Sulfone-Linked Paracyclophanes via Macrocyclic Aromatic Thioethers: Synthetic and Structural Investigations

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Abstract: Reaction of 4,4′-sulfonylbis-(benzenethiol) with 4,4′-dichlorodiphenylsulfone under pseudo-high-dilution conditions leads to macrocyclic thioethersulfones [-S-Ar-SO_2-Ar-]$_n$ (Ar = 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 entirely different conformations in the crystalline state, one having molecular D_{2d} ("tennis-ball-seam") symmetry. The same type of reaction is successful using 4,4′-thiobis(benzenethiol) instead of 4,4′-sulfonylbis(benzenethiol) and affords macrocycles with a higher ratio of thioether to sulfone linkages. Exhaustive oxidation of macrocyclic thioethersulfones with hydrogen peroxide affords a series of sulfone-linked paracyclophanes, [-Ar-SO_2-]$_4$, [-Ar-SO_2-]$_6$, [-Ar-SO_2-]$_8$ and [-Ar-SO_2-]$_{12}$. Single crystal X-ray analysis reveals [Ar-SO_2-]$_4$ to be a near-perfect square box, whilst the cyclic hexamer [-Ar-SO_2-]$_6$ adopts a much more irregular conformation, and [-Ar-SO_2-]$_8$ displays a "double-box" structure clearly related to that of [Ar-SO_2-]$_4$.

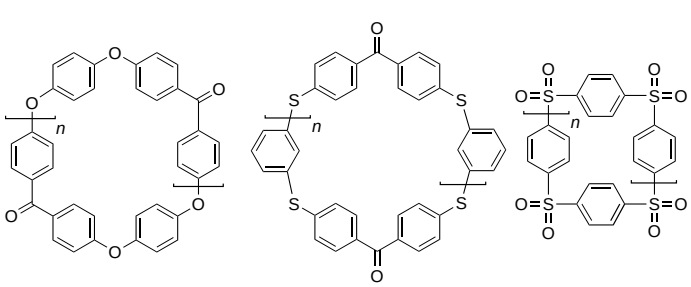
Keywords: arenes · macrocycles · nucleophilic aromatic substitution · oxidations · sulfur

Introduction

There is considerable and growing interest in the synthesis and ring-opening polymerisation of macrocyclic aromatic ethers and thioethers such as **1** and **2**.[1, 2] The very low melt-viscosities of such macrocycles and the absence of by-products during polymerisation offer new possibilities for microfabrication of high-performance materials and the production of fibre-reinforced composite structures.[3] Furthermore the in situ ring-opening polymerisation of macrocyclic oligomers may allow the fabrication of crystalline polymers which are currently intractable because of extreme insolubilty and/or a melting point which exceeds the polymer decomposition temperature.

The crystalline melting point of poly(1,4-phenylenesulfone) is reported to exceed 500 °C,[4] and we have thus sought to develop routes to *macrocyclic oligomers* of this material (sulfone-linked paracyclophanes, **3**), to investigate their potential for ring-opening polymerisation. An additional point of interest is that the strongly electron-withdrawing and exceptionally rigid nature of the diarylsulfone unit, with its preferred "open-book" conformation,[5] suggests that such macrocycles, if they can be synthesised, may behave as π-electron deficient molecular receptors. Unlike analogous systems based on the cationic 4,4′-bipyridinium unit,[6] they would not require counterions and should, in addition, afford a high degree of pre-organisation in any non-covalent complexation process.

In the present paper we report synthetic and crystallographic studies of the first sulfone-linked paracyclophanes, sulfur-based analogues of, for example, [1.1.1.1]paracyclo-



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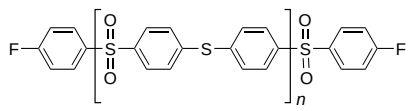
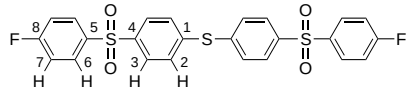
phane and [1.1.1.1.1.1]paracyclophane.[7] The new macrocycles are obtained by a three-step synthesis, which involves i) nucleophilic cyclocondensation of an aromatic dithiol with 4,4′-dichlorodiphenylsulfone, ii) chromatographic separation and purification of the resulting family of macrocyclic thioethersulfones, and finally iii) oxidation of the thioether groups to sulfone linkages with hydrogen peroxide in acetic or trifluoroacetic acid. Part of this work has been reported in preliminary communications.[8, 9]

Results and Discussion

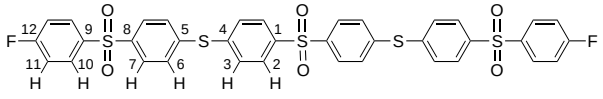
Our initial attempts to generate macrocyclic thioethersulfones involved nucleophilic polycondensation between sodium sulfide (Na_2S) and 4,4′-difluorodiphenylsulfone (**4a**) in dimethylacetamide (DMAc) under heterogeneous, high-dilution conditions. Analysis of the product mixture by HPLC indicated that a series of oligomers was indeed formed in this reaction, but MALDI-TOF and FAB mass spectrometry suggested that these were predominantly *linear* rather than macrocyclic species. This was confirmed by preparative chromatographic fractionation, which led to the isolation, albeit in low yield, of four linear fluorine-ended oligomers **5a–5d**, together with trace amounts of a compound eventually identified as the *cyclic* tetramer **6c**.



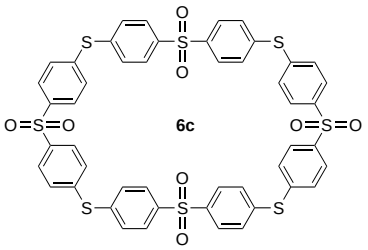
4a (*n* = 0), **5a** (*n* = 1), **5b** (*n* = 2), **5c** (*n* = 3), **5d** (*n* = 4)



5a



5b



6c

Oligomers **5a–5d** and **6c** were fully characterised by ^1H and ^{13}C NMR spectroscopy and by FAB-MS, and the structures of the linear trimer **5b** and cyclic tetramer **6c** (as its benzene solvate, hereafter referred to as form **I**) were determined by single crystal X-ray methods. The X-ray analysis of **5b** showed that the molecule has an extended, sinusoidal conformation with crystallographic C_2 symmetry about an axis passing through the central sulfone group (Figure 1, top). There are significant deviations from the normal "open-book" conformation for the two independent diarylsulfone units, both of which display distinctly skewed geometries. The combined effect of these conformational features is to impose a helical twist upon the oligomer chain as a whole producing an F(1)-S(8)-S(8A)-F(1A) molecular torsion angle of 57°. Analysis of the packing of the oligomer chains reveals an electrostatic interaction between each of the central sulfone oxygen atoms of one oligomer and ring A of another (interaction *a* in Figure 1, bottom). The distance

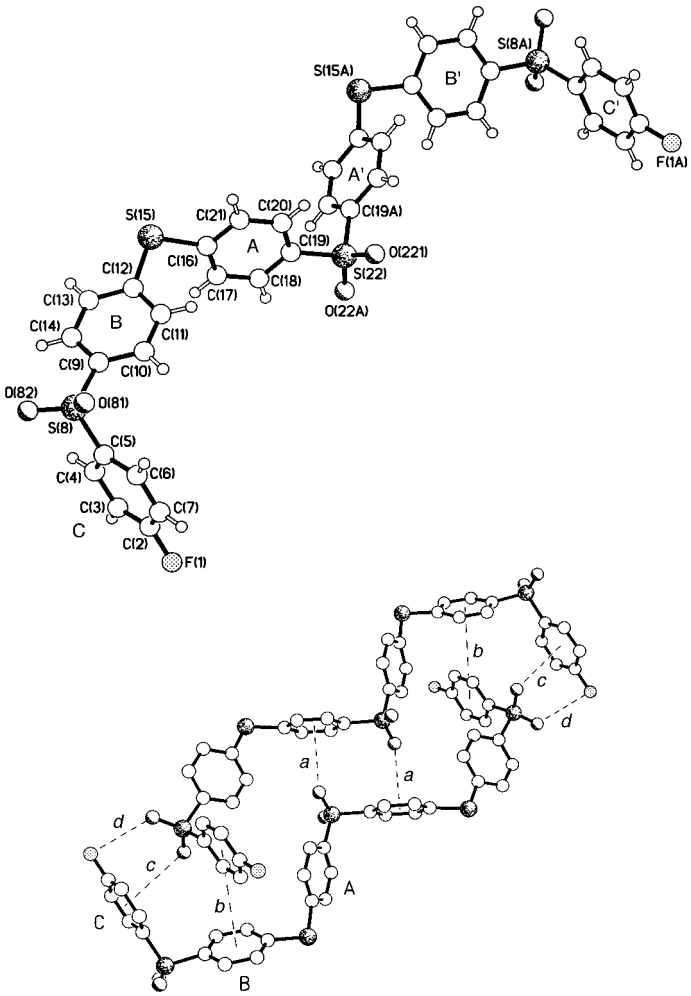


Figure 1. Top: The molecular structure of **5b**. The in-chain angles [°] at the sulfur atoms are: S(8) = 105.9(2), S(15) = 103.6(2), S(22) = 104.1(2). The mean torsional twists [°] in the molecular backbone are C(5)–S(8) = 76, S(8)–C(9) = 62, C(12)–S(15) = 36, S(15)–C(16) = 60 and C(19)–S(22) = 71. Bottom: Interactions between adjacent molecules of **5b** in the crystal. The geometries of the interactions are: *a*: O ··· ring-centroid 3.17 Å; vector inclined by 86° to ring plane; *b*: centroid ··· centroid separation 4.95 Å; rings inclined by 77°; *c*: O ··· ring-centroid 3.59 Å; *d*: S=O ··· F separation is 3.08 Å.

between the sulfone oxygen and the aromatic ring centre is only 3.17 Å, with the O ··· ring-centroid vector being inclined by 86° to the ring plane. This contact is directly analogous to

