

Electrochemical oxidative coupling of 1,4-bis(1,4-dithiafulven-6-yl)-benzene cyclophanes

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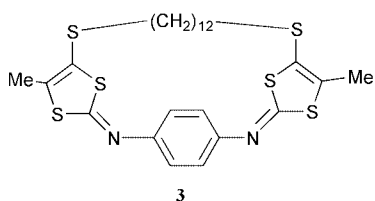
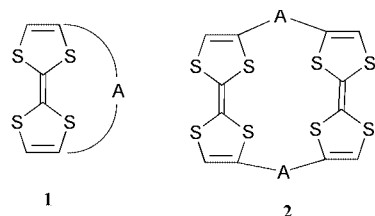
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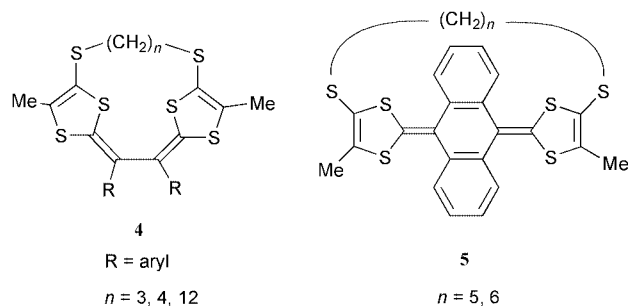
The synthesis and the redox behavior of π -redox cage-like molecules incorporating one or two 1,4-bis(1,4-dithiafulven-6-yl)benzene are reported. The shape of the voltammograms indicates that **6** and **9** undergo an oxidative coupling. The X-ray crystal structure of compound **6** is presented.

Donor properties of electroactive units such as tetrathiafulvalene (TTF) can be radically modified within a cyclic structure.¹ For example, depending on the length of the side linker in tetrathiafulvalenophanes **1**, two different redox behaviors have

behavior as interactions of the donor cores bring about multiple oxidation stages.⁴ So far only a few examples of their extended analogues (**3–5**) with a conjugated spacer moiety between the two dithiole rings have been described.^{5–7} Consistently, within these extended π -redox cage-like systems similar trends in the influence of the side linker size on the donor properties are expected.⁷ In an earlier study we reported the electrochemical synthesis of the cage molecules **4** by an intramolecular oxidative coupling of bis(1,4-dithiafulvene)s.⁶ Thus, it was of interest to investigate the preparation of cyclophanes (**6**,⁵ **7**, **9**) incorporating one or two 1,4-bis(1,4-dithiafulven-6-yl)benzene units and their redox behavior upon oxidation. We also set out the structural arrangements of the cage molecule containing one 1,4-bis(1,4-dithiafulven-6-yl)-benzene (**6**).



A = alkyl of various length, aryl



R = aryl

n = 3, 4, 12

5

n = 5, 6

been observed. On the one hand, a short side linker induces distortion in the donor core and such constrained tetrathiafulvalenophanes **1** exhibit higher oxidation potentials and mainly irreversible processes.² On the other hand, increasing the length of the side chain leads to an essentially planar TTF skeleton and the two traditionally reversible oxidation waves are observed, moreover *trans-cis* isomerization can be detected.^{2a,3} Otherwise, short linkers between two TTF belonging to the same macrocycle **2** influence also the redox

