Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Organic and Biomolecular Chemistry - SUPPORTING INFORMATION

Manuscript Title: Macrocyclic aromatic polysulfones: synthesis and structural characterisation of molecular pentagons and rectangles

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X-Ray Crystallography

The structure of the pentagonal macrocycle **2** was refined using the centrosymmetric space group $P2_1/m$, resulting in the presence of a mirror plane through the middle of the molecule. It is evident from the thermal ellipsoid plot that there is noticeable elongation of the thermal ellipsoids for the S(1) SO_2 unit and the adjacent C(1)-C(6) phenyl ring perpendicular to the plane of the mirror. This suggests that the macrocycle might not have perfect mirror symmetry, and instead be disordered across the mirror plane. The simplest way to handle this kind of disorder (if present) is to remove the mirror plane, *i.e* change the space group to $P2_1$, and this indeed was tried. Though the *R*-factor dropped to *ca.* 4.1% (*cf.* 4.6%), the elongation of the thermal ellipsoids was still present, so the refinement in the higher symmetry centrosymmetric space group was retained. The solvent present in the structure of **2** was found to be highly disordered, and so the SQUEEZE procedure of the PLATON program[S1] was used, suggesting 176 electrons per macrocycle. Before the use of SQUEEZE, the solvent had not been identified, so it was assumed to be the crystallisation solvent, dimethylacetamide, which has 48 electrons per molecule. The 176 electrons per macrocycle suggested by SQUEEZE closely corresponds to 3.75 dimethylacetamide molecules (180 electrons) per macrocycle, so the contents of the unit cell were adjusted on the basis of this being the solvent present.

The solvent present in the structure of **3** was found to be highly disordered, and so the SQUEEZE procedure of the PLATON program[S1] was used, suggesting 154 electrons per macrocycle. Before the use of SQUEEZE, the solvent present had most resembled a molecule of $COCl_2$ inside the macrocycle, and two chloroform molecules outside. A molecule of $COCl_2$ contains 48 electrons, whilst a molecule of chloroform contains 58 electrons, so $COCl_2$·2CHCl3 comprises 164 electrons. This is close to the 154 electrons per macrocycle

suggested by SQUEEZE so the contents of the unit cell were adjusted on the basis of this being the solvent present.

The structure of **6** was found to contain three crystallographically independent macrocycles, one in a general position (**6-A**) and two with C_i symmetry (**6-B** and **6-C**). In each of the molecules, disorder was found in the sulfur-based moieties at the corners of the macrocycles. For macrocycle **6-A**, electron density corresponding to SO_2 oxygen atom positions were seen around all four sulfur centres, but with those adjacent to S(1) and S(2) of much higher occupancy (*ca.* 81%) than those near S(3) and S(4) (*ca.* 19%), consistent with the species present always being the expected disulfide-disulfone macrocycle (though other interpretations are possible). For both of the centrosymmetric macrocycles **6-B** and **6-C**, the oxygen atoms of the unique portions of the molecules were found to be of only 50% occupancy, again consistent with the expected disulfide-disulfone macrocycle. The C(1) to C(12) biphenyl ring system of macrocycle **6-A** was found to be substantially disordered. Two orientations were identified of *ca.* 67 and 33% occupancy, and in each case the six-membered rings were refined as optimised rigid bodies. The C(1) to C(6) phenyl ring of macrocycle **6-C** was also found to be substantially disordered. Again, two orientations were identified of *ca.* 62 and 38% occupancy, and both six-membered rings were refined as optimised rigid bodies. For each of the disorders detailed above, only the major occupancy non-hydrogen atoms were refined anisotropically. The solvent present in the structure of **6** was found to be highly disordered, and so the SQUEEZE procedure of the PLATON program[S1] was used, suggesting 45 electrons per macrocycle. Before the use of SQUEEZE, the solvent had not been identified, so it was assumed to be the crystallisation solvent, dichloromethane, which has 42 electrons per molecule. This is close to the 45 electrons per macrocycle suggested by SQUEEZE so the contents of the unit cell were adjusted on the basis of this being the solvent present.

