# Sulfone-linked paracyclophanes

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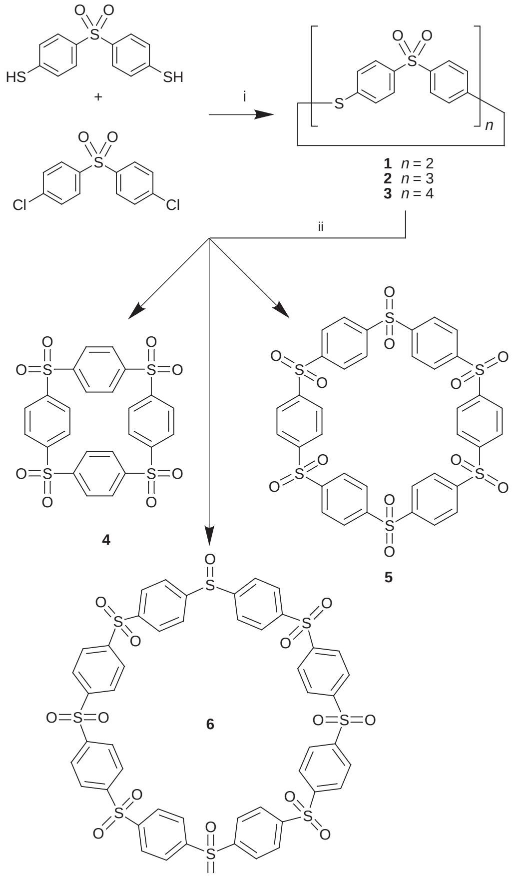
**Oxidation of the macrocyclic thioether sulfones $(S\phi SO_2\phi)_n$ ($\phi$ = 1,4-phenylene; $n$ = 2 or 3) affords sulfone-linked paracyclophanes $(\phi SO_2)_4$ and $(\phi SO_2)_6$; single crystal X-ray analysis reveals the tetramer, $(\phi SO_2)_4$, to be a near-perfect square box, whilst the hexamer, $(\phi SO_2)_6$, adopts a much more irregular conformation; exhaustive oxidation of $(S\phi SO_2\phi)_4$, leads not to the expected octamer, $(\phi SO_2)_8$, but to the heptasulfone sulfoxide $[(\phi SO_2)_7(\phi SO)]$.**

The recent discovery of a route to macrocyclic aromatic thioether sulfones containing from four to (at least) 24 aromatic rings has opened up the possibility of converting these, by oxidation, to their all-sulfone analogues (Scheme 1).[1] The strongly electron-withdrawing nature of the sulfone group compared to the electron-donating thioether linkage offers the potential to create a new family of $\pi$-electron deficient receptors which, unlike those based on bipyridinium systems,[2] would obviate the need for counterions. Moreover, the exceptionally rigid nature of the diphenyl sulfone unit, coupled with its preferred 'open-book' conformation,[3] should provide a high degree of pre-organisation in any non-covalent complexation process. From a materials perspective, these all-sulfone macrocycles could provide a new approach (ring-opening polymerisation)[4] to the extremely stable but very high-melting and currently unprocessable linear poly(1,4-phenylene sulfone).[5]



**Scheme 1** *Reagents and conditions*: i, $K_2CO_3$, DMA, 150 °C, 48 h; ii, $H_2O_2$, AcOH, 60 °C

Here we report that peroxide oxidation of the macrocyclic thioethersulfones **1** and **2** in glacial acetic acid does indeed afford the sulfone-linked paracyclophanes **4** and **5** (sulfur analogues of the known [1.1.1.1]paracyclophane and [1.1.1.1.1.1]paracyclophane, respectively).[6] Oxidation of **3** cannot however be driven to completion under these conditions,** the reaction ceasing at the heptasulfone sulfoxide stage (**6**) rather than affording the expected cyclic octasulfone.

The symmetrical aromatic substitution pattern in macrocycles **4** and **5** 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 sulfide sulfone substitution patterns of **1** and **2**. However, in keeping with the presence of a sulfoxide linkage in **6**, the $^1$H NMR spectrum of this material comprises an AA′BB′ system integrating as two aromatic rings, together with a single resonance representing the remaining six rings, at $\delta$ 8.21, superimposed on the lower field component. Confirmation that compound **6** is a single oxidation product (rather than a mixture) was provided by the unchanging ratio of the integration values in its $^1$H NMR spectrum on repeated recrystallisation from DMA, and by MALDI-TOF mass spectrometry of **6** (anthracene-1,8,9-triol matrix, LiBr as cationising agent) which showed a strong parent ion at *m/z* 1111, corresponding to $[(C_6H_4SO_2)_7(C_6H_4SO)Li]^+$.