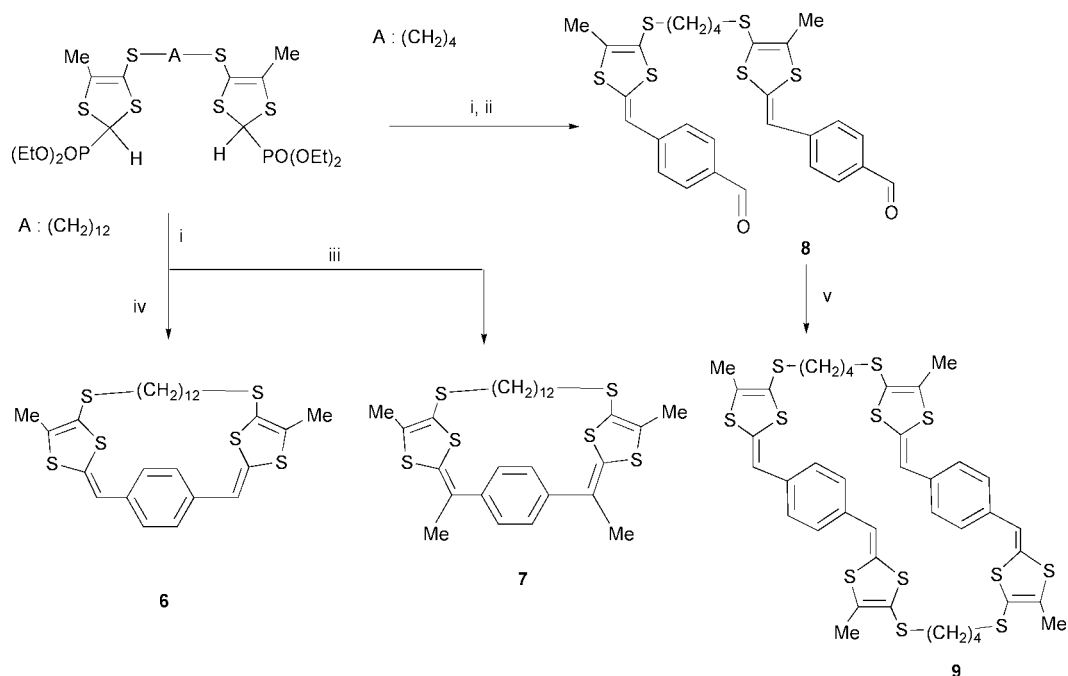
Results and discussion

Synthesis

The syntheses of cyclophanes **6**, **7** and **9** were achieved by Wittig–Horner olefination as outlined in Scheme 1. For the cyclic donors **6**⁵ and **7**, a stoichiometric amount of the carbonyl derivative, terephthalaldehyde or 1,4-diacetylbenzene, was added to the bis(dithiolylphosphonate) dianion. In the presence of an excess of terephthalaldehyde, the bisaldehyde **8** was obtained and, condensation of the latter with the bis(dithiolylphosphonate) dianion affords cyclophane **9** with two extended donor cores.

X-Ray crystal structure of cyclophane **6**

The compound **6** crystallises with two molecules in the asymmetric unit. Despite the same *cis* configuration, as can be seen in Fig. 1, these two molecules have different conformational arrangements. The dihedral angles between the dithiole rings are 42.8(2) and 47.0(2)° for molecules A and B respectively. Additionally, the dihedral angles between the central benzene ring and the two dithiole moieties are 32.7(2) and 10.6(3)° for molecule A and 31.1(3) and 16.0(2)° for molecule B. One can observe also different conformations of the lateral chain which is also more disordered in the case of the molecule B. These results are reminiscent of the structures we previously described for their imino analogues **3**, although in this latter case we



Scheme 1 Reagents and conditions: i, BuLi in THF, $-78\text{ }^{\circ}\text{C}$; ii, terephthalaldehyde (excess); iii, 1,4-diacetylbenzene (1 equiv.); iv, terephthalaldehyde (1 equiv.); v, bis(dithiolylphosphonate) dianion (1 equiv.).

