

Macrocyclic aromatic thioether sulfones

Ian Baxter,^a Howard M. Colquhoun,^{b†} Philip Hodge,^{c‡} Franz H. Kohnke,^{c§} and David J. Williams^a

^a Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY

^b Science Research Institute and Department of Chemistry, University of Salford, Salford, UK M5 4WT

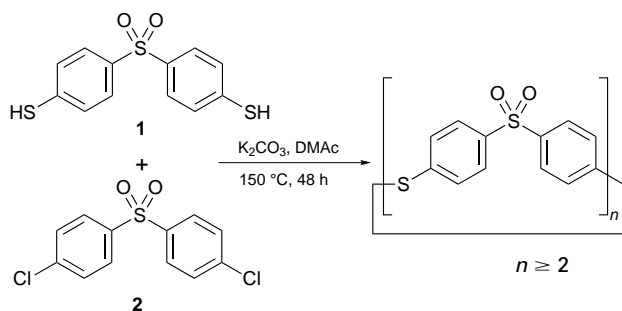
^c Department of Chemistry, University of Manchester, Manchester, UK M13 9PL

Reaction of 4,4'-sulfonylbis(thiophenol) with 4,4'-dichlorodiphenyl sulfone under pseudo-high-dilution conditions leads to a novel family of all-*para* macrocyclic thioether sulfones $[-S\phi SO_2\phi-]_n$ ($\phi = 1,4$ -phenylene); these include a highly strained [1 + 1] cyclodimer ($n = 2$), a cyclotrimer resulting from thioether exchange reactions, and a [2 + 2] cyclotetramer which can adopt two distinctly different conformations, one having molecular D_{2d} ('tennis-ball-seam') symmetry, in the crystalline state.

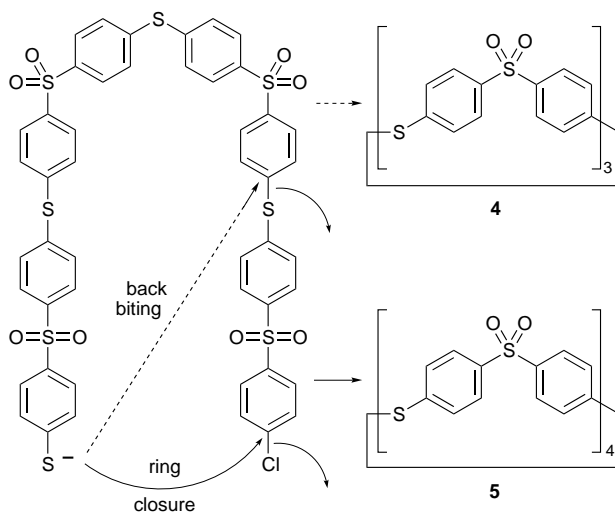
There is considerable and growing interest in the synthesis and ring-opening polymerisation chemistry of macrocyclic aromatic ethers¹ and thioethers.² The very low viscosities of such macrocycles, together with the absence of by-products during polymerisation, offer new possibilities for *in situ* fabrication of high-performance materials. We now report the discovery of a new class of potentially polymerisable macrocyclic aromatic thioethers, including an extremely strained cyclodimer, formed by polycondensation of 4,4'-sulfonylbis(thiophenol) **1** with 4,4'-dichlorodiphenyl sulfone **2** under pseudo-high-dilution conditions.

A dimethylacetamide (DMA) solution containing equimolar quantities of **1** and **2** (0.13 M in each) was added *via* syringe-pump over 48 h to a refluxing suspension of K_2CO_3 in DMA–benzene (7.5:1, v/v). By-product water from the reaction was continuously removed by azeotropic distillation of benzene. After a further 2 h the reaction mixture was cooled and the products precipitated in water. Analysis by HPLC and FAB-mass spectrometry demonstrated the formation of a new family of macrocyclic oligomers $[-S\phi SO_2\phi-]_n$ ($\phi = 1,4$ -phenylene) in *ca.* 30% yield (Scheme 1), the remaining material being high molecular weight polymer. The principal macrocyclic product (*ca.* 15% yield) is the cyclic trimer, a result which indicates that cyclisation must be accompanied by extensive thioether exchange. Macrocycles where n is odd cannot be formed directly by condensation of **1** and **2**, and must therefore arise by redistribution or back-biting reactions (Scheme 2).

Extraction of the product mixture with $CHCl_3$ followed by gradient elution column chromatography on silica gel with CH_2Cl_2 –EtOAc as eluent allowed several of the macrocyclic oligomers to be isolated as pure crystalline compounds, including the cyclodimer $[-S\phi SO_2\phi-]_2$ **3**, the cyclotrimer **4** and the cyclic tetramer **5**. Macrocycles were identified by ^{13}C and



Scheme 1



Scheme 2

1H NMR spectroscopy and FAB-mass spectrometry. The cyclic trimer and tetramer give 1H NMR spectra virtually identical to that of the linear polymer $[-S\phi SO_2\phi-]_n$, which shows a well-resolved AA'BB' system at δ 7.85, 7.82, 7.44 and 7.41. In contrast, the 1H NMR resonances for cyclic dimer **3**, where the effects of ring-closure are likely to be greatest, occur in a very much narrower range at δ 7.61, 7.58, 7.55, and 7.52.