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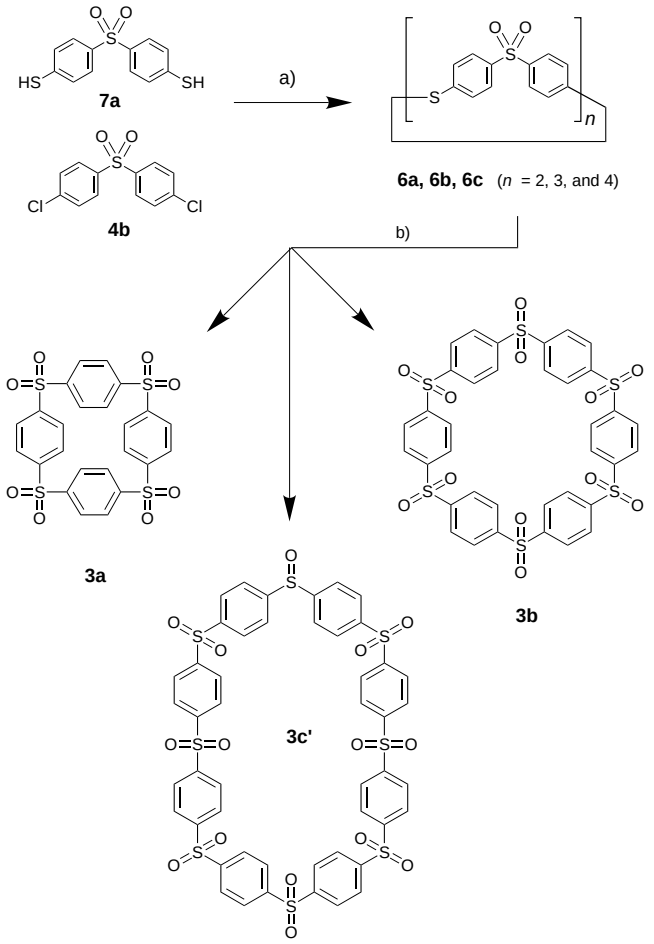
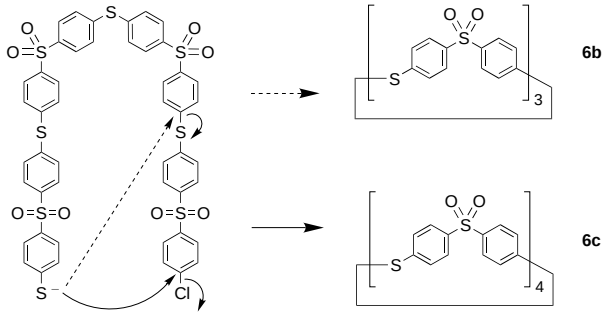
those previously observed between oxygen atoms and *para*-substituted tetrafluorophenylene rings,[10] and is in fact very close to the minimum of the distribution of ring···oxygen distances observed for the latter type of interaction.

It seemed possible that our initial attempts to generate significant quantities of macrocyclic oligomers might be due to unfavourable reaction kinetics associated with the very low solubility of sodium sulfide in DMAc. We therefore changed our approach to one involving reactants which are fully soluble in the reaction medium, namely 4,4′-dichlorodiphenylsulfone (**4b**), 4,4′-sulfonylbis(benzenethiol) (**7a**), and 4,4′-thiobis(benzenethiol) (**7b**) (Schemes 1 and 3).



Scheme 1. Synthesis of sulfone-linked paracyclophanes. a) K_2CO_3, DMAc, 150 °C, 48 h. b) H_2O_2/AcOH, 60 °C.

A dimethylacetamide solution containing equimolar quantities of **4b** and **7a** (0.13 M each) was added through a syringe-pump over a period of 48 h to a refluxing suspension of potassium carbonate in a mixture of dimethylacetamide and benzene. Water formed as a by-product was continuously removed from the reaction mixture by azeotropic distillation. After a further 2 h the reaction mixture was cooled and the products were precipitated by adding the solution to water. Analysis by FAB-MS demonstrated that a family of macrocyclic oligomers [-S-Ar-SO_2-Ar-]$_n$ (Ar = 1,4-phenylene, n = 2–6) had been formed in about 30% total yield (Scheme 1). The major macrocyclic product (15% yield) is the cyclic trimer **6b**, which was an initially surprising result since macrocycles where n is an odd number cannot be built directly by condensation of **4b** and **7a**, and must therefore arise by redistribution or "backbiting" reactions (Scheme 2).



Scheme 2. Formation of macrocyclic thioethersulfones **6c** and **6b**, by end/end ring-closure and by "backbiting", respectively.

Although "ether-scrambling" is a well-established feature of poly*ether*sulfone chemistry,[11] this is the first evidence for analogous processes occurring in a *thioether*sulfone system.

Extraction of the reaction mixture with chloroform followed by gradient-elution column chromatography on silica gel with dichloromethane/ethyl acetate as eluent allowed the isolation of several macrocyclic oligomers as pure crystalline compounds; these included cyclodimer [-S-Ar-SO_2-Ar-]$_2$ (**6a**), cyclotrimer **6b**, and cyclotetramer **6c** (in two crystallographically distinct forms, **I** and **II**, see below). The individual macrocycles were identified by ^{1}H, ^{13}C NMR and by FAB mass spectrometry. The cyclic trimer and tetramer give ^{1}H NMR spectra virtually identical to that of the linear polymer [-S-Ar-SO_2-Ar-]$_n$, which shows a well-resolved AA′BB′ system at $\delta = 7.85$, 7.82, 7.44 and 7.41.[12] In contrast, ^{1}H NMR resonances for the cyclodimer **6a**, where the effects of ring-closure are likely to be greatest, occur in a very much narrower range at $\delta = 7.61$, 7.58, 7.55, and 7.52. The structures of **6a**, **6b**, and the two cyclotetramer forms **6c(I)** and **6c(II)** were investigated by single crystal X-ray methods (Table 1).

The cyclic dimer **6a** (Figure 2, top) has a C_i-symmetric, box-like geometry in the solid state, with the four sulfur atoms coplanar and the phenylene spacer groups aligned almost orthogonally (88° for ring A and 81° for ring B) to this plane. Although this "open-book" type of conformation is well established in diarylsulfones,[5] diarylthioethers have until now invariably displayed a "skewed" conformation, even in the closely related cyclic oligomer [-Ar-S-]$_4$.[13] It thus appears to be the conformational preferences of the sulfone linkage which dominate the present structure. Ring strain results in each of the sides of the "box" being noticeably bowed, the S–Ar bonds associated with each ring being mutually inclined by about 9°. The rather low yield of cyclodimer **6a** (<2%) clearly reflects the high strain energy associated with formation of a cyclic thioethersulfone oligomer with only two repeating units. As a consequence of the different valence angles at the thioether and sulfone sulfur atoms [96.4(2)° at S(7) and 101.4(2) at S(1)], a slight rhombic distortion of the macrocycle is observed, the transannular thioether···

Table 1. Crystal data, data collection and refinement parameters.[a]

Data	**5b**	**6a**	**6b**	**6c(I)**	**6c(II)**
formula	$C_{36}H_{24}F_2O_6S_5$	$C_{24}H_{16}O_4S_4$	$C_{36}H_{24}O_6S_6$	$C_{48}H_{32}O_8S_8$	$C_{48}H_{32}O_8S_8$
solvent	–	–	$3\,CHCl_3$	$5\,C_6H_6$	$5\,CHCl_3 \cdot 0.5\,CH_2Cl_2$
formula weight	750.9	496.6	1103.0	1383.8	1632.5
colour, habit	colourless needles	colourless blocks	colourless plates	colourless needles	colourless plates
crystal size [mm]	$0.03 \times 0.07 \times 0.67$	$0.13 \times 0.27 \times 0.53$	$0.13 \times 0.43 \times 0.73$	$0.03 \times 0.03 \times 0.23$	$0.10 \times 0.33 \times 0.33$
lattice type	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group, no.	*C*2/*c*, 15	$P2_1/c$, 14	*Ia*, 9	$P\bar{1}$, 2	$P\bar{1}$, 2
T [K]	293	203	203	203	203
cell dimensions					
a [Å]	35.365(3)	9.912(1)	11.355(1)	8.289(2)	15.147(1)
b [Å]	9.494(1)	13.085(1)	32.209(2)	13.049(1)	15.892(2)
c [Å]	9.801(1)	10.007(1)	13.475(2)	16.705(2)	16.591(2)
α [°]	–	–	–	103.58(1)	72.68(1)
β [°]	96.02(7)	117.67(1)	105.00(1)	101.88(1)	66.14(1)
γ [°]	–	–	–	90.85(1)	79.81(1)
V [Å^3]	3272.7(5)	1149.7(2)	4760.5(10)	1714.9(5)	3479.3(6)
Z	4[b]	2[c]	4	1[c]	2
D_c [g cm^{-3}]	1.524	1.435	1.539	1.340	1.558
F(000)	1544	512	2232	722	1646
radiation used	$Cu_{K\alpha}$[d]	$Cu_{K\alpha}$[d]	$Cu_{K\alpha}$[d]	$Cu_{K\alpha}$[d]	$Cu_{K\alpha}$
μ [mm^{-1}]	3.78	4.05	7.67	2.87	8.44
θ range [°]	2.5 – 60.0	5.0 – 62.0	2.7 – 62.5	2.8 – 63.0	2.9 – 60.0
no. of unique refl.					
measured	2438	1799	3861	5492	9496
observed[e]	1911	1558	3489	4002	5967
no. of variables	222	146	560	425	937
*R*1[F]	0.0500	0.0398	0.0693	0.0565	0.0894
*wR*2[g]	0.1205	0.1003	0.1833	0.1347	0.2135
largest diff. peak, hole [e Å^{-3}]	0.25, −0.32	0.28, −0.28	0.79, −0.64	0.42, −0.35	0.79, −0.55