The solvent present in the structure of **7** was found to be highly disordered, and so the SQUEEZE procedure of the PLATON program[S1] was used, suggesting 38 electrons per macrocycle. Before the use of SQUEEZE, the solvent present had most resembled a molecule of CH_2Cl_2, which comprises 42 electrons. This is close to the 38 electrons per macrocycle suggested by SQUEEZE so the contents of the unit cell were adjusted on the basis of this being the solvent present.

References

S1 P. v.d. Sluis and A.L. Spek, *Acta Crystallogr., C*, 1990, **A46**, 194.

Fig. S1 The molecular structure of the C_s-symmetric macrocycle **2** (30% probability ellipsoids). Atoms with the suffix "A" are related to their counterparts without the "A" by the operation of the mirror plane (x, $-y+1/2$, z).

Fig. S2 The molecular structure of the C_i-symmetric macrocycle **3** (50% probability ellipsoids). Atoms with the suffix "A" are related to their counterparts without the "A" by the operation of the inversion centre ($-x+1$, $-y+1$, $-z$).

Fig. S3 The molecular structure of **5** (50% probability ellipsoids).

Fig. S4 The molecular structure of **6-A**, one of the three crystallographically independent macrocycles present in the crystal of **6**, showing the sulfone-sulfide disorder.

Fig. S5 The molecular structure of **6-A**, one of the three crystallographically independent macrocycles present in the crystal of **6**, showing the sulfone-sulfide disorder (30% probability ellipsoids).

Fig. S6 The molecular structure of **6-B**, one of the three crystallographically independent macrocycles present in the crystal of **6**, showing the sulfone-sulfide disorder.

Fig. S7 The molecular structure of **6-B**, one of the three crystallographically independent macrocycles present in the crystal of **6**, showing the sulfone-sulfide disorder (30% probability ellipsoids). Atoms with the suffix "C" are related to their counterparts with the suffix "A" by the operation of the inversion centre ($-x+2$, $-y$, $-z+1$).

Fig. S8 The molecular structure of **6-C**, one of the three crystallographically independent macrocycles present in the crystal of **6**, showing the sulfone-sulfide disorder.

Fig. S9 The molecular structure of **6-C**, one of the three crystallographically independent macrocycles present in the crystal of **6**, showing the sulfone-sulfide disorder (30% probability ellipsoids). Atoms with the suffix "D" are related to their counterparts with the suffix "B" by the operation of the inversion centre ($-x+1$, $-y$, $-z+2$).

Fig. S10 The molecular structure of **7** (30% probability ellipsoids).