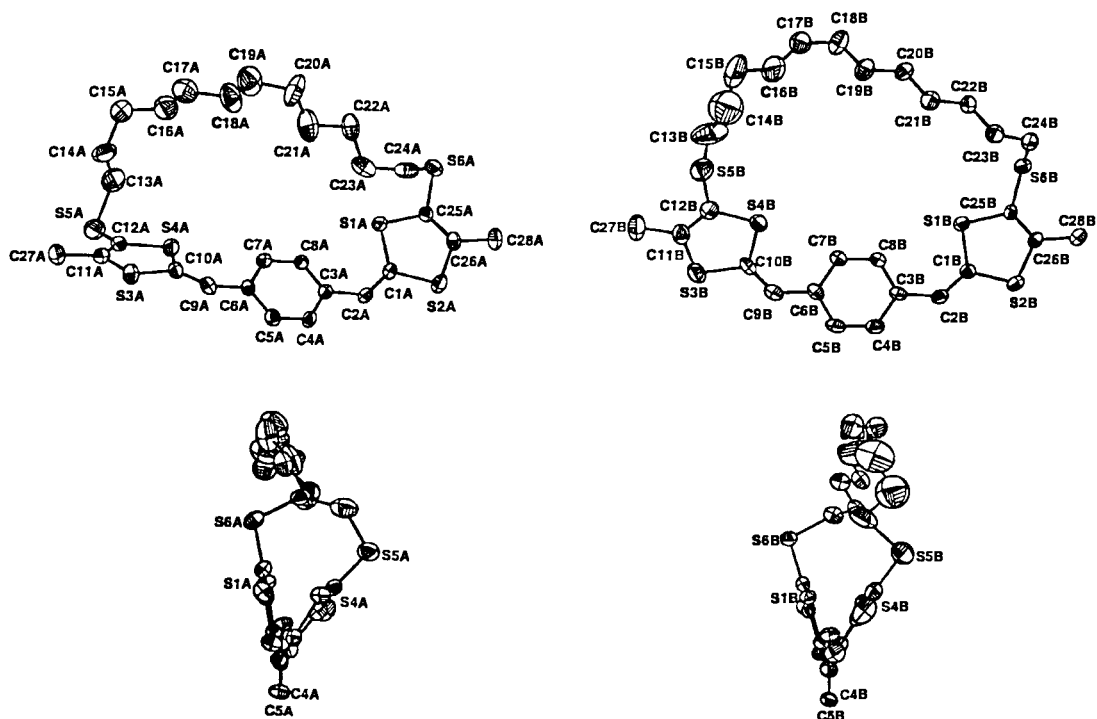


Fig. 1 View of the molecular structure of the two conformers A and B of **6**.

observed two polymorphic modifications in crystals with different morphologies.⁵

Electrochemical studies

The redox behavior of these cyclophanes was first studied by cyclic voltammetry. Analytical investigations of **7** show that this derivative exhibits one reversible electrochemical system corresponding to a two-electron transfer process (Table 1). The shape of this voltammogram is not modified upon recurrent sweeps. Due to reduced coulombic repulsion in the dication species, the introduction of the aromatic spacer group between the dithiole rings induces the coalescence of the two oxidation potentials traditionally observed for a TTF. In the case of

Table 1 Cyclic voltammetry data, E in V vs. SCE, Pt working electrode with 0.1 M $n\text{-Bu}_4\text{NPF}_6$, scan rate 0.1 V s^{-1} in CH_2Cl_2

Compound	E_{pa}^1/V	E_{pa}^2/V
6	0.53	0.87
7		0.67^a
9	0.50	0.83

^a Two-electron reversible process.

1,4-bis(1,4-dithiafulven-6-yl)benzene **6**, where the two dithiole rings are linked together by a dithioalkyl chain of the same length, two irreversible peaks are observed at a lower oxidation potential than for **7**. This difference in the redox behavior of **7**