Data	**3a**	**3b**	**3c′**	**8b**
formula	$C_{24}H_{16}O_8S_4$	$C_{36}H_{24}O_{12}S_6$	$C_{48}H_{32}O_{15}S_8$	$C_{48}H_{32}O_4S_8$
solvent	$2\,(CH_3)_2SO$	$2.5\,(CH_3)_2CO$	$6\,(CH_3)_2SO$	$1.5\,CH_2Cl_2$
formula weight	716.9	986.1	1574.0	1056.6
colour, habit	colourless prisms	colourless needles	colourless plates	colourless plates
crystal size [mm]	$0.13 \times 0.13 \times 0.27$	$0.13 \times 0.23 \times 0.57$	$0.03 \times 0.17 \times 0.57$	$0.08 \times 0.26 \times 0.47$
lattice type	monoclinic	orthorhombic	triclinic	monoclinic
space group, no.	$P2_1/c$, 14	*Pbca*, 60	$P\bar{1}$, 2	$P2_1/n$, 14
I [K]	293	293	203	293
cell dimensions:				
a [Å]	9.966(5)	11.220(3)	11.479(2)	11.534(1)
b [Å]	18.003(5)	29.432(3)	11.583(2)	10.750(1)
c [Å]	10.391(4)	29.860(4)	15.936(3)	19.366(2)
α [°]	–	–	80.34(2)	–
β [°]	118.22(2)	–	78.63(2)	95.04(1)
γ [°]	–	–	62.78(1)	–
V [Å^3]	1642.7(11)	9861(3)	1840.0(6)	2391.9(4)
Z	2[c]	8	1[c]	2[c]
D_c [g cm^{-3}]	1.449	1.328	1.421	1.467
F(000)	744	4096	820	1086
radiation used	$Cu_{K\alpha}$	$Cu_{K\alpha}$	$Cu_{K\alpha}$[d]	$Cu_{K\alpha}$[d]
μ [mm^{-1}]	4.31	3.10	4.42	5.37
θ range [°]	4.9 – 62.2	3.0 – 62.0	2.8 – 60.0	4.3 – 64.0
no. of unique refl.				
measured	2419	7741	5401	3760
observed[e]	1461	3718	3969	2864
no. of variables	235	605	452	316
*R*1[f]	0.0793	0.0778	0.0821	0.0576
*wR*2[g]	0.1968	0.2037	0.2156	0.1471
largest diff. peak, hole [e Å^{-3}]	0.75, −0.52	0.62, −0.24	1.06, −0.84	0.25, −0.35

[a] Details in common: Graphite monochromated radiation, ω scans, Siemens P4 diffractometer, refinement based on F^2. [b] C_2 symmetry. [c] C_i symmetry. [d] Rotating anode source. [e] $|F_o| > 4\sigma(|F_o|)$. [f] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [g] $wR2 = \sqrt{[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]}$.

thioether and sulfone···sulfone distances being 9.00 and 8.81 Å, respectively. The molecules pack to form slightly stepped $\pi - \pi$ stacks, with ring B of one molecule overlaying its symmetry related counterpart in the next (the mean interplanar and centroid···centroid separations are 3.41 and 3.89 Å, respectively). Adjacent stacks are arranged in a parquet-like pattern to form a pseudo-close-packed-hexagonal array (Figure 2, bottom).

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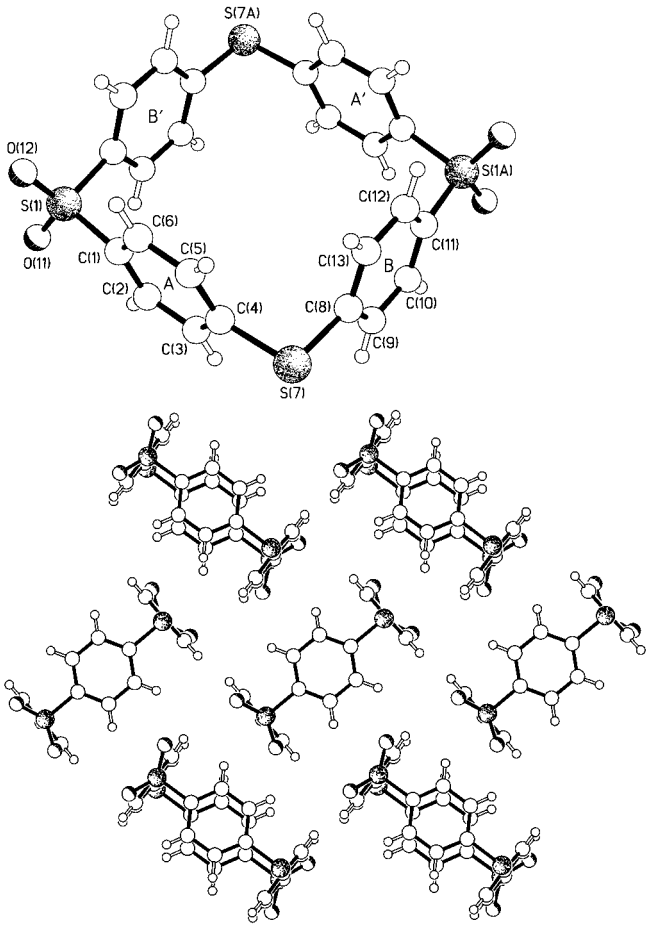

Figure 2. Top: The solid state structure of the cyclic dimer **6a**. The in-chain angles [°] at the sulfur atoms are: S(1) 101.4(2) and S(7) 96.4(2). The mean torsional twists [°] about the S–C bonds are: S(1)–C(1) 88, C(4)–S(7) 88, S(7)–C(8) 81, C(11)–S(1A) 81. Bottom: The pseudo-hexagonal-close-packed, parquet-like array of molecules of **6a** in the solid state.

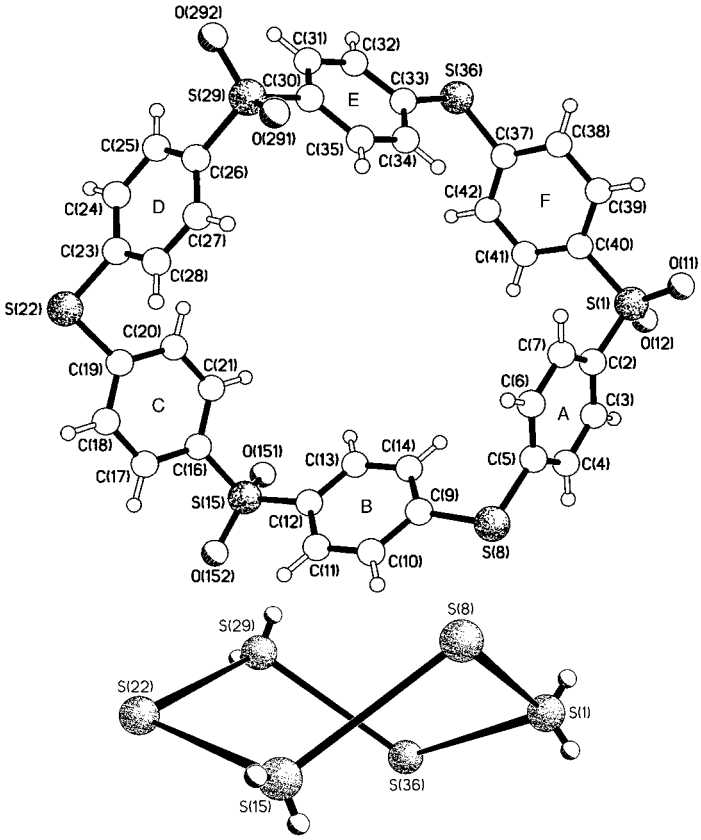

Figure 3. Top: The molecular structure of **6b**. The in-chain angles [°] at the sulfur atoms are: S(1) 105.7(4), S(8) 101.5(4), S(15) 106.5(4), S(22) 101.1(5), S(29) 105.1(5), S(36) 103.0(5). The mean torsional twists [°] about the S–C bonds are: S(1)–C(2) 50, C(5)–S(8) 88, S(8)–C(9) 7, C(12)–S(15) 87, S(15)–C(16) 75, C(19)–S(22) 40, S(22)–C(23) 62, C(26)–S(29) 78, S(29)–C(30) 84, C(33)–S(36) 7, S(36)–C(37) 77, C(40)–S(1) 49. Bottom: The twist conformation of the S6 ring in **6b**.

The cyclotrimer **6b** and cyclotetramer **6c** were isolated in much higher yields (ca. 15% and 10%). In the solid state the cyclotrimer **6b** (Figure 3, top) has a distinctly folded geometry which approximates to a flattened and twisted tennis-ball-seam conformation. There is, however, a significant free pathway (ca. 4.6 Å) through the macrocycle. The six-membered ring constructed by linking the sulfur atoms has a twist-type conformation (Figure 3, bottom). The C-S-C bond angles at thioether and sulfone are compressed by about 8 and 3°, respectively from their normal open-chain values. Two of the diarylsulfone units, those containing S(15) and S(29), adopt geometries that approximate to the conventional open-book conformations whilst the third [centred on S(1)] has a skewed geometry with torsional twists of about 50° about the two S–Ar bonds. Similarly, two of the diarylthioether units have typical near-orthogonal geometries between their ring systems whilst the third [based on S(22)] is skewed. Accompanying the orthogonal geometries are characteristic enlargements and contractions of the external angles at the carbon atoms C(9) and C(33) analogous to those observed in diaryl ethers.[14] With the exception of ring A, where the thioether and sulfone sulfur atoms lie approximately equidistant above and below the aromatic ring plane, each of the other rings exhibit small degrees of bowing, as their associated S–Ar bonds subtend angles between 3 and 5°.

The packing of the molecules is to some extent influenced by the presence of three chloroform molecules per macrocycle. There are C-H···O hydrogen bonds to five of the six sulfone oxygen atoms: one of them from a chloroform solvent molecule, and the other four involving aromatic hydrogens (the C-H···O distances range between 2.29 and 2.42 Å).

The cyclic tetramer **6c** is found to crystallise in two distinct forms (**I** and **II**) both of which are heavily solvated. The first form, **I**, crystallised from benzene, has an open, extended, C_i-symmetric conformation (Figure 4, top) and contains two of the five solvating benzene molecules, which appear to be held within the macrocycle by C-H···π interactions. The "eight-membered ring" constructed by linking the sulfur atoms has a chair-like conformation (Figure 4, bottom) with deviations of up to 2.27 Å from the mean plane of the eight sulfur atoms. The packing of the molecules in **6c(I)** is complex and dominated by π–π and C-H···π interactions between symmetry-related tetramers and with the entrapped molecules of benzene (both the molecules located within the macrocycle and those positioned between macrocycles). The principal interaction between the macrocycles is a parallel π–π interaction between rings B to form stacks; the centroid···centroid and interplanar separations are 4.01 and 3.76 Å.