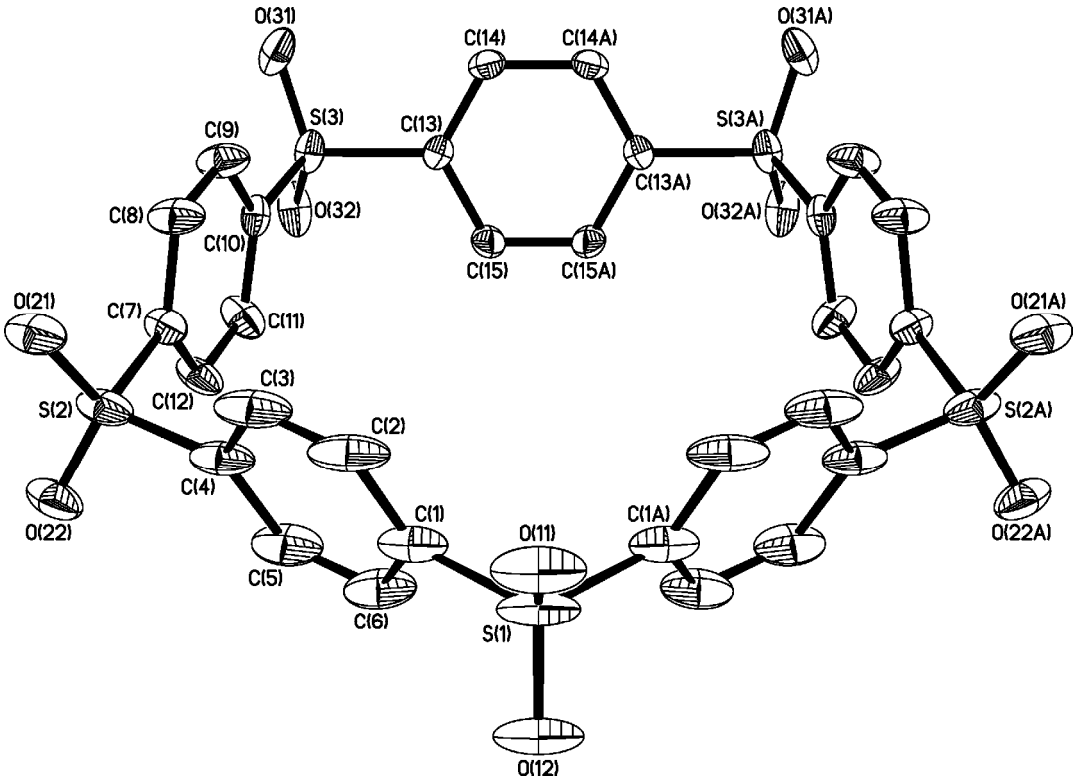
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Fig. S1

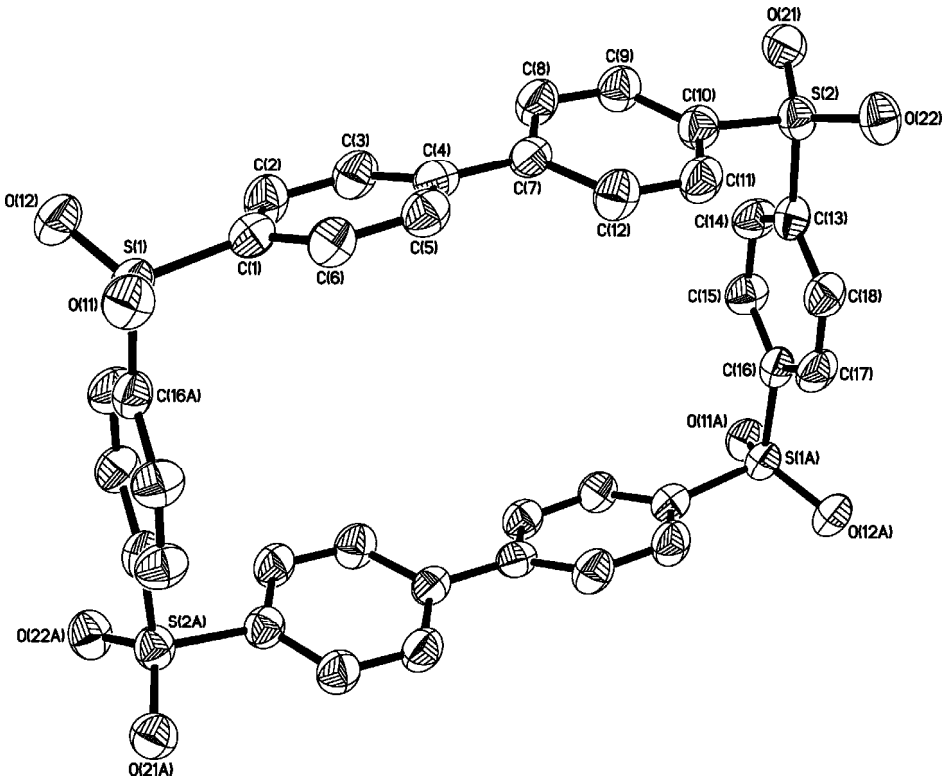
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Fig. S2