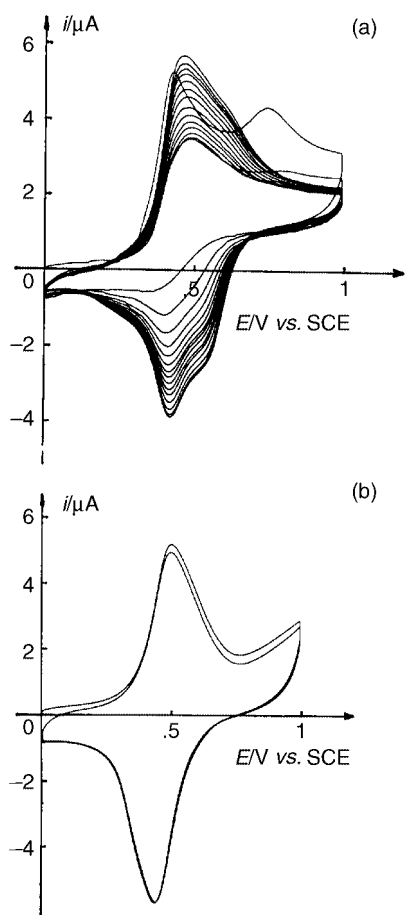
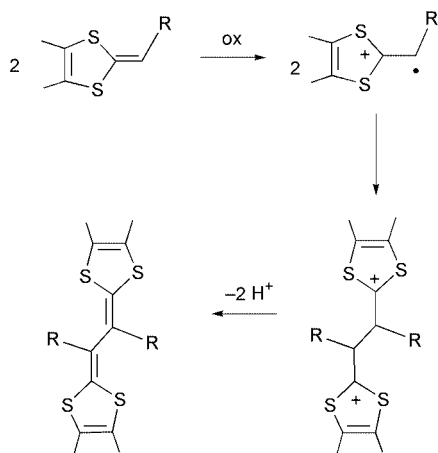


Fig. 2 (a) Cyclic voltammogram of compound **9** upon several scans; (b) electrochemical behaviour of the film formed at the electrode.

compared to **6** is due to the presence of the methyl substituents located on the double bonds. Unlike **7**, oxidation of the dithiafulvene moiety in the case of **6** generates a cation radical which couples irreversibly into a protonated dimer. Deprotonation of the latter yields a vinylogous TTF core following the mechanism described in Scheme 2. In accordance, two irreversible



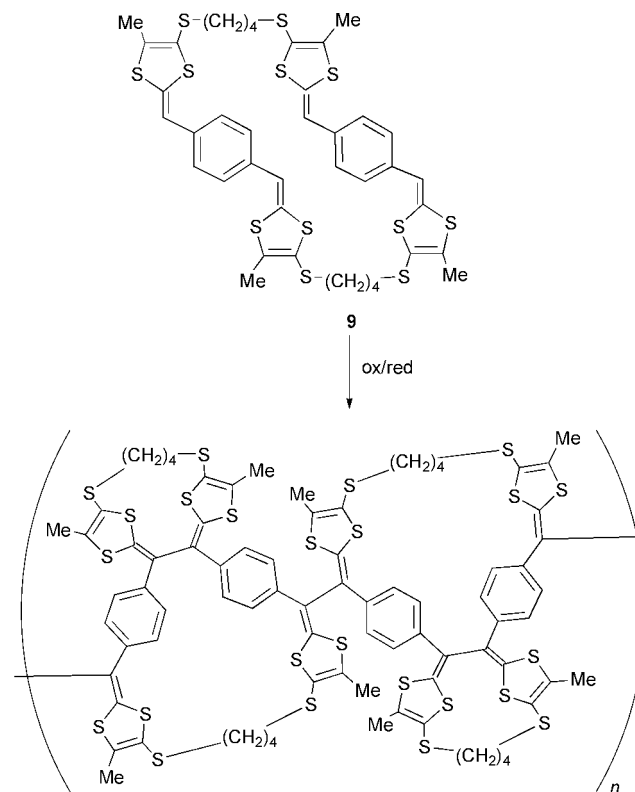
Scheme 2 Oxidative dimerization mechanism of dithiafulvene.

oxidation peaks are observed for the cyclophane **9**, with two 1,4-bis(1,4-dithiafulven-6-yl)benzene units.