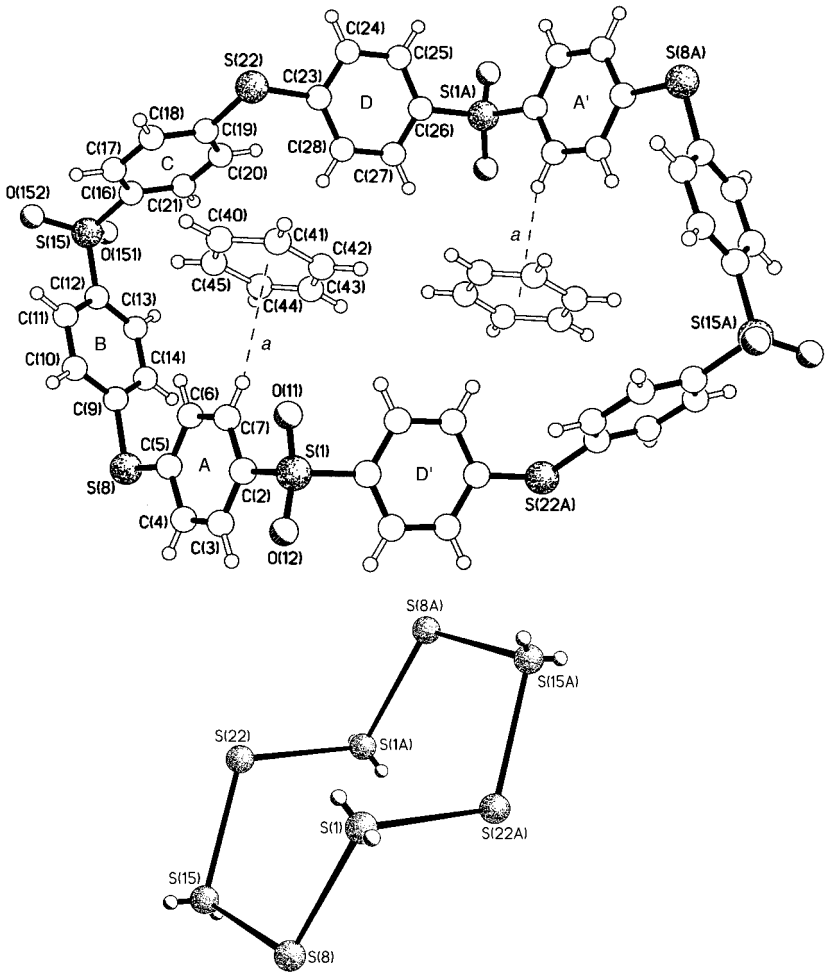

Figure 4. Top: The molecular structure of **6c** (form **I**) showing also the included benzene molecules. The geometry of the C-H$\cdots\pi$ interaction *a* is: H$\cdots\pi$ = 2.85 Å, C-H$\cdots\pi$ = 144°, the H$\cdots\pi$ vector inclined by 82° to ring-plane. The in-chain angles [°] at the sulfur atoms are: S(1) 105.1(2), S(8) 104.5(2), S(15) 103.2(2), S(22) 104.8(2). The backbone torsion angles [°] are C(26A)–S(1) 85, S(1)–C(2) 88, C(5)–S(8) 2, S(8)–C(9) 79, C(12)–S(15) 88, S(15)–C(16) 88°, C(19)–S(22) 11, S(22)–C(23) 53. Bottom: The chair-like conformation of the S8 ring of macrocycle **6c** (form **I**).

Form **II** of the cyclic tetramer **6c**, obtained by crystallisation from dichloromethane/chloroform, has a tennis-ball-seam-like conformation with approximate D_{2d} symmetry (Figure 5, top). The eight-membered ring constructed by linking the sulfur atoms (Figure 5, middle) has S(8), S(22), S(36), and S(50) coplanar within 0.04 Å, with S(1) and S(29) lying 4.00, 3.83 Å above and S(15) and S(43) 3.58, 3.79 Å below this plane, respectively. The four diarylsulfone units all have almost ideal open-book conformations while the diarylthioether components are skewed. Despite the very different conformation adopted by **6c** in form **II** compared with that in form **I** there is still a significant free pathway (of ca. 4.0 Å) through the macrocycle. This cavity is filled by one of the included, but disordered, chloroform molecules. The cavity is capped by a sulfone group [based on S(29)] of a symmetry-related molecule, which is held in place by C-H$\cdots$O hydrogen bonds [*a*–*c* in Figure 5, bottom].

A second series of macrocyclic thioethersulfones **8** was obtained by cyclocondensation of 4,4′-dichlorodiphenylsulfone (**4**) with 4,4′-thiobis(benzenethiol) (**7b**) (Scheme 3) under conditions very similar to those described above for synthesis of the macrocycles **6**. Analysis of the product mixture by FAB-MS gave evidence for cyclic oligomers ranging from the [1 + 1] cyclic monomer **8a** to the [5 + 5] cyclic pentamer **8e**. The relative proportions of macrocycles **8a, 8b, 8c, 8d** and **8e** were quantified by GPC (in chloroform) as 1:7.5:4.7:2.6:2.4. Fractionation of the mixture by gradient chromatography (dichloromethane/ethyl acetate as eluent) afforded all five macrocycles as pure compounds, with the highest yield for the eight-ring cyclic dimer **8b**. Note that, although "backbiting" is certainly possible in this system, the central thioether linkage in 4,4′-thiobis(benzenethiol) (**7b**) is essentially non-activating towards nucleophilic aromatic substitution. As a result, the macrocycles **8** formed by backbiting are indistinguishable from those arising by end/end ring-closure (Scheme 3), in contrast to the synthesis of macrocycles **6** discussed above, in which the major product, **6c**, can *only* arise from backbiting (Scheme 2) or other type of redistribution reaction. After exhaustive desolvation under high vacuum, macrocycles **8a**–**8c** were found to be crystalline by DSC, but the higher macrocycles **8d** and **8e**, containing sixteen and twenty aromatic rings, respectively, proved to be amorphous glasses.

The [2 + 2] cyclodimer **8b** has an open, C_i-symmetric conformation (Figure 6, top) with the three unique diarylthioether units adopting near-orthogonal geometries, while the diarylsulfone fragment is skewed. All four unique S-Ar-S units are bent, the folding being greatest for rings A and D where the S–Ph bonds subtend angles of 11°. The central void within the macrocycle is occupied by disordered dichloromethane molecules. Despite the geometrical differences in the diarylthioether and diarylsulfone components the chair-like conformation of the "eight-membered ring" formed by the sulfur atoms (Figure 6, bottom) is very similar to that observed in form **I** of macrocycle **6c** (Figure 4, bottom). The macrocycles pack in stepped stacks, with adjacent "chains" linked by C-H$\cdots\pi$ interactions between the C(18) protons in one chain and rings B (B′) in the next (the H$\cdots\pi$ distance is 2.77 Å and C-H$\cdots\pi$ angle 175°).

Peroxide-oxidation of the macrocyclic dimer **6a** and trimer **6b** in glacial acetic acid at 60 °C (with sonication) afforded the sulfone-linked paracyclophanes **3a** and **3b**. However, the

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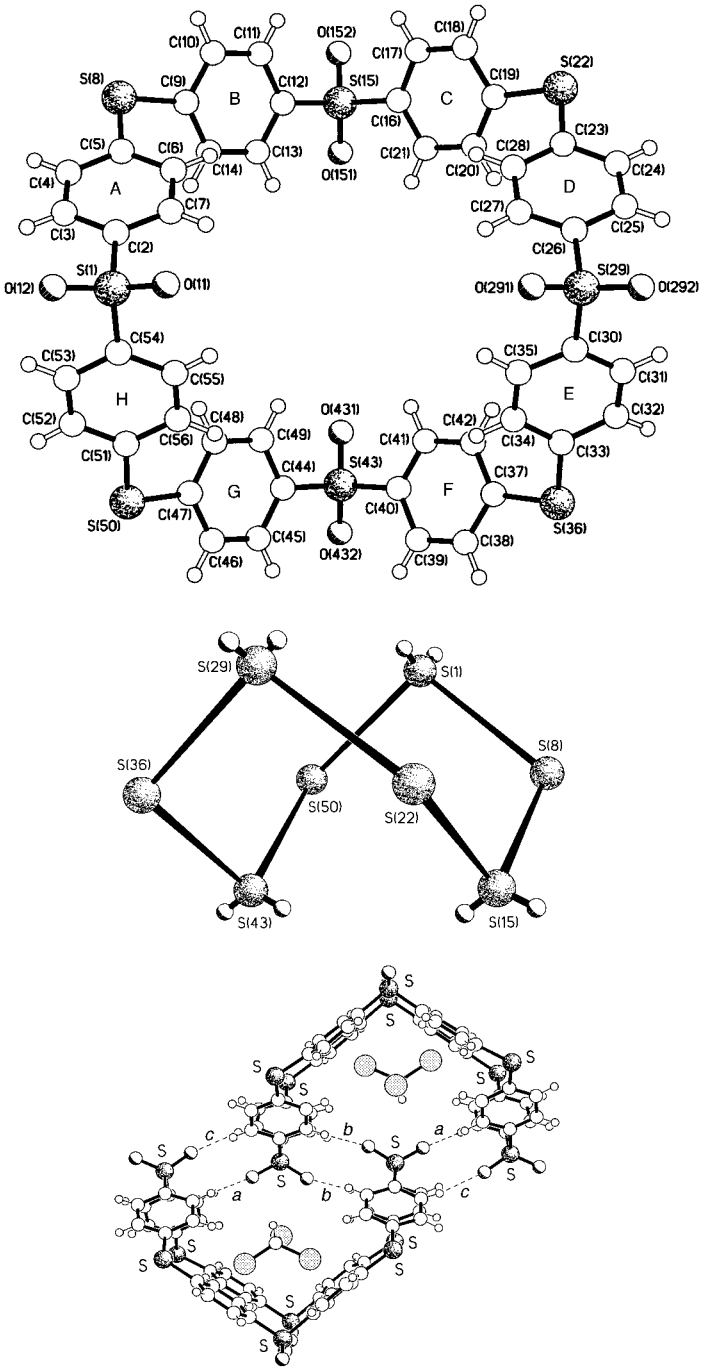


Figure 5. Top: The molecular structure of **6c** (form **II**). The in-chain angles [°] at the sulfur atoms are: S(1) 103.7(4), S(8) 104.5(4), S(15) 104.9(3), S(22) 104.3(4), S(29) 103.9(3), S(36) 104.0(3), S(43) 104.6(3), S(50) 106.3(3). The torsional twists [°] about the S–C bonds are: S(1)–C(2) 89, C(5)–S(8) 27, S(8)–C(9) 44, C(12)–S(15) 85, S(15)–C(16) 85, C(19)–S(22) 42, S(22)–C(23) 28, C(26)–S(29) 86, S(29)–C(30) 87, C(33)–S(36) 40, S(36)–C(37) 33, C(40)–S(43) 84, S(43)–C(44) 87, C(47)–S(50) 26, S(50)–C(51) 33, C(54)–S(1) 88. Middle: The tennis-ball-seam-like conformation of the S8 ring observed in form **II** of **6c**. Bottom: The stacked dimer pairs of molecules of form **II** of **6c**, showing also the entrapped $CHCl_3$ solvent. The C-H···O geometries are, H···O distance [Å] and C-H···O [°]: *a*: 2.34, 168, *b*: 2.44, 165, *c*: 2.65, 170.