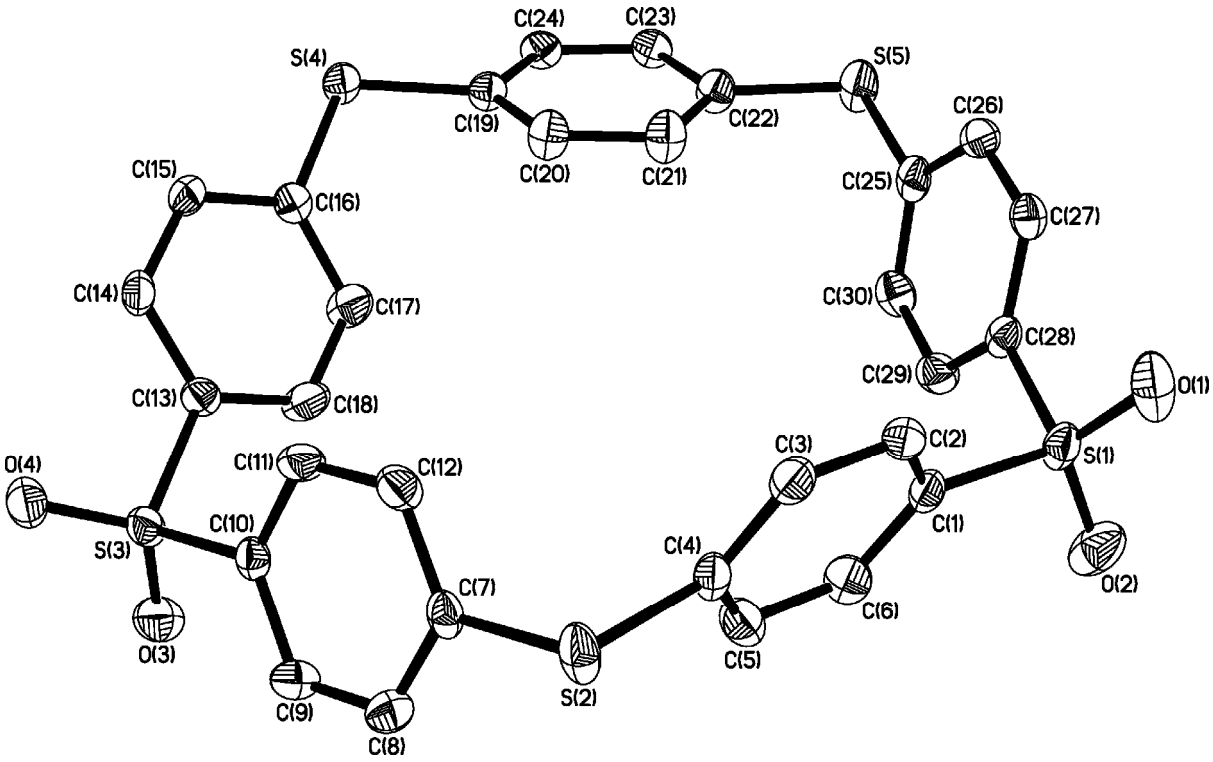
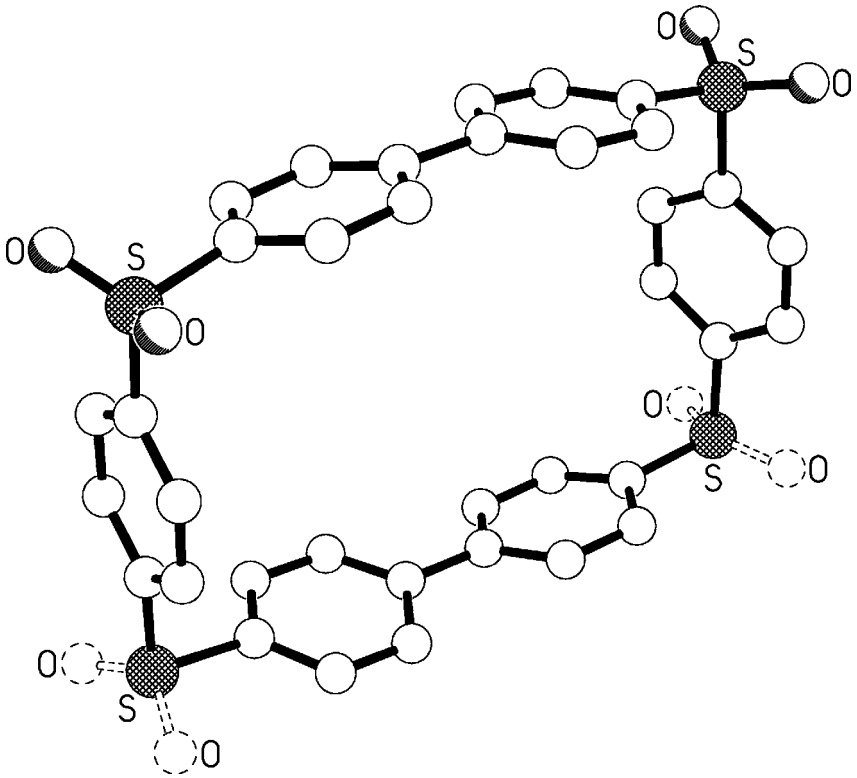