Upon successive scans, modifications appear on the cyclic voltammograms of **6** and **9** which are reminiscent of those observed for dithiafulvene.⁸ The electrochemical behavior is quite similar for cyclophanes **6** and **9**. As can be seen in Fig. 2a, after several scans a reversible system replaces the previous

irreversible ones. Indeed this voltammogram shape indicates that coupling reaction occurs upon oxidation. Application of the recurrent potential scans to the cyclophane **9** solution led to the formation of a film at the electrode. The electrode was rinsed with dichloromethane in order to remove cyclophane **9** and the redox behavior of the film was examined. The cyclic voltammogram obtained under the same experimental conditions exhibits a reversible surface wave (Fig. 2b).

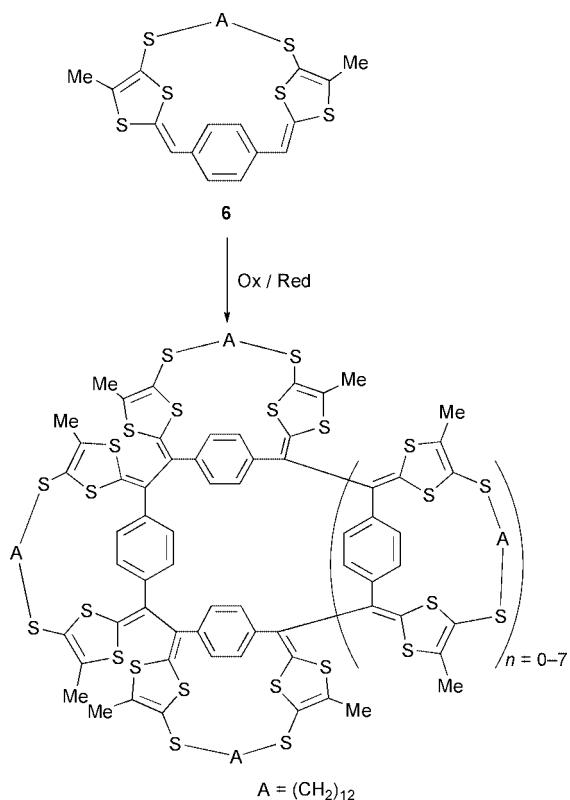
Considering the structure of molecule **6**, only intermolecular coupling upon oxidation can take place. Despite the similar cyclic voltammograms obtained for **6** and **9**, what occurs upon oxidation for **9** could be different from that in the case of **6**. Indeed we reported that bis(dithiafulvene)s, where the two dithiafulvenes are linked with a dithioalkyl chain of varying length, undergo intramolecular coupling even when the bridging chain is short, to afford **4**.⁶ Cyclophane **9**, where the donors are linked by a dithioalkyl chain of the same length, could undergo intramolecular and intermolecular reactions upon oxidation as illustrated in Scheme 3. Electrogeneration of related polymers has recently been reported.^{9–12}



Scheme 3 Electrochemical oxidative coupling of cyclophane **9**.

Macroscale electrolysis of cyclophane **6**

In order to have an insight into the coupling reaction which occurs upon oxidation, we performed a preparative electrolysis of **6**. This one-pot procedure consists of the oxidation of a solution containing **6** and tetrabutylammonium hexafluorophosphate as the supporting electrolyte at 1.3 V vs. SCE and then, after complete oxidation of the solution, reduction at -0.2 V vs. SCE. After removal of the supporting electrolyte we separated by column chromatography two main fractions. Compared with the cyclophane **6**, ¹H NMR analyses of these fractions reveal the disappearance of the vinylogous protons. This implies a cyclooligomerisation rather than a polymerisation (Scheme 4). Analyses of the FAB spectrum provided evidence of the presence of several macrocyclophanes. The first fraction leads mainly to the macrocycles including 3, 4 and 5 bis(dithiafulvenyl)benzene units. In the last one several macrocyclophanes can be detected with up to 10 bis(dithiafulvenyl)benzene units.