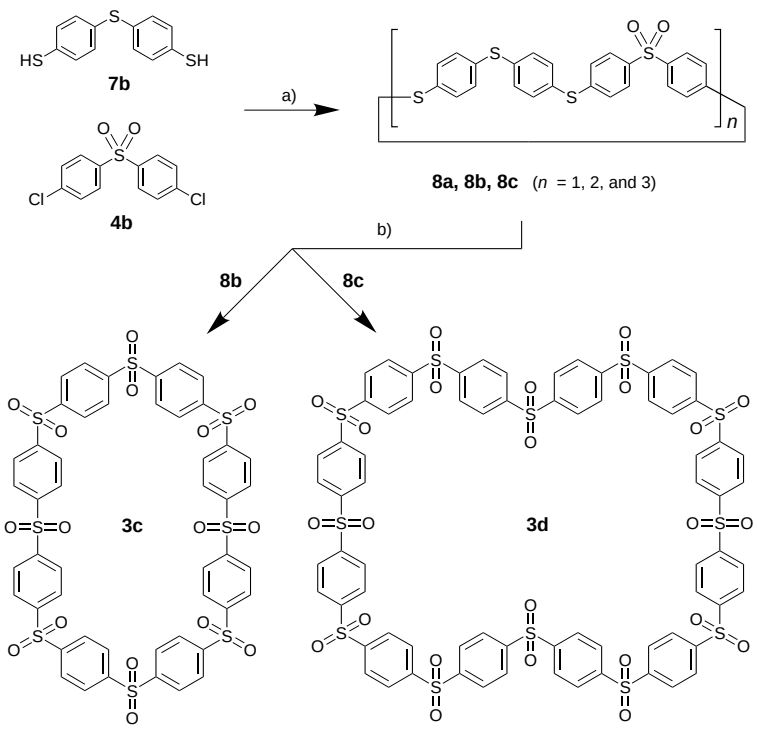
oxidation of **6c** could not be driven to completion under these conditions (nor by extending the reaction time to 24 h and increasing the temperature to 90 °C). The reaction in fact, for reasons discussed below, ceases at the heptasulfone-sulfoxide stage **3c′** rather than affording the expected cyclic octasulfone. For macrocycles **6a** and **6c** the reaction mixture remained heterogeneous throughout the oxidation process, but the oxidation of **6b** gave a homogeneous intermediate solution from which the hexasulfone **3b** finally precipitated as a microcrystalline powder.

The symmetrical aromatic substitution pattern in macrocycles **3a** and **3b** results in the observation of only a *single* ^{1}H NMR resonance ($\delta = 8.21$) for each compound, replacing the AA′BB′ pattern associated with the 1,4-thioether-sulfone substitution patterns of **6a** and **6b**. However, in keeping with the presence of a sulfoxide linkage in **3c′**, the ^{1}H NMR spectrum of this compound comprises a weak AA′BB′ system, which gives two aromatic rings equivalents, together with a strong singlet resonance at δ 8.21 for the remaining six rings; this signal is superimposed on the lower field component of the AA′BB′ system. Confirmation that compound **3c′** is a single oxidation product was provided by the constant ratio of the integration values from its ^{1}H NMR spectrum upon repeated recrystallisation from dimethylacetamide, and by MALDI-TOF mass spectrometry (dithranol matrix, LiBr as cationising agent) which showed a strong parent ion at $m/z =$ 1111 for $[(C_6H_4SO_2)_7(C_6H_4SO)\cdot Li]^+$.

All three macrocyclic sulfones have very high melting points. For example, DSC analysis of the cyclic hexamer **3b** revealed an endothermic crystal–crystal (solid state) transition at 442 °C, followed by melting peak at 495 °C, and finally a strong exothermic transition at 502 °C associated with decomposition. The very close proximity of melting and decomposition temperatures would seem to rule out any possibility of achieving melt-phase ring-opening polymerisation of this macrocyclic sulfone. The solubilities of macrocycles **3a** and **3c** in conventional organic solvents are very low indeed and, although ^{1}H and ^{13}C NMR spectra of **3a** were obtained (with some difficulty) in [D$_6$]DMSO solution, a solvent mixture of trifluoroacetic acid and CD_2Cl_2 was required to obtain NMR spectra of compound **3c′**. The cyclic hexamer **3b**, in contrast, is moderately soluble in acetone, CS_2 and DMSO.

Subsequent work established that replacement of acetic acid by trifluoroacetic acid as the solvent in the peroxide-oxidation of the macrocyclic thioethersulfones enabled more rapid and complete oxidation to be achieved. Thus, for example, oxidation of **8b** in trifluoroacetic acid gave the cyclic octasulfone **3c**, as evidenced by the presence of only a single resonance ($\delta = 8.0$) in its ^{1}H NMR spectrum ($CDCl_3$/CF_3COOH). Oxidation of **8c** under similar conditions gave an extremely insoluble compound believed to be **3d**, the cyclic dodecamer of poly(1,4-phenylenesulfone). A very weak singlet resonance at $\delta = 8.16$ could be observed in its ^{1}H NMR spectrum ($CDCl_3$/CF_3COOH), but no mass spectrum or other analytical data have yet been obtained for this highly intractable material. Neither **3c** nor **3d** showed any evidence of a crystal melting transition below 550 °C.

In order to establish the conformational characteristics of the diarylsulfone unit as a function of ring size, single crystal X-ray structures were determined for **3a** (DMSO solvate), **3b** (acetone solvate), and **3c′** (DMSO solvate). The *p*-phenyl-



Scheme 3. Cyclocondensation of 4,4′-dichlorodiphenylsulfone with 4,4′-thiobis(benzenethiol), and subsequent oxidation.

enesulfone cyclotetramer **3a** has a C_i-symmetric box-like structure (Figure 7) in the solid state. The four sulfur atoms are coplanar and rings A (A′) and B (B′) are inclined by 86 and 89° to this plane. The transannular A···A′ and B···B′ centroid–centroid distances are 6.64 and 6.54 Å, respectively. The rhombic distortion seen in the thioether-sulfone analogue **6a** is now almost eliminated, the internal angles at S(1) and S(8) being 98.7(3) and 100.4(3)°, respectively. Both of the crystallographically independent SO_2-Ar-SO_2 units are bowed, their S–Ar bonds subtending angles of 11° (ring A) and 9° (ring B), respectively. The molecules pack to form continuous π–π stacks that extend in the crystallographic *c* direction, with ring B of one molecule partially overlaying ring B′ of the next, the mean interplanar separation being 3.54 Å. Viewed down the *c* axis the stacks are arranged in herring-bone fashion. The crystal is solvated with DMSO, the disordered molecules of which are located between adjacent stacks, leaving the central region within each macrocycle vacant. The cyclic oligomer **3a** thus provides a rare example of a structurally characterised organic molecular square.[15] The mutually orthogonal orientation of the four aromatic rings results in a cylindrical free pathway through the macrocycle (based on van der Waals surfaces) of a diameter of about 3.3 Å. The presence of this electrophilic binding site suggests the possibility of complexation with first-row anions such as fluoride or cyanide, and pseudo-rotaxane formation with linear, electron-rich species such as the polyalkynes. Complexation studies with **3a** are currently in progress.

X-ray analysis of the *p*-phenylenesulfone hexamer **3b** shows an open conformation for the macrocycle (Figure 8, top, middle) with a central free pathway about 5.2 Å in diameter. The SO_2-Ar-SO_2 units all exhibit varying degrees of bowing, the angles subtended by their S–Ph bonds ranging between 11° in the case of ring F to 3° for ring E. Three of the rings, A, B and F, are bowed in towards the macrocyclic centre whilst the other three are folded outwards. Although there are no intermolecular π–π stacking interactions there is evidence for the formation of "embryonic" homodimers (Figure 8, bottom) similar to those seen in form **II** of **6c**; this is analogous to those observed for the very much larger cyclic trimer of bisphenol-A polysulfone.[16] In the structure of **3b**, the sulfone group based on S(29) of one molecule is inserted into the cavity of its centrosymmetric related counterpart (and vice versa), this geometry being stabilised by a pair of weak aromatic···aromatic edge-to-face interactions between ring E in one molecule and ring D in the next (and vice versa); the centroid···centroid separations are 5.26 Å.

The pseudo-octamer **3c′** has a C_i-symmetric "double-box" or "figure-of-eight-like" conformation in the solid state (Figure 9) in which all the diarylsulfone units adopt near-open-book conformations. The in-chain angles at the four independent sulfur atoms are in the range 101.4(3) to 103.(3)°, values that are significantly contracted from those observed in the hexamer (see above). Three of the four independent diphenylsulfone units are bowed outwards by between 1 and 7°, the fourth (that associated with ring D is planar. The "waisting" of the macrocycle results in a transannular S(22)···S(22′) separation of 5.36 Å and a contact distance of 3.27 Å between their two inwardly directed sulfone oxygen atoms. This conformation is stabilised by the cooperative action of four weak transannular C-H···O hydrogen bonds between the inwardly directed *ortho* hydrogen atoms of rings C, D, C′ and D′ and the inwardly directed sulfone oxygen atoms; the H···O distances are 2.51 and 2.63 Å with angles at H of 176 and 170°, respectively. It is remarkable that the observed structure in fact represents that of the originally anticipated cyclo-octa(*p*-phenylensulfone) (**3c**). It appears that when oxidation reaches the heptasulfone-sulfoxide stage the present compound is able to adopt the crystal lattice of the octasulfone. The vacancy associated with the missing oxygen atom is then disordered over all sixteen possible sites. At this point crystallisation from acetic acid prevents final oxidation to the "true" octasulfone. In keeping with this idea, refinement of the occupancies of the sulfone oxygen atoms converged to a value (0.96) which compares well with the figure of 0.94 expected for 15/16 occupancy.