Fig. S3



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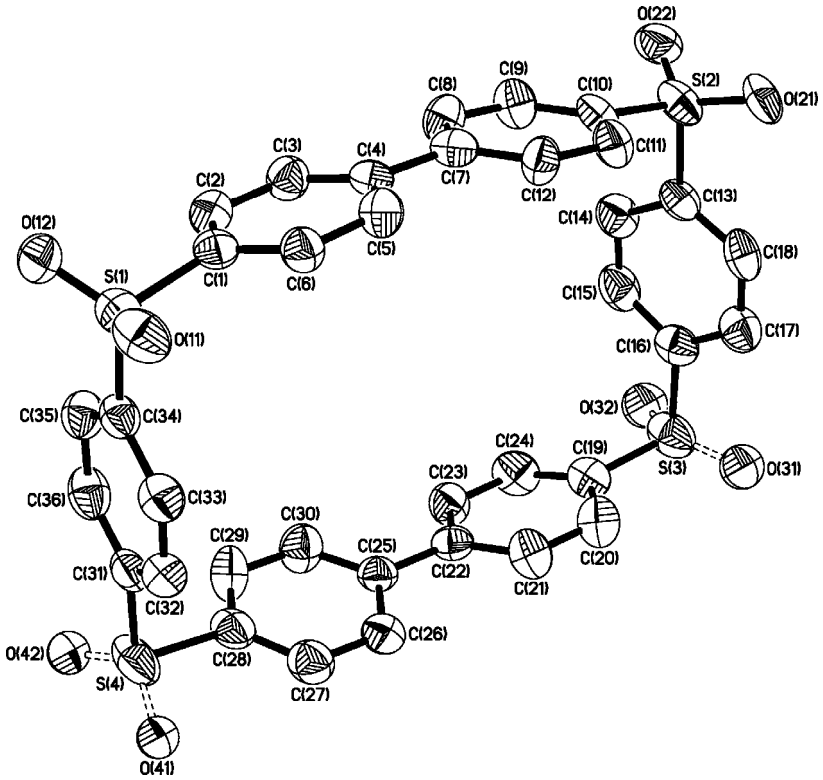
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Fig. S5

