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Perfluorinated *cyclo*-tetrakis(phenylene sulfides): synthesis and structure

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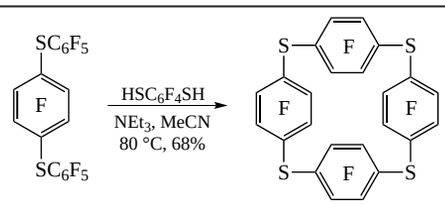
Perfluoro-*cyclo*-tetrakis(1,4-phenylene sulfide) has been synthesized by the reaction of tetrafluorobenzene-1,4-dithiol with perfluoro-1,4-bis(phenylthio)benzene. The reaction of tetrafluorobenzene-1,4-dithiol with perfluoro-*m*-xylene gives a macrocycle with 1,3- and 1,4-arrangement of bridged sulfur atoms.



Keywords: macrocycles, perfluoro-*cyclo*-tetrakis(phenylene sulfides), hexafluorobenzene, tetrafluorobenzene-1,4-dithiol, perfluoro-*m*-xylene, organofluorine compounds, organosulfur compounds, X-ray analyses.

Sulfur-containing macrocycles are widely used as platforms in supramolecular chemistry. However, the majority of them belongs to thiacalixarenes which have a 1,3-arrangement of bridged sulfur atoms in aromatic nuclei.[1,2] Macrocycles with a 1,4-arrangement of sulfur atoms have not been widely used, probably, due to the lack of convenient synthetic methods.[2] On the other hand, the effect of macrocyclization using 1,4-sulfur-containing polyfluoroarenes is proposed for the study of protein structures.[3] Cyclotetra(*p*-phenylene sulfide), along with cyclopenta(*p*-phenylene sulfide), was initially isolated in low yield from commercially available linear poly(*p*-phenylene sulfide).[4] Subsequently, a method was proposed for the synthesis of various macrocyclic *p*-phenylene sulfides (n = 4–8) using α,ω-dihalogenodiaryl sulfides as starting compounds.[5] Macrocycles containing bridged SO_2,[6] S–S[7–10] and S–CH_2[9,10] groups with 1,4-arrangement in aromatic nuclei are also known.

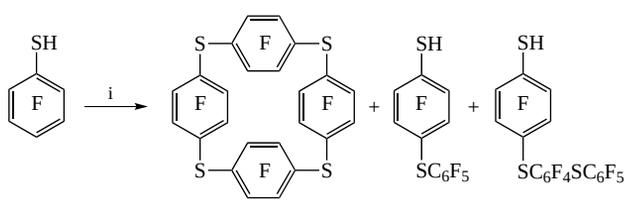
We have previously synthesized polyfluorinated thia- and oxathia calixarenes using perfluoro-*m*-xylene and 2,5-difluoro-4,6-bis(trifluoromethyl)benzene-1,3-dithiol.[11] In this paper, we report on the synthesis of perfluorinated macrocycles using tetrafluorobenzene-1,4-dithiol **1** as the starting compound. Similar macrocycles with S–S bridge groups were obtained earlier by oxidation of compound **1**.[7,8]

It is known that pentafluorothiophenol in the reaction with hexafluorobenzene easily forms perfluorinated poly(*p*-phenylene sulfide). The assumption about the linear structure of that polymer and the chain length (~10 aromatic nuclei) was made on the basis of the ratio (1 : 4) between pentafluorobenzene and 2,3,5,6-tetrafluorobenzene formed upon desulfurization under the action of Raney nickel.[12] It is also known that pentafluorothiophenol itself would readily polymerize under the action of bases.[13] To test the possibility of the formation of four-membered perfluorocyclotetrakis(*p*-phenylene sulfide) **2**, we carried out this reaction under conditions favorable for cyclooligomerization (Scheme 1). Indeed, the formation of macrocycle **2** was recorded when a dilute DMF solution (~0.08 mol dm^{-3}) of pentafluorothiophenol was kept at 20 °C for 52 h and then heated at 80 °C for 4 h. The resulting soluble mixture of oligomerization products contained, according to GC–MS, 9% of macrocycle **2** along with compounds **3**, **4** having possibly two (65%) and three (6%) aromatic nuclei.