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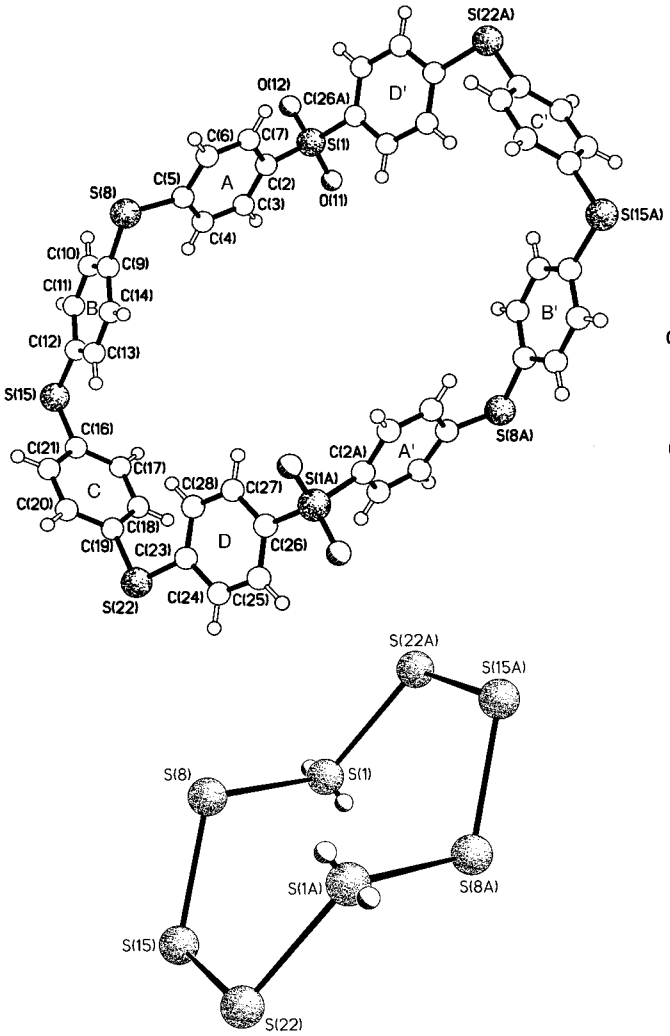


Figure 6. Top: The molecular structure of **8b**. The in-chain angles [°] at the sulfur atoms are: S(1) 106.9(2), S(8) 104.3(2), S(15) 102.7(2), S(22) 102.9(2). The backbone torsion angles [°] are C(26A)–S(1) 75, S(1)–C(2) 38, C(5)–S(8) 3, S(8)–C(9) 74, C(12)–S(15) 14, S(15)–C(16) 86, C(19)–S(22) 76, S(22)–C(23) 10. Bottom: The chair-like conformation of the S8 ring in the structure of **8b**.

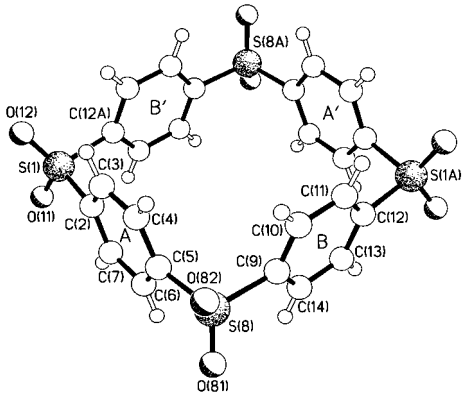
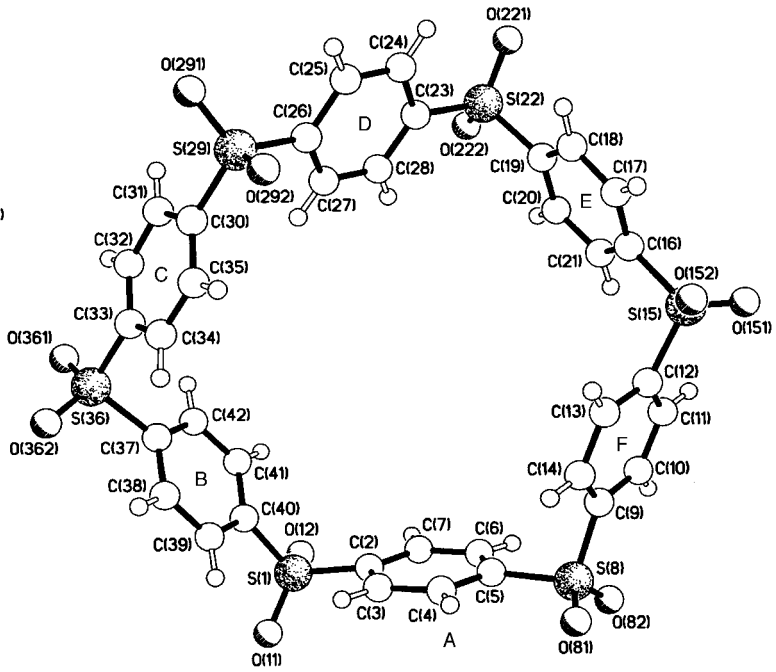
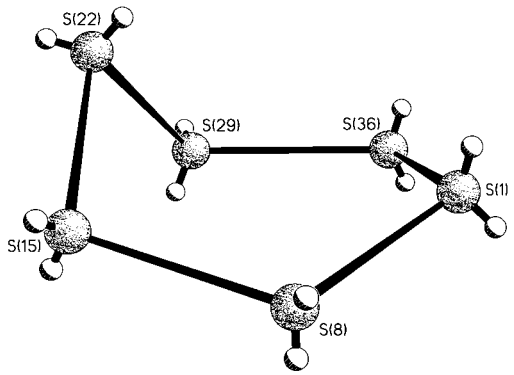


Figure 7. The solid state structure of the cyclic tetramer **3a**. The in-chain angles [°] at the sulfur atoms are: S(1) 98.7(3) and S(8) 100.4(3). The mean torsional twists [°] about the S–C bonds are: S(1)–C(2) 85, C(5)–S(8) 82, S(8)–C(9) 90, C(12)–S(1A) 89.





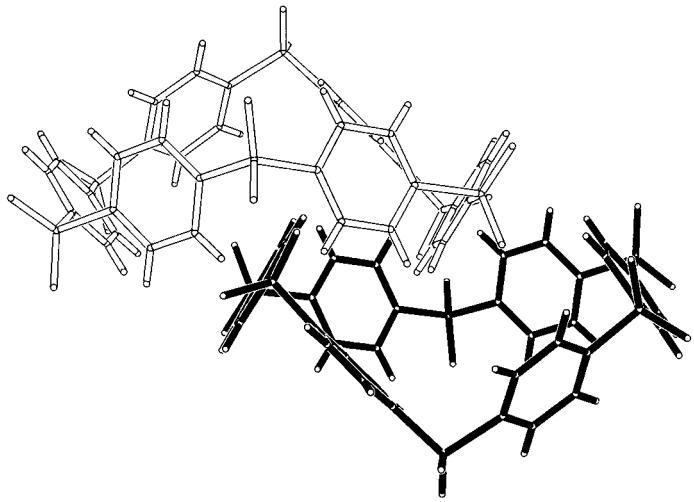


Figure 8. Top: The molecular structure of the phenylsulfone hexamer **3b**. The in-chain angles [°] at the sulfur atoms are: S(1) 106.1(3), S(8) 105.1(3), S(15) 106.4(4), S(22) 102.0(4), S(29) 104.8(4), S(36) 105.3(3). The mean torsional twists [°] about the S–Ph bonds are: S(1)–C(2) 65, C(5)–S(8) 81, S(8)–C(9) 76, C(12)–S(15) 88, S(15)–C(16) 45, C(19)–S(22) 69, S(22)–C(23) 76, C(26)–S(29) 8, S(29)–C(30) 71, C(33)–S(36) 66, S(36)–C(37) 80, C(40)–S(1) 86. Middle: The conformation of the S6 ring in **3b**. Bottom: An "embryonic" homodimer formed by centrosymmetrically related pairs of cyclic hexamers in the crystal of **3b**.

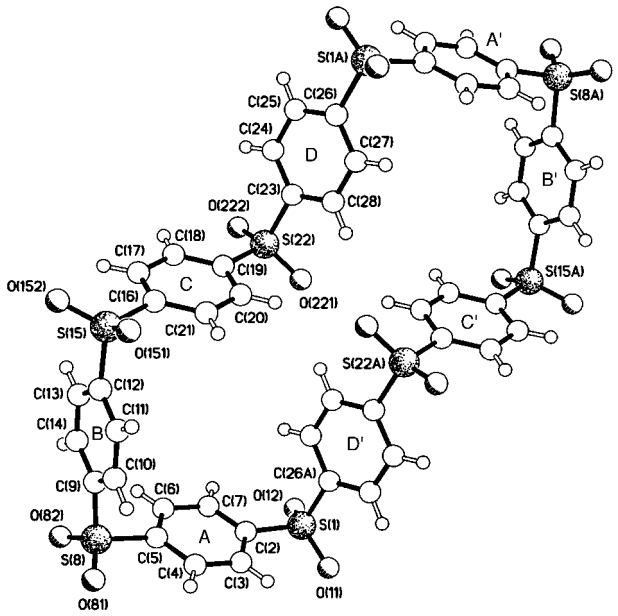


Figure 9. The solid state structure of the pseudo-octamer **3c′**. The in-chain angles [°] at the sulfur atoms are: S(1) 101.4(3), S(8) 102.1(3), S(15) 101.8(3), S(22) 103.3(3). The backbone torsion angles [°] are C(26A)–S(1) 67, S(1)–C(2) 86, C(5)–S(8) 77, S(8)–C(9) 88, C(12)–S(15) 69, S(15)–C(16) 83, C(19)–S(22) 79, S(22)–C(23) 85.