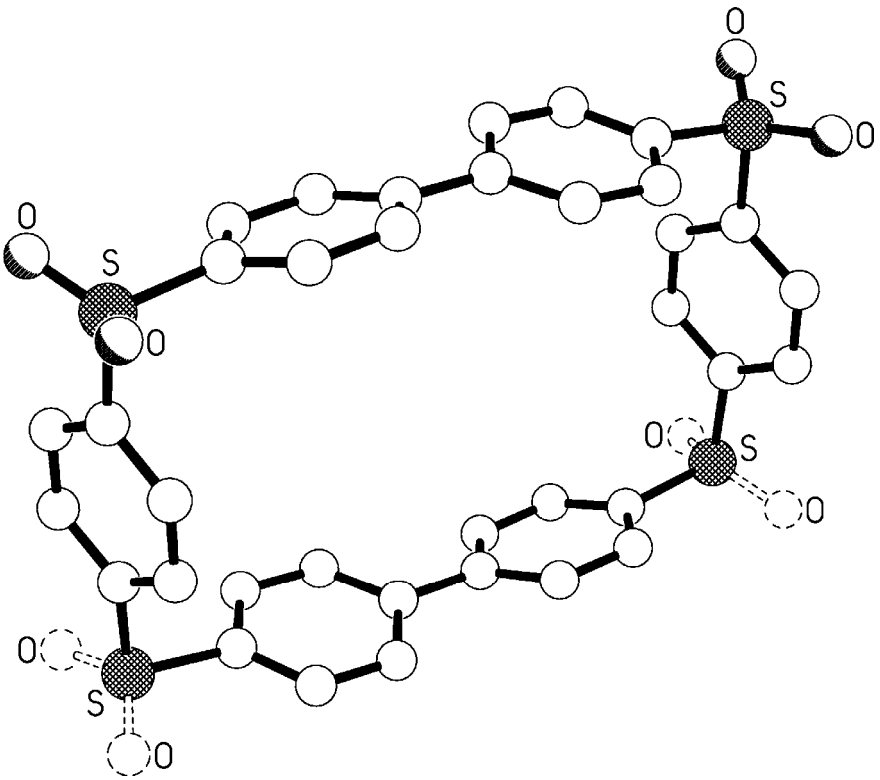
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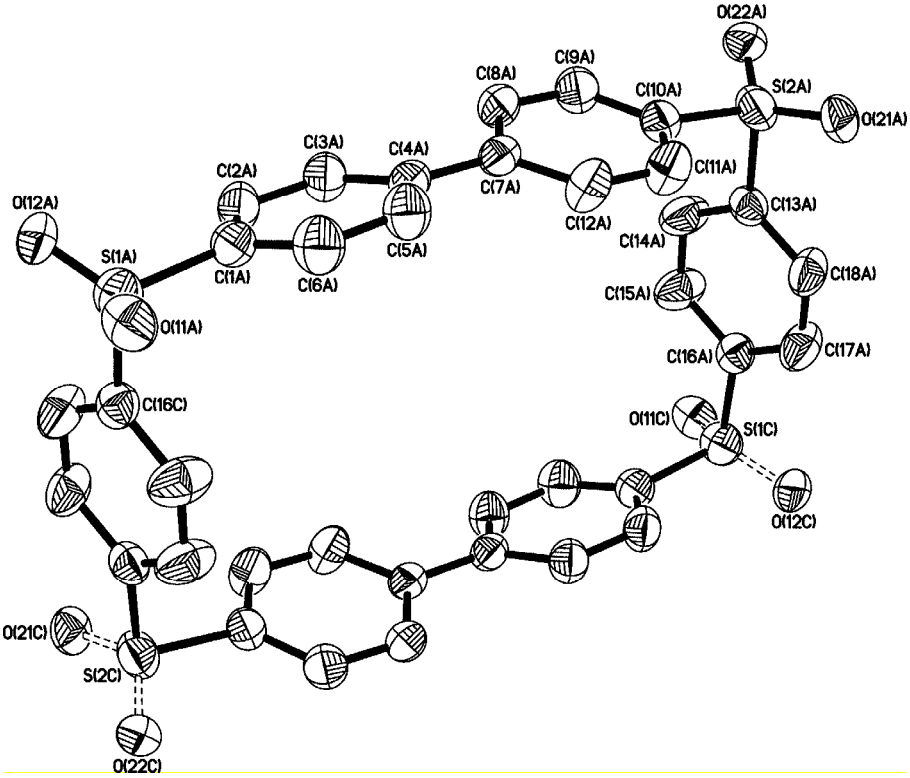
Fig. S6