The structures of **3**, **4** and **5** were investigated by single crystal X-ray methods.[¶] The cyclic dimer **3** adopts a centrosymmetric, box-like conformation (Fig. 1) in which adjacent aromatic rings are orthogonal to within 1° . Although this 'open-book' type of conformation is well established in diaryl sulfones,⁴ diaryl thioethers have up until now invariably displayed a 'skewed' conformation, even in the related cyclic oligomer $[1,4-C_6H_4S]_4$.⁵ It thus appears to be the conformational preferences of the sulfone linkage which dominate the present structure.

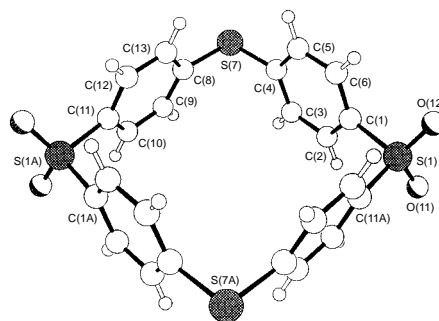


Fig. 1 Molecular structure of the cyclic dimer **3**: bond angles within the macrocycle at S(1) and S(7) are 101.4(2)° and 96.4(2)°; the C(1)–C(6) and C(8)–C(13) rings are inclined by 88° and 81°, respectively, to the plane of the four sulfur atoms

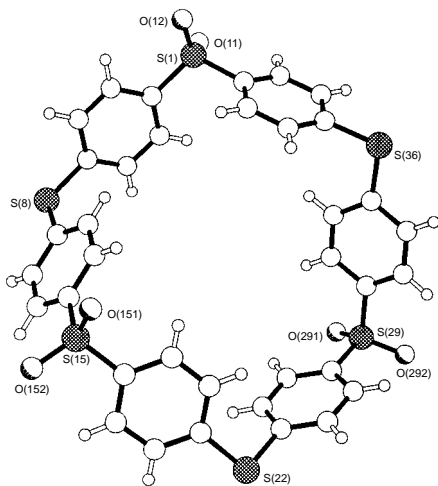


Fig. 2 Molecular structure of the cyclic trimer **4**: bond angles within the macrocycle at the sulfone sulfur atoms S(1), S(15) and S(29) are 105.7(4), 106.5(4) and 105.1(5)°, and those at the thioether sulfur atoms S(8), S(22) and S(36) are 101.5(4), 101.1(5) and 103.0(5)°

In the cyclic dimer **3**, C–S–C bond angles at thioether and sulfone are compressed by some 8 and 3°, respectively, from their normal open-chain values around 105°. Moreover, a distinct ‘bowing’ of the macrocycle is evident such that 1,4-related C–S bonds, which would normally be co-linear, here subtend an angle of *ca.* 171°. The very low yield of cyclodimer **3** (< 1%) thus clearly reflects the high strain-energy associated with formation of a cyclic thioether–sulfone oligomer containing only two repeat units.

The cyclotrimer **4** and cyclotetramer **5** were isolated in very much higher yields (*ca.* 15 and 10%, respectively), but despite the increased ring size, there is still evidence of some steric strain in the structure of **4**, all three independent thioether C–S–C bond angles being compressed by *ca.* 3° (Fig. 2).

The cyclic tetramer **5** adopts two entirely different conformations in the solid state, depending on the solvent of crystallisation. In the benzene solvate (**5a**) the oligomer displays a rather flattened conformation with the macrocyclic cavity being occupied by two of the five solvating benzene molecules. In another solvate (**5b**), however, the macrocycle adopts a ‘tennis-ball-seam’ conformation having non-crystal-

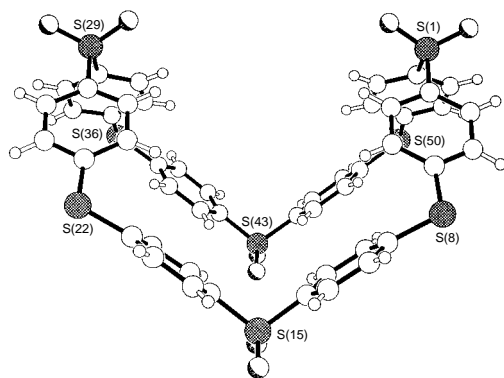


Fig. 3 The D_{2d} (‘tennis-ball-seam’) conformation adopted by the cyclic tetramer **5** in solvate **5b**: bond angles within the macrocycle at the sulfone sulfur atoms S(1), S(15), S(29) and S(43) are 103.7(4), 104.9(3), 103.9(3) and 104.6(3)°, and those at the thioether sulfur atoms S(8), S(22), S(36) and S(50) are 104.5(4), 104.3(4), 104.0(3), and 106.3(3)°