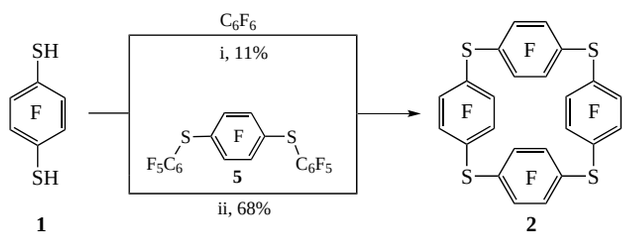
Another approach to the synthesis of macrocycle **2** and other similar macrocycles is to use tetrafluorobenzene-1,4-dithiol **1** as one of the initial components. We investigated herein the reaction of dithiol **1** with hexafluorobenzene and with perfluoro-1,4-bis(phenylthio)benzene **5**. In the first case, compound **2** was isolated in 11% yield, whereas the second method provided 68% yield (Scheme 2, for synthetic details, see Online Supplementary Materials).

The assembling of dithiol **1** with perfluoro-*m*-xylene **6** in two separate stages affords perfluoro-1,4-bis(2,4-dimethylbenzene-thio)benzene **7** and macrocycle **8** in 55% yield (Scheme 3).

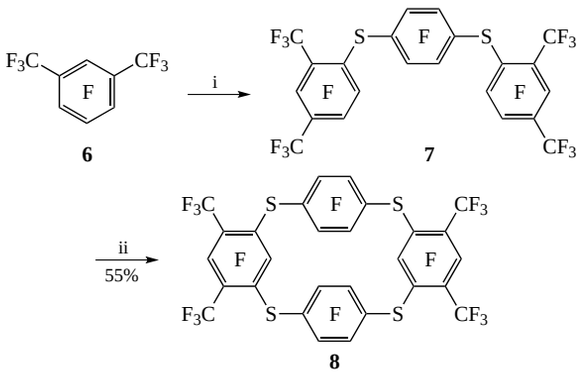
The structures of compound **7** and macrocycles **2**, **8** were determined on the basis of analytical and spectral data. Macrocycle **2** has one singlet signal in the ^{19}F NMR spectrum (δ –133.7), which is expected for a highly symmetric molecule. Macrocycle **8** can exist in solution as two ('boat' and 'chair') conformers. The possibility of implementing these conformers



Scheme 1 *Reagents and conditions*: i, DMF, ~0.08 mol dm^{-3} dilution, 20 °C, 52 h, then 80 °C, 4 h.



Scheme 2 *Reagents and conditions*: i, NEt_3, DMF, 80 °C; ii, NEt_3, MeCN, 80 °C.



Scheme 3 *Reagents and conditions*: i, *p*-HSC_6H_4SH **1**, NEt_3, acetone, 20 °C; ii, *p*-HSC_6H_4SH **1**, NEt_3, MeCN, 80 °C.

for the hydrocarbon analogue of compound **8** has been discussed.[10,14] One set of four sharp signals in the NMR spectra of macrocycle **8** at room temperature can indicate both the realization of one symmetric conformation as well as a very fast conformational equilibrium in the NMR time scale. Unfortunately, it is not possible to carry out a detailed conformational analysis by NMR methods for compound **8**, similar to those described for tetrathiacalixarenes,[15] due to the extremely low solubility of this compound.

The structures of macrocycles **2**, **8** were also confirmed by the X-ray data (Figure 1).†

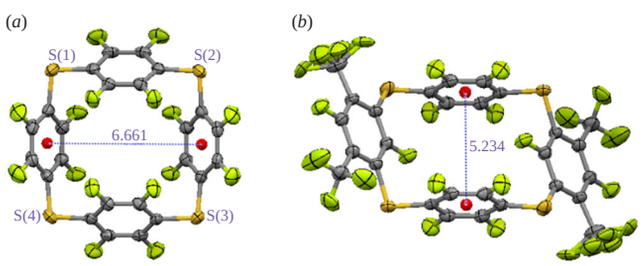


Figure 1 Molecular structures of (*a*) macrocycle **2** and (*b*) macrocycle **8**.