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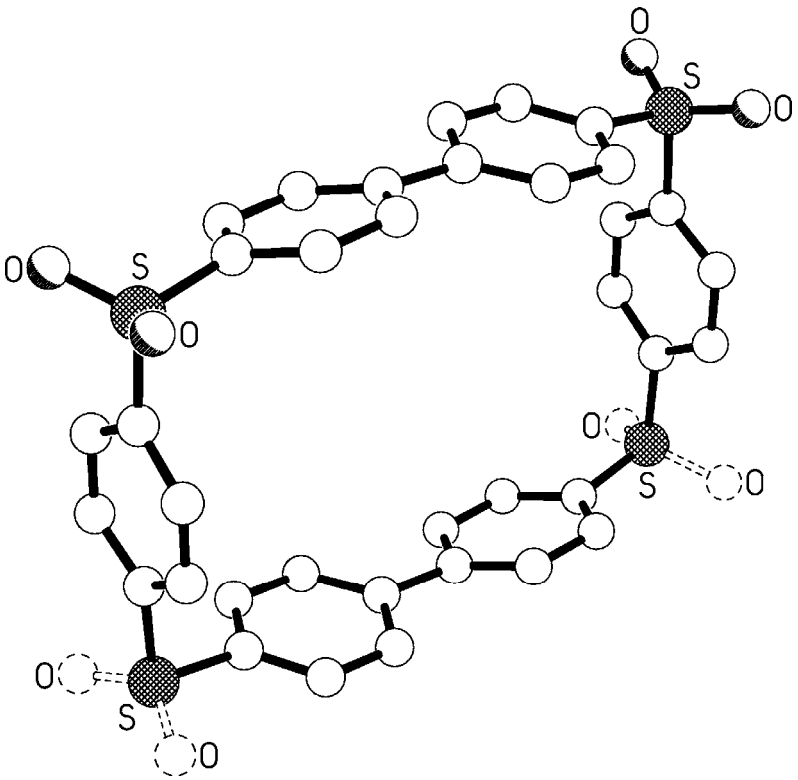
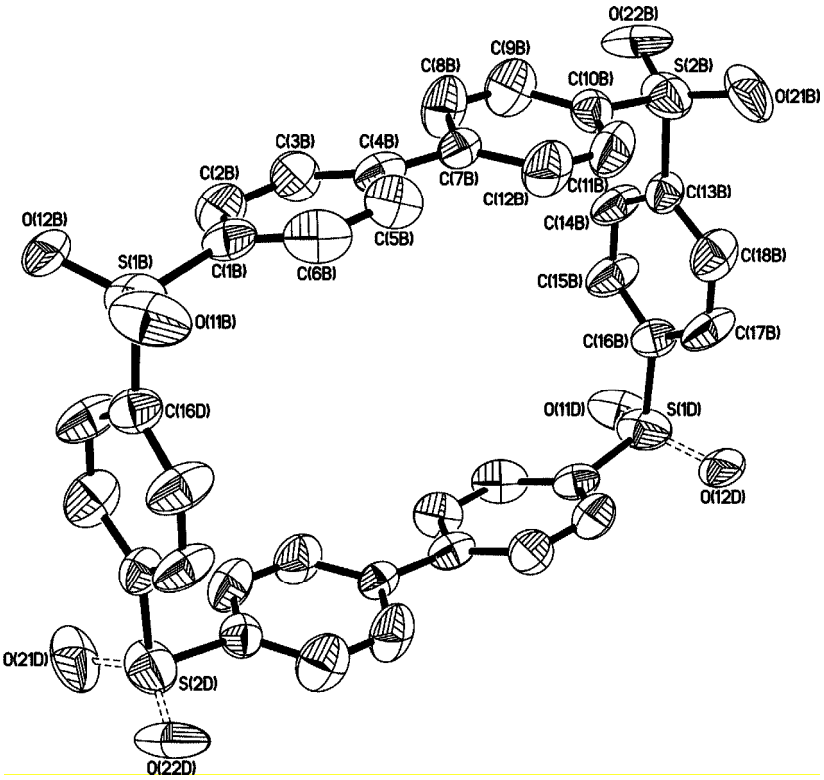