lographic D_{2d} symmetry (Fig. 3). The solvent in **5b** is very substantially disordered and appears to comprise a mixture of both solvents used in its recrystallisation (CHCl_3 and CH_2Cl_2), limiting the overall precision of the structure. It is nevertheless evident from their bond and torsion angles that both **5a** and **5b** are virtually unstrained. In both conformers all diphenyl sulfone units have the conventional open-book geometry, so that interconversion between the two structures may be achieved simply by rotation about the thioether linkages.

We have found that peroxide oxidation of the cyclic thioether sulfones $[-\text{S}\phi\text{SO}_2\phi-]_n$ affords a further series of macrocycles $[-\phi\text{SO}_2-]_{2n}$. These novel, cyclic oligomers of the highly crystalline and intractable polymer poly(1,4-phenylene sulfone)⁶ will be described in a future communication.

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Footnotes and References

† E-mail: h.m.colquhoun@chemistry.salford.ac.uk

‡ E-mail: philip.hodge@man.ac.uk

§ On leave from the Department of Organic and Biological Chemistry, University of Messina, I-98166, Messina, Italy.

¶ *Crystal data* for **3**: $\text{C}_{24}\text{H}_{16}\text{O}_4\text{S}_4$, $M = 496.61$, monoclinic, space group $P2_1/c$, $a = 9.912(1)$, $b = 13.085(1)$, $c = 10.007(1)$ Å, $\beta = 117.67(1)^\circ$, $Z = 2$, $U = 1149.7(2)$ Å³, $T = 203$ K, $D_c = 1.435$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 4.05$ mm⁻¹, $F(000) = 512$. $R_1 = 0.0398$, $wR_2 = 0.1003$ for 1558 independent observed reflections [$2\theta < 126^\circ$, $I > 2\sigma(I)$]. For **4**: $\text{C}_{36}\text{H}_{24}\text{O}_6\text{S}_6 \cdot 3\text{CHCl}_3$, $M = 1103.02$, monoclinic, space group Ia , $a = 11.355(1)$, $b = 32.209(2)$, $c = 13.475(2)$ Å, $\beta = 105.00(1)^\circ$, $Z = 4$, $U = 4760.5(10)$ Å³, $T = 203$ K, $D_c = 1.529$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 7.67$ mm⁻¹, $F(000) = 2232$. $R_1 = 0.0693$, $wR_2 = 0.1833$ for 3861 independent observed reflections [$2\theta < 126^\circ$, $I > 2\sigma(I)$]. For **5a**: $\text{C}_{48}\text{H}_{32}\text{O}_8\text{S}_8 \cdot 5\text{C}_6\text{H}_6$, $M = 1383.76$, triclinic, space group $P\bar{1}$, $a = 8.289(2)$, $b = 13.049(1)$, $c = 16.705(2)$ Å, $\alpha = 103.58(1)$, $\beta = 101.88(1)$, $\gamma = 90.85(1)^\circ$, $Z = 1$, $U = 1714.9(5)$ Å³, $T = 203$ K, $D_c = 1.340$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 2.87$ mm⁻¹, $F(000) = 722$. $R_1 = 0.0579$, $wR_2 = 0.1360$ for 4002 independent observed reflections [$2\theta < 126^\circ$, $I > 2\sigma(I)$]. For **5b**: $\text{C}_{48}\text{H}_{32}\text{O}_8\text{S}_8 \cdot 5\text{CHCl}_3 \cdot 0.5\text{CH}_2\text{Cl}_2$, $M = 1632.52$, triclinic, space group $P\bar{1}$, $a = 15.147(1)$, $b = 15.892(2)$, $c = 16.591(2)$ Å, $\alpha = 72.68(1)$, $\beta = 66.14(1)$, $\gamma = 79.81(1)^\circ$, $Z = 2$, $U = 3479.3(6)$ Å³, $T = 203$ K, $D_c = 1.558$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 8.44$ mm⁻¹, $F(000) = 1646$. $R_1 = 0.089$, $wR_2 = 0.214$ for 5967 independent observed reflections [$2\theta < 120^\circ$, $I > 2\sigma(I)$]. Data for all four compounds were measured on a Siemens P4/RA diffractometer with graphite-monochromated Cu-K α radiation using ω -scans. The data were absorption-corrected and the structures were solved by direct methods. Major-occupancy non-hydrogen atoms were refined anisotropically on F^2 data using the SHELXTL program package. CCDC 182/685.

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