Conclusion

Macrocyclic oligomers of poly(1,4-phenylenesulfone), the first sulfone-linked paracyclophanes, have been obtained by cyclocondensation of 4,4′-dichlorodiphenylsulfone with aromatic dithiols, followed by fractionation and oxidation of the isolated and purified thioethersulfone macrocycles with hydrogen peroxide. Crystallographic analyses of sulfone-linked paracyclophanes suggest that the smaller macrocycles, containing four or six aromatic rings, have significant potential for complexation of electron-rich species. These cyclophanes are, however, somewhat intractable, with very high crystal melting points restricting their potential for ring-opening polymerisation.

Experimental Section

General methods and instrumentation: All chemicals were standard reagent grade and were used without further purification. All air-sensitive and/or moisture-sensitive reactions were conducted under a dry argon or nitrogen atmosphere. Thin layer chromatography (TLC) was conducted on Polygram SIL G/UV_{254} Macherey–Nagel GmbH silica gel coated plastic plates. Compounds were visualised with iodine or by examination under UV light. Column chromatography was conducted on Aldrich silica gel, 230–400 mesh, 60 Å. ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini-200, Varian Unity Inova-300 and Varian Unity-500 spectrometers. Conventional mass spectra (EI/CI/FAB) were run on a Kratos Concept spectrometer, and MALDI-TOF MS analyses were obtained on Kratos Kompact and Micromass Tofspec instruments. Elemental analyses were provided by the analytical service of Manchester University. Differential scanning calorimetry (DSC) was performed under nitrogen using a Mettler DSC20 system. Conditions for HPLC analyses were: Perkin–Elmer LC-480 diode-array system, phenosphere silica gel column 8 mm × 10 cm, eluent 5% EtOAc in CH_2Cl_2, flow rate 2 mL min^{-1}.

Reaction of 4,4′-difluorodiphenylsulfone with Na_2S to prepare linear oligomers 5: Hydrated sodium sulfide, $Na_2S \cdot 9H_2O$ (2.83 g, 11.8 mmol), was added to DMAc (150 mL) and toluene (50 mL) in a flask fitted with a Dean–Stark apparatus. The mixture was heated under nitrogen to remove the water and allowed to cool to room temperature before 4,4′-difluorodiphenylsulfone (3.00 g, 11.8 mmol) was added in one portion. The mixture was heated at reflux for 24 h and allowed to cool before adding water (500 mL). The pale yellow precipitate was filtered off, dried and extracted with CH_2Cl_2 (3 × 100 mL; each time the insoluble material was filtered off and used in the subsequent extraction). The combined organic extracts were washed with water, dried and concentrated to give a residue (0.730 g) which was subjected to column chromatography (CH_2Cl_2/EtOAc; 0 to 5% EtOAc) to give, in order of elution:[17]

Compound **5a** (0.042 g, 1.4%); m.p. 196 °C (MeOH); ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C, TMS): $\delta = 7.12$ (t, 4H; H-7), 7.34 (d, 4H, H-2), 7.75 (d, 4H, H-3), 7.85 (m, 4H, H-6); ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C, TMS): $\delta =$ 116.4 (d, $^2J_{C,F} = 23$ Hz, C-7), 127.7 (C-3), 129.8 (d, $^3J_{C,F} = 10$ Hz, C-6), 130.5 (C-2), 136.6 (C-5), 139.8/140.5 (C-1, C-4), 164.8 (d, $^1J_{C,F} = 256$ Hz, C-8); anal. calcd (%) for $C_{24}H_{16}F_2O_4S_3$: C 57.36, H 3.21; found C 57.33, H 3.20; HR-MS: *m*/*z*: 502.0179; found 502.0182 $[M]^+$.

Compound **5b** (0.105 g, 3.5%); m.p. 239.6 °C (DSC, from CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): $\delta = 7.12$ (t, 4H, H-11), 7.31–7.37 (m, 8H, H-3,6), 7.76–7.81 (m, 8H, H-2,7), 7.88 (m, 4H, H-10); ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C, TMS): $\delta = 116.7$ (d, $^2J_{C,F} = 23$ Hz, C-11), 128.4/128.5 (C-2,7), 131.0/131.3 (C-3,6), (d, $^3J_{C,F} = 10$ Hz, C-6), 130.5 (C-2), 136.6 (C-5), 139.8/140.5 (C-1, C-4), 164.8 (d, $^1J_{C,F} = 256$ Hz, C-8); anal. calcd (%) for $C_{36}H_{24}F_2O_6S_5$: C 57.58, H 3.22; found C 57.56, H 3.27; HR-MS: *m*/*z*: 750.0144; found 750.0142.

Compound **5c** (0.128 g, 4.3%); m.p. 213.1 °C (DSC, from CH_2Cl_2/EtOAc); $T_g = 105.0$ °C (DSC); ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C, TMS): $\delta = 7.21$–7.28 (br, 4H, H-15), 7.45–7.49 (d, 12H, H-2,7,10), 7.89–7.91 (d, 12H, H-3,6,11), 7.96–8.01 (m, 4H, H-14); ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C, TMS): $\delta = 116.4$ (d, $^2J_{C,F} = 23$ Hz, C-15), 127.5, 127.7, 127.8 (C-3,6,11), 129.8 (d, $^3J_{C,F} = 10$ Hz, C-14), 130.4, 130.5, 130.6 (C-2, 7, 10), 136.6 (C-13), 139.5, 139.6, 140.0 140.3, 140.6, 140.8 (C-1,4,5,8,9,12), 164.9 (d, $^1J_{C,F} = 256$ Hz, C-8); anal. calcd (%) for $C_{48}H_{32}F_2O_8S_7$: C 57.70, H 3.23, S 22.46; found C 57.79, H 3.15, S 22.51; FAB-MS: *m*/*z*: 999 $[M]^+$, 1021 $[M + Na]^+$.

Compound **5d** (0.127 g, 4.3%); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS) $\delta = 7.15$–7.20 (br, 4H, H-19), 7.37–7.41 (m, 16H, H-3,6,11,14), 7.82–7.87 (m, 16H, H-2,7,10,15), 7.92–7.95 (m, 4H, H-18); ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C, TMS, selected resonances): $\delta = 116.8$ (C-19), 128.3, 128.5, 128.6, 128.6 (C-2,7,10,15), 130.5 (C-18), 131.0, 131.2, 131.3, 131.4 (C-3,6,11,14), 140.1, 140.3, 140.4, 140.7, 140.9, 141.2, 141.3, 141.5 (C-1,4,5,8,9,12,13,16); anal. calcd (%) for $C_{60}H_{40}F_2O_9S_{10}$: C 57.69, H 3.21; found C 58.04, H 3.57; FAB-MS: 1247 $[M]^+$, 1269 $[M + Na]^+$.

Cyclic oligomers 6: 4,4′-Dichlorodiphenylsulfone (**4b**) (5.0 g, 17.4 mmol) and 4,4′sulfonylbis(benzenethiol) (**7a**) (4.8 g, 17.4 mmol) were dissolved in DMAc (135 mL) and added with a syringe pump over 48 h to a refluxing suspension of K_2CO_3 in DMAc (500 mL) and benzene (66 mL) under nitrogen in a flask fitted with a Dean–Stark apparatus. The heating was maintained for further 2 h, and then the mixture was allowed to cool before adding water (1500 mL). The precipitate was filtered off, dried and extracted with chloroform in a Soxhlet apparatus. A sample taken before extraction was analysed by FAB-MS which revealed the presence of $[M + 1]^+$ molecular ions at *m*/*z*: 497, 745, 993, 1242, and 1490, corresponding to cyclodimer, -trimer, -tetramer, -pentamer and -hexamer. The chloroform extract was concentrated to dryness and the solid re-extracted into CH_2Cl_2 (ca. 100 mL) before being subjected to column chromatography (CH_2Cl_2/EtOAc 0 to 5% EtOAc) to give, in order of elution:

Compound **6a** (0.06 g, 0.7%); m.p. >375 °C (from CH_2Cl_2/EtOAc); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): $\delta = 7.52$, 7.55, 7.58, 7.61 (AA′ BB′ system, 2 × 8H, H-*ortho*(-SO_2-,-S-)); ^{13}C NMR (CD_2Cl_2, 75 MHz): $\delta =$ 127.9 (CH *ortho*(-SO_2-)), 135.1 (CH *ortho*(-S-)), 142.0 (Cq), 143.6 (Cq); EI-MS: anal. calcd for $C_{24}H_{16}O_4S_4$: 495.9931; found 496 $[M]^+$; CIMS: found 514 $[M + NH_4]^+$; HRMS: found 495.9943. Crystals suitable for X-ray analysis were grown from solution in dichloromethane/ethyl acetate.

Compound **6b** (1.47 g, 17%); m.p. 412.1 °C (DSC, from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): $\delta = 7.41$, 7.44, 7.82, 7.85 (AA′ BB′, 2 × 8H, H-*ortho*(-SO_2-,-S-)); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): $\delta = 128.6$ (CH *ortho*(-SO_2-)), 131.5 (CH *ortho*(-S-)), 140.0 (Cq), 141.0 (Cq); anal.

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calcd (%) for $C_{36}H_{24}O_6S_6$: C 58.04, H 3.24, S 25.82; found C 58.09, H 3.22, S 26.01; FAB-MS: *m/z*: 744.9682; found 745 $[M+1]^+$, 898 $[M+m\text{NBA}]^+$; crystals suitable for X-ray analysis were obtained from chloroform.

Compound **6c** (0.786 g, 9%); m.p. 441.4 °C (by DSC, form **I**+**II**); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): $\delta = 7.39$, 7.42, 7.84, 7.87 (AA′BB′ system, 2×8H, H-*ortho* (-SO_2-,-S-)); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): $\delta =$ 128.6 (CH *ortho* (-SO_2-)), 131.0 (CH *ortho*(-S-)), quaternary carbons not detectable because of the low solubility of the compound; anal. calcd for $C_{48}H_{32}O_8S_8$: C 58.04, H 3.24, S 25.82; found C 57.70, H 3.51, S 25.84. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution in CH_2Cl_2/$CHCl_3$ (form **II**) and by vapour diffusion of benzene into $CHCl_3$ (form **I**). The DSC trace of **6c(II)** shows a complex set of curves (corresponding to loss of solvent and recrystallisation) before the final melting point is reached. The melting point thus appears to be independent of the solvent of crystallisation.