Fig. S8



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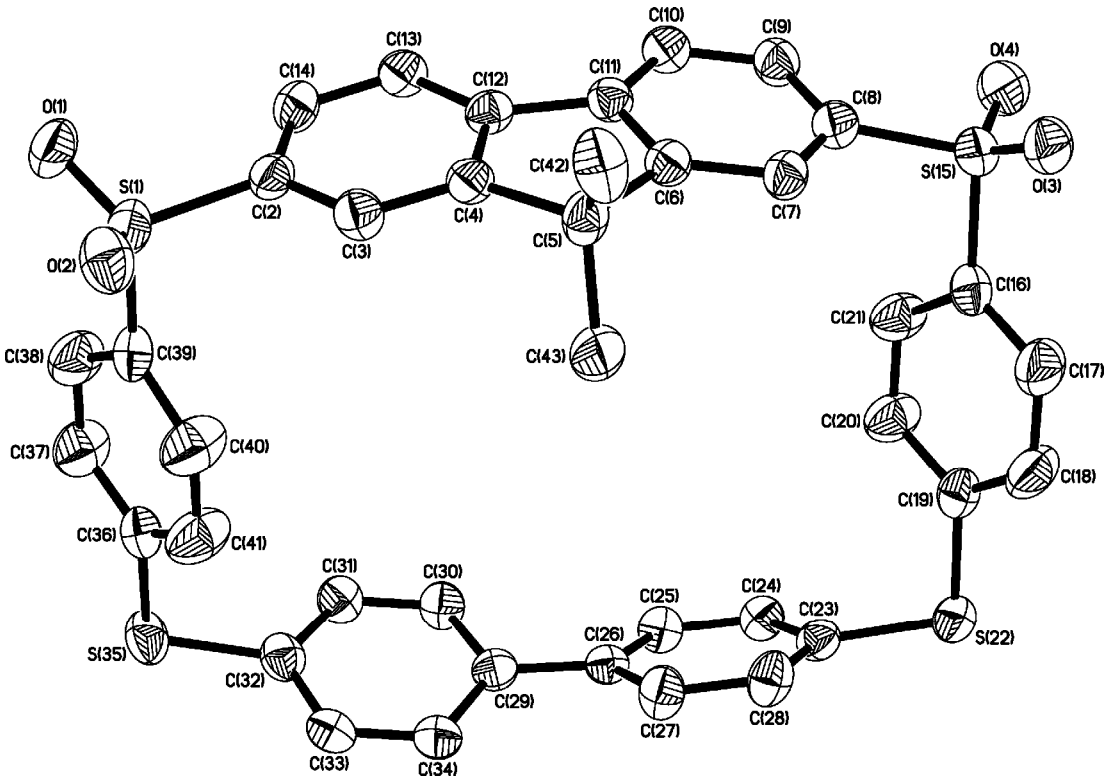

Fig. S10