† *Crystal data for* **2**. Crystals of $C_{24}F_{16}S_4$ (M = 720.48) are triclinic, space group $P\bar{1}$, at 296(2) K, a = 11.0558(6), b = 11.2166(6) and c = 12.3849(6) Å, α = 109.591(2)°, β = 103.895(2)°, γ = 109.990(2)°, V = 1245.8(1) Å^3, Z = 2, d_{calc} = 1.921 g cm^{-3}, μ(MoKα) = 0.518 mm^{-1}, F(000) = 704. 42407 reflections were measured (θ < 30°) and 7308 independent reflections (R_{int} = 0.0365) were used for further refinement. The refinement converged to wR_2 = 0.1198 and GOF = 1.007 for all independent reflections [R_1 = 0.0419 was calculated against F for 5630 observed reflections with $I > 2\sigma(I)$].

Crystal data for **8**. Crystals of $C_{28}F_{24}S_4$ (M = 920.52) are triclinic, space group $P\bar{1}$, at 296(2) K: a = 6.0190(6), b = 9.2675(9) and c = 13.9188(14) Å, α = 103.573(4)°, β = 100.727(4)°, γ = 98.416(4)°, V = 726.71(13) Å^3, Z = 1, d_{calc} = 2.103 g cm^{-3}, μ(MoKα) = 0.507 mm^{-1}, F(000) = 448. 11991 reflections were measured (θ < 28°) and 3484 independent reflections (R_{int} = 0.1602) were used for further refinement. The refinement converged to wR_2 = 0.1984 and GOF = 1.126 for all independent reflections [R_1 = 0.0649 was calculated against F for 2816 observed reflections with $I > 2\sigma(I)$]. The CF_3 group is disordered in a ratio of 0.508(5) : 0.492(5).

The X-ray diffraction experiments for **2** and **8** were carried out on a Bruker KAPPA APEX II diffractometer with graphite monochromated MoKα (λ = 0.71073 Å) radiation. The structures were solved by direct methods and refined by full-matrix least-squares method against all F^2 in anisotropic approximation using the SHELXT-2014 and SHELXL-2018 set of programs. Absorption corrections were applied using the empirical multi-scan method with the SADABS program.

CCDC 2161158 (**2**) and 2161159 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

According to the X-ray data of macrocycle **2**, the bridged sulfur atoms are located practically in the same plane, the dihedral angle between the planes S1S3S2 and S1S3S4 being 1.8°, whereas in the hydrocarbon analogue it was 16.0°.[16,17] The C–S–C angle is in average 97.1°, which is a few less than in hydrocarbon analogues with S[16,17] and SO_2[6] bridge groups. In large unstrained S-containing macrocycles, this value lies in the range of 100–105°.[6,16,17] In macrocycle **2**, in contrast to the hydrocarbon analogue with the SO_2[6] bridge group, the opposite aromatic nuclei are inclined to each other. The dihedral angles between these nuclei are 67.1 and 70.9°, and the distances between the corresponding centroids are 6.66 and 6.55 Å. The bridged S atoms have a slight deviation inward from the plane of the aromatic nuclei (0.03–0.20 Å).

According to the X-ray data, macrocycle **8** has the 'chair' conformation. The bridging sulfur atoms lie in the same plane. Tetrafluorophenylene aromatic nuclei are arranged in parallel, the distance between the centroids is 5.23 Å. Perfluoroxylene fragments are at an angle of 45.7° to the plane of sulfur atoms. The C–S–C angle is 102.9 and 103.0°. The bridged S atoms have a slight deviation of 0.11–0.12 Å outward from the plane of tetrafluorophenylene nuclei and 0.17–0.20 Å from the plane of perfluoroxylene fragments. The length of the C–S bond in both macrocycles **2** and **8** is 1.77–1.78 Å, which corresponds to the literature data for S-containing macrocycles.[11,16,17]

Macrocycle **2**, as well as the hydrocarbon analogue with SO_2 bridge groups,[6] provides a rare example of organic molecular squares having a cylindrical free pathway through the macrocycle but with a small diameter of about 3.3 Å.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.11.027.

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