Scheme 4 Cyclooligomerisation of cyclophane **6**.

In summary we investigated the synthesis of novel bridged bis(dithiafulvenyl)benzenes. These cyclophanes incorporating one or two donor units exhibit similar redox behavior and they both undergo electrochemical coupling upon oxidation. The main difference lies in the nature of the coupling step: either intermolecular or intramolecular. Despite the steric strain due to the bithioalkyl link, as demonstrated by X-ray analysis for the cyclophane with one redox active moiety, cyclooligomerisation does occur. It would be of interest to examine the redox behavior of this donor in the presence of an acceptor molecule, indeed cyclooligomerisation could offer the possibility of encapsulating the latter.

Experimental

¹H NMR spectra were recorded at 300 MHz and ¹³C NMR spectra at 75 MHz on a Bruker AM 300 spectrometer with tetramethylsilane as internal reference. Mass spectra were determined with a Varian Mat 311 Spectrometer (Centre de Mesures Physiques de l'Ouest). Melting points were measured using a Kofler hot stage apparatus and are uncorrected. Elemental analysis results were obtained from the Laboratoire Central de Microanalyse du CNRS (Lyon). Solvents were dried using standard procedures. Column chromatography was performed on Merck silica gel 60 (0.040–0.063 mm). Electro-analytical investigations were carried out on a 10⁻³ M solution of substrate in dichloromethane, containing a 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Voltammograms were recorded at 0.1 V s⁻¹ at a platinum disk electrode (*A* = 1 mm²). The potentials were measured *versus* a saturated calomel electrode (SCE).

General procedure for cyclophanes **6** and **7**

Bis(phosphonate) (1 g, 1.35 mmol) was dissolved in 70 mL of dry THF in a three-necked flask and BuLi (3 mmol from a 1.6 M solution in hexane) was added at -8 °C under nitrogen. After 15 min the carbonyl derivative (1.3 mmol of terephthalaldehyde or 1,4-diacetylbenzene) in 40 mL of THF was added

dropwise to the solution. The reaction mixture was stirred at low temperature during 1 h and then allowed to reach room temperature. After three hours, THF was removed *in vacuo*, the reaction mixture was extracted with methylene chloride, and the extract was washed with water, dried over Na₂SO₄, and evaporated. Chromatography of the residue, on a silica gel column using methylene chloride–petroleum ether (1 : 1) as the eluent, gave the corresponding cyclophane, **6** and **7**, crystallized on addition of methanol to the eluate.

Compound 6. Yellow crystals; yield 31%; mp 158 °C; ¹H NMR δ 1.30 (m, 16H), 1.69 (m, 4H), 2.12 (s, 6H), 2.72 (t, 4H), 6.39 (s, 2H), 7.21 (s, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 14.48, 28.42, 28.61, 29.16, 29.38, 29.85, 36.21, 112.78, 118.07, 126.69, 132.39, 132.62, 133.82. HRMS Calcd for C₂₈H₃₆S₆: 564.1141. Found: 564.1131. Anal. Calcd for C₂₈H₃₆S₆: C, 59.52; H, 6.42; S, 34.05. Found: C, 59.50; H, 6.35; S, 35.61%.

Compound 7. Yellow crystals; yield 15%; mp 160 °C; ¹H NMR δ 1.18 (m, 16H), 1.52 (m, 4H), 1.99 (s, 6H), 2.06 (s, 6H), 2.56 (t, 4H), 7.27 (s, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 14.98, 22.54, 28.29, 28.60, 28.76, 29.23, 29.90, 35.78, 117.98, 126.35, 127.68, 132.87, 140.04. HRMS Calcd for C₃₀H₄₀S₆: 592.1454. Found: 592.1467. Anal. Calcd for C₃₀H₄₀S₆: C, 60.75; H, 6.79; S, 32.44. Found: C, 60.71; H, 6.71; S, 31.96%.