The solubilities of macrocycles **4** and **6** in conventional organic solvents are very low indeed and, although $^1$H and $^{13}$C NMR spectra of **4** were obtained (with some difficulty) in [$^2H_6$]DMSO solution, a solvent mixture of TFA and $CD_2Cl_2$ was required to obtain NMR spectra of compound **6**. The cyclic hexamer **5**, in contrast, was easily soluble in a wide range of organic solvents including $CHCl_3$ and acetone.

In order to establish the conformational characteristics of the diaryl sulfone unit as a function of ring size, single crystal X-ray structures were determined for **4** (DMSO solvate), **5** (acetone

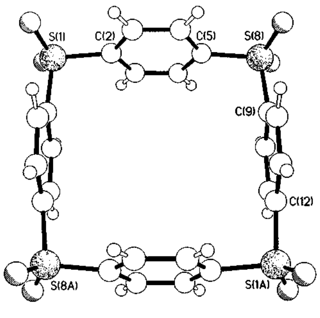


**Fig. 1** Molecular structure of the cyclic tetrasulfone **4**. There is a very slight tilting from orthogonality of the aromatic rings with respect to the $S_4$ plane; the C(2)–C(7) ring is inclined at 86° and the C(9)–C(14) ring at 89° to this plane.

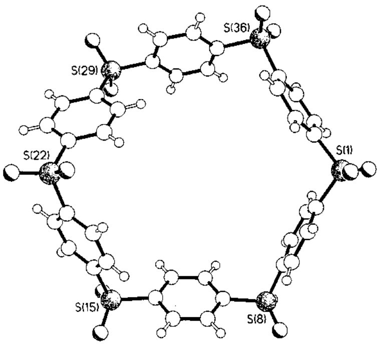


**Fig. 2** Molecular structure of the cyclic hexasulfone **5**. Torsion angles about the S–phenyl linkages are in the range 45–88°, with the exception of an 8° torsion angle at S(29).

solvate) and **6** (DMSO solvate).†† The C–S–C bond angles in **5** and **6** lie very close to the conventional unstrained value[3] of 105° but in the effectively *square* cyclic tetramer **4** (Fig. 1) these angles are sharply reduced to an average value of 99.5°. Commensurate distortions are evident in the aromatic ring systems, which in **4** undergo a distinct outward bowing such that 1,4-related C–S bonds, which would normally be co-linear, here subtend angles averaging 10°. In contrast, the aromatic rings of oligomer **5** (Fig. 2) are bowed *inwards*, with the corresponding angle averaging −7.5°.

Remarkably, the structure of compound **6** in fact represents that of the originally-expected octasulfone [(1,4-$C_6H_4SO_2)_8$]. It thus appears that, when oxidation reaches the heptasulfone sulfoxide stage, this compound is able to crystallise *as though it were* the octasulfone, with the 'missing' oxygen atom being disordered over all sixteen possible sites. In keeping with the identification of macrocycle **6** as a *pseudo*-octasulfone, the average crystallographic occupancy of the oxygen atoms in the molecule refined to a value significantly less than one (*ca.* 0.96; *cf.* a calculated value of 0.94 for 15/16 occupancy). Macrocycle **6** adopts a 'figure-of-eight' conformation (Fig. 3) which is essentially strain-free, the two halves of the molecule each approximating the box-like structure of oligomer **4**. Contacts between the sulfone oxygen atoms at S(22) and S(22A) are avoided by a relative shearing of the two sides of the macrocycle, though there is evidence for weak but co-operative C–H···O hydrogen bonding interactions between these sulfone oxygens and transannular C–H groups (Fig. 3).

The cyclic tetramer **4** provides a rare example of a structurally characterised organic molecular square.[7] 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 diameter *ca.* 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 of rotaxane formation with linear, electron-rich species such as the polyalkynes. Complexation studies with **4** are currently in progress.

