1.0), 402 (10.8): M^+, intensities in accordance with proposed formula.

1,3,5-Triamino-2,4-dinitro-6-trifluoromethylsulfonylaniline (**6**): Ammonia was bubbled through a solution of the trichloro compound **36** (205 mg, 0.508 mmol) in dry CH_2Cl_2. The mixture soon turned yellow, and a cloudy precipitate was formed. The mixture was kept in a tightly closed container for 1.5 d, during which time the triamine **6** crystallized as yellow platelets, which were removed by filtration and washed with water to remove ammonium chloride (170 mg, 0.492 mmol, 96.9 %), m.p. 273–274 °C. Recrystallization from either acetonitrile or nitromethane did not alter the observed m.p.. ^{1}H NMR ([D$_6$]DMSO): 9.19 (brs); ^{13}C NMR ([D$_6$]DMSO): $\delta = 78.38$ (q, $J = 2.1$ Hz), 113.77, 120.40 (q, $J = 328.5$ Hz), 149.71, 151.86; anal. calcd for $C_7H_6F_3N_5O_6S$ (345.22): C 24.35, H 1.75, N 20.29, S 9.29; found: C 24.33, H 1.78, N 20.22, S 9.28.

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