Cyclic oligomers 8: 4,4′-Dichlorodiphenylsulfone (**4b**) (2.47 g, 8.63 mmol) and 4,4′-thiobis(benzenethiol) (**7a**) (2.16 g, 8.63 mmol) were dissolved in DMAc (100 mL) and added dropwise over 5 h to a stirred, refluxing (145 °C) suspension of K_2CO_3 in DMAc (200 mL) and toluene (40 mL) under nitrogen, in a flask fitted with a Dean–Stark apparatus. At the end of the addition, the temperature of the reaction was raised to 155 °C by removal of toluene and maintained at this temperature for a further 15 h. The mixture was then allowed to cool before filtering to remove precipitated salts. The filtrate was concentrated to about 60 mL and added slowly to dilute hydrochloric acid (300 mL) with vigorous stirring. The precipitate was filtered off, washed with water until the washings were neutral, and then re-suspended in methanol at 60 °C. After stirring for 30 min the solid was recovered by filtration and dried under vacuum at 70 °C to yield 4.31 g of the product. Analysis by FAB-MS showed $[M+1]^+$ molecular ions at *m/z*: 464, 929, 1393, 1857, and 2324, corresponding to cyclomonomer **8a**, -dimer **8b**, -trimer **8c**, -tetramer **8d**, and -pentamer **8e**. The product mixture was subjected to column chromatography (CH_2Cl_2/EtOAc, 0 to 5% EtOAc) to give, in order of elution:

Compound **8a** (0.01 g, 0.25%); m.p. 362 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS) $\delta = 7.64$ (d, $J = 8.8$ Hz, 4H, H-*ortho*(-SO_2-)), 7.54 (d, $J =$ 8.8 Hz, 4H, H-*meta*(-SO_2-)), 7.10 (s, 8H, H-*ortho*-/-*meta*-(-S-)); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): $\delta = 127.6$, 127.7 129.9, 131.4, 134.9, 137.3, 138.5, 141.3; anal. calcd for $C_{24}H_{16}O_2S_4$: C 62.04, H 3.47, S 27.60; found C 62.08, H 3.48, S 27.82; FAB-MS: *m/z* (%): 464 $[M]^+$ (100).

Compound **8b** (0.35 g, 9%); m.p. 378.4 °C (DSC); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): $\delta = 7.75$ (d, 8H, H-*ortho*(-SO_2-)), 7.44 (d, 8H, H-*meta*(-SO_2-)), 7.36 (d, 8H, H-*ortho*-/-*meta*-(-S-)), 7.18 (d, 8H, H-*ortho*-/-*meta*-(-S-)); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): $\delta = 126.8$, 127.8 129.7, 131.6, 135.0, 136.6, 138.2, 145.3; anal. calcd (%) for $C_{24}H_{16}O_2S_4$: C 62.04, H 3.47, S 27.60; found C 62.29, H 3.28, S 27.67 FAB-MS: *m/z* (%): 929 $[M+H]^+$ (100).

Compound **8c** (0.18 g, 4.5%); m.p. 158.3 °C (DSC); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): $\delta = 7.76$ (d, 8H, H-*ortho*(-SO_2-)), 7.40 (d, 8H, H-*meta*(-SO_2-)), 7.35 (d, 8H, H-*ortho*-/-*meta*-(-S-)), 7.23 (d, 8H, H-*ortho*-/-*meta*-(-S-)); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): $\delta = 127.8$, 127.9 130.4, 131.7, 134.3, 136.3, 138.5, 144.8; anal. calcd (%) for $C_{24}H_{16}O_2S_4$: C 62.04, H 3.47, S 27.60; found: C 62.14, H 3.23, S 27.41; FAB-MS: 1394 $[M+H]^+$ (100).

Compound **8d** (0.04 g, 1%); $T_g = 134$ °C (DSC); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): $\delta = 7.78$ (d, 8H, H-*ortho*(-SO_2-)), 7.44 (d, 8H, H-*meta*(-SO_2-)), 7.38 (d, 8H, H-*ortho*-/-*meta*-(-S-)), 7.25 (d, 8H, H-*ortho*-/-*meta*-(-S-)); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): $\delta = 127.8$, 127.9 130.5, 131.8, 134.4, 136.4, 138.6, 144.9; anal. calcd (%) for $C_{24}H_{16}O_2S_4$: C 62.04, H 3.47, S 27.60; found C 62.01, H 3.45, S 27.82; FAB-MS: *m/z* (%): 1859 $[M+H]^+$ (100).

Compound **8e** (0.025 g, 0.6%); $T_g = 128$ °C (DSC); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): $\delta = 7.78$ (d, 8H, H-*ortho*(-SO_2-)), 7.43 (d, 8H, H-*meta*(-SO_2-)), 7.37 (d, 8H, H-*ortho*-/-*meta*-(-S-)), 7.25 (d, 8H, H-*ortho*-/-*meta*-(-S-)); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, TMS): $\delta = 127.8$, 127.9 130.5, 131.8, 134.4, 136.4, 138.6, 144.9; anal. calcd (%) for $C_{24}H_{16}O_2S_4$: C 62.04, H 3.47, S 27.60; found C 62.08, H 3.54, S 27.33; FAB-MS: *m/z* (%): 2323 $[M+H]^+$ (100).

General procedure for the oxidation of the cyclic oligomers 6 to give oligomers 3: The cyclic oligomer (**6a**, **6b** or **6c)** was suspended in glacial acetic acid (2 mL acid for 50 mg compound) using a ultrasonic bath, and an excess of hydrogen peroxide (30%, 1 mL for 50 mg compound) was added to the suspension. In the cases of **6a** and **6b** the hydrogen peroxide was added in one portion and the mixtures were sonicated at 50 °C for 6 h. In the case of the **6c** the hydrogen peroxide was added in four portions over a period of 24 h and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. During this time the mixture was sonicated at 85–90 °C. The work-up consisted of the addition of water to the mixtures followed by filtration, which afforded quantitative yields of the sulfonated macrocycles **3a** and **3b** and of the heptasulfone-sulfoxide **3c′**. These compounds were recrystallised from DMSO, acetone and DMSO, respectively.

Compound **3a**: M.p. >375 °C (DMSO); ^{1}H NMR ([D_6]DMSO, 300 MHz, 25 °C, TMS): $\delta = 8.21$ (s, 16H); ^{13}C NMR ([D_6]DMSO, 75 MHz, 25 °C, TMS): $\delta = 130.0$ (C-H), 145.1 (Cq); anal. calcd for $C_{24}H_{16}O_4S_8$: 559.9728; EI-MS: *m/z*: 560 $[M]^+$; HRMS: 559.9730; crystals suitable for X-ray analysis were obtained by the slow cooling of a DMSO solution.

Compound **3b**: M.p. 495.0 °C (by DSC, acetone); ^{1}H NMR ([D_6]DMSO, 300 MHz, 25 °C, TMS) $\delta = 8.21$ (s, 24H); ^{13}C NMR ([D_6]DMSO, 75 MHz, 25 °C, TMS): $\delta = 129.6$ (C-H), 144.6 (Cq); calcd for $C_{36}H_{24}O_{12}S_6$: C 51.42, H 2.87, S 22.87; found C 51.64, H 2.79, S 22.57; ES-MS (neg. KCl/acetone): 839.96; found 874 $[M+Cl]^-$; crystals suitable for X-ray analysis were obtained by very slow cooling of a solution in acetone.

Compound **3c′**: ^{1}H NMR ([D_6]DMSO, 300 MHz, 25 °C, TMS): $\delta = 8.21$ (s, 24H), 8.24–8.16/7.78–7.90 (AA′BB′, 8H); ^{13}C NMR ([D_6]DMSO, 75 MHz, 25 °C, TMS): $\delta = 129.4$ (C-H), 144.7 (Cq); anal. calcd for $C_{48}H_{32}O_{15}S_8$: 1103.95; MALDI-TOF: *m/z*: 1111 $[M+Li]^+$, 1127 $[M+Na]^+$, 1143 $[M+K]^+$; crystals suitable for X-ray analysis were obtained by slow cooling of a DMSO solution.

General procedure for the oxidation of the cyclic oligomers 8 to give oligomers 3: The cyclic oligomer [**8b** (0.25 g) or **8c** (0.20 g)] was suspended in trifluoroacetic acid (12 mL) at 60 °C and hydrogen peroxide (30%, 10 mL) was added dropwise to the stirred suspension over a period of 15 min. The temperature was then raised to 80 °C and kept for 3 h, before filtering the solid product, which was washed with water and then methanol, and finally dried at 100 °C under vacuum. The yields for **3c** and **3d** were essentially quantitative.

Compound **3c**: ^{1}H NMR ($CDCl_3$/CF_3COOD, 300 MHz): $\delta = 8.08$ (s, 32H); anal. calcd for (%) $C_{48}H_{32}O_{16}S_8$: C 51.41, H 2.87, S 22.87; found C 51.20, H 2.69, S 22.52; m.p. >550 °C (DSC).

Compound **3d**: ^{1}H NMR ($CDCl_3$/CF_3COOD, 300 MHz): $\delta = 8.16$ (s, 48H); anal. calcd for $C_{72}H_{48}O_{24}S_{12}$: C 51.41, H 2.87, S 22.87; found C 50.67, H 2.42, S 22.40; m.p. >550 °C (DSC).

X-ray crystallography: Table 1 provides a summary of the crystal data, data collection, and refinment parameters for compounds **5b**, **6a**, **6b**, **6c(I)**, **6c(II)**, **3a**, **3b**, **3c′**, and **8b**. The data were corrected for Lorentz and polarisation effects and for absorption (with ψ-scans). The structures were solved by direct methods and refined anisotropically by full matrix least-squares based on F^2. Hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent atoms. Major occupancy solvent molecules were refined anisotropically, minor components isotropically. Computations were carried out using the SHELXTL PC program system.[18]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-182685, -182970, -142878 (**5b**), -142879 (**8b**). 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).

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