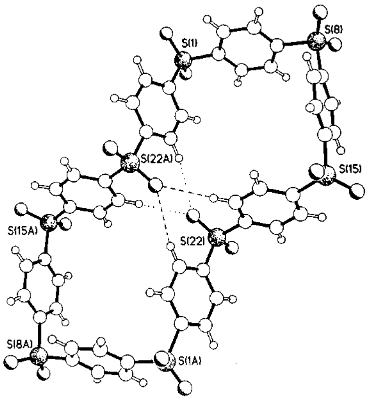


**Fig. 3** Molecular structure of the cyclic *pseudo*-octasulfone **6** showing the transannular C–H···O interactions; the two independent sets of C–O and H–O distances and C–H···O angles are: 3.46 and 2.53 Å, 176°; 3.58 and 2.65 Å, 170°

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## Notes and References

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** The macrocyclic sulfide sulfone **1**, **2** or **3** (ref. 1) (0.30 g) was suspended in a mixture of glacial AcOH (15 $cm^3$) and 30% aq. $H_2O_2$ (7.5 $cm^3$) and heated at 60 °C for 8 h with continuous sonication. For macrocycle **3**, further 30% $H_2O_2$ (7.5 $cm^3$) was then added to the reaction mixture and oxidation continued at 85 °C for 16 h. Yields were essentially quantitative. *Selected data* for **4**: $\delta_H$([$^2H_6$]DMSO) 8.21 (s); $\delta_C$([$^2H_6$]DMSO) 130.0, 145.1 (Found: 559.9730. Calc.for $C_{24}H_{16}S_4O_8$: 559.9728). For **5**: $\delta_H$([$^2H_6$]DMSO) 8.21 (s); $\delta_C$([$^2H_6$]DMSO) 129.6, 144.5; *m/z* (ES-MS, −ve) 874–877 ([M+Cl]$^-$). For **6**: $\delta_H$($CD_2Cl_2$–TFA) 8.21 (s+m, 28H), 7.94 (m, 4H); *m/z* (LiBr-doped MALDI-TOF) 1011 [$(C_6H_4SO_2)_7(C_6H_4SO)Li]^+$ and 1027 [$(C_6H_4SO_2)_7(C_6H_4SO)Na]^+$.

†† *Crystal data* for **4**: [$C_{24}H_{16}O_8S_4\cdot 2DMSO$]: $M$ = 716.86, monoclinic, $a$ = 9.966(5), $b$ = 18.003(5), $c$ = 10.391(4) Å, $\beta$ = 118.22(2)°, $V$ = 1643(1) Å$^3$, space group $P2_1/c$, $Z$ = 2, $\rho_{calc}$ = 1.449 g cm$^{-3}$, $\mu$(Cu-K$\alpha$) = 43.1 cm$^{-1}$, $F(000)$ = 744, $T$ = 293 K, 2419 unique reflections ($2\theta \leqslant 124°$), of which 1461 were observed [$I_o > 2\sigma(I_o)$]. $R_1$ = 0.0793, $wR_2$ = 0.1968. For **5**: [$C_{36}H_{24}O_{12}S_6\cdot 2.5(CH_3)_2CO$)]: $M$ = 986.11, orthorhombic, $a$ = 11.220(3), $b$ = 29.432(3), $c$ = 29.860(4) Å, $V$ = 9861(3) Å$^3$, space group $Pbca$, $Z$ = 8, $\rho_{calc}$ = 1.328 g cm$^{-3}$, $\mu$(Cu-K$\alpha$) = 31.0 cm$^{-1}$, $F(000)$ = 4096, $T$ = 293K, 7741 unique reflections ($2\theta \leqslant 124°$), of which 3718 were observed [$I_o > 2\sigma(I_o)$]. $R_1$ = 0.0778, $wR_2$ = 0.2037. For **6**: [$C_{48}H_{32}O_{15}S_8\cdot 6DMSO$]: $M$ = 1573.98, triclinic, $a$ = 11.479(2), $b$ = 11.583(2), $c$ = 15.936(3) Å, $\alpha$ = 80.34(2), $\beta$ = 78.63(2), $\gamma$ = 62.78(1)°, $V$ = 1840(1) Å$^3$, space group $P\bar{1}$, $Z$ = 1, $\rho_{calc}$ = 1.421 g cm$^{-3}$, $\mu$(Cu-K$\alpha$) = 44.2 cm$^{-1}$, $F(000)$ = 820, $T$ = 203 K, 5401 unique reflections ($2\theta \leqslant$ 120°), of which 3969 were observed [$I_o > 2\sigma(I_o)$]. $R_1$ = 0.0821, $wR_2$ = 0.2156.

Data for all structures were collected on Siemens P4 diffractometers using graphite monochromated Cu-K$\alpha$ radiation ($\lambda$ = 1.54178 Å; rotating anode source for **6**) and $\omega$-scans. The data were corrected for Lorentz and polarisation effects and for absorption (using $\psi$-scans). The structures were solved by direct methods and refined by least-squares based on $F^2$. All computations were carried out using the SHELXTL 5.03 package. CCDC 182/970.

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