Bis(dithiafulvenylbenzaldehyde) **8** and cyclophane **9**

These were prepared by the same procedure as for **6** using an excess of terephthalaldehyde (4 mmol). Purification of the bisaldehyde **8** was achieved by chromatography on a silica gel column using methylene chloride–petroleum ether (4 : 1). Orange powder; yield 30%; mp 134 °C; ¹H NMR δ 1.74 (m, 4H), 2.17 (s, 6H), 2.75 (m, 4H), 6.48 (m, 2H), 7.30 (d, 2H), 7.82 (d, 2H), 9.92 (s, 2H). The bisaldehyde **8** was used without further purification in the synthesis of **9**, following the same procedure as for **6** using a stoichiometric amount of bis(phosphonate). Chromatography of the residue obtained after the work up, on a silica gel column with methylene chloride as the eluent, afforded cyclophane **9** as a yellow powder, mp >250 °C (yield 30%); ¹H NMR δ 1.64 (m, 8H), 2.04 (s, 12H), 2.64 (m, 8H), 6.31 (m, 4H), 7.09 (m, 8H); ¹³C NMR δ 14.35, 27.55, 34.25, 112.05, 116.08, 125.68, 130.92, 132.70, 133.09. HRMS Calcd for C₄₀H₄₀S₁₂: 903.9779. Found: 903.9770. Anal. Calcd for C₄₀H₄₀S₁₂·0.5 CH₂Cl₂: C, 51.30; H, 4.35; S, 40.58. Found: C, 51.44; H, 4.34; S, 40.68%.

Macroscale electrolyses of **6**

This was performed under controlled potential in a divided cell, the working electrode being a platinum grid. 100 mL of a dichloromethane solution containing 1 mmol of **6** (590 mg) and 1 M tetrabutylammonium hexafluorophosphate were introduced in the working compartment. The solution was then oxidized under controlled potential (1.3 V *vs.* SCE). The highly coloured solution was then, without any treatment, reduced at -0.2 V *vs.* SCE. The solvent was removed *in vacuo*, the addition of toluene–methylene chloride (2 : 3) to the residue induced the precipitation of tetrabutylammonium hexafluorophosphate which was filtered off. The organic phase was evaporated and the residue was chromatographed on a silica gel column using methylene chloride as eluent. Two main fractions were separated exhibiting the same ¹H NMR spectra: ¹H NMR δ 1.38 (m), 1.63 (m), 2.07 (m), 2.72 (m), 7.35 (m). The macrocyclophanes in both fractions were obtained as an inseparable mixture.

MS(FAB) *m/z* first fraction: 1688.2 (100, *n* = 0), 2251.0 (32, *n* = 1), 2814.3 (28, *n* = 2).

MS(FAB) *m/z* second fraction: 1688.5 (17, *n* = 0), 2251.5 (28, *n* = 1), 2815.0 (96, *n* = 2), 3378.0 (84, *n* = 3), 3941.2 (72, *n* = 4), 4504.3 (59, *n* = 5), 5067.7 (25, *n* = 6), 5631.0 (17, *n* = 7).

Crystal structure determination of cyclophane 6[†]

C₂₈H₃₆S₆, $M = 564.95$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.510(2)$, $b = 13.225(3)$, $c = 22.293(5)$ Å, $\alpha = 88.29(2)$, $\beta = 89.88(2)$, $\gamma = 72.94(2)^\circ$, $U = 2960.8(10)$ Å³, $Z = 4$, $T = 293(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.478$ mm⁻¹, 17225 reflections measured, 7734 unique ($R_{\text{int}} = 0.050$) which were used in all calculations. The final reliability factors are $wR_2(F_0^2) = 0.123$ (all data) and $R_1 = 0.053$ ($F_0 > 4\sigma(F_0)$).

[†] CCDC reference number 207/448. See <http://www.rsc.org/suppdata/p1/b0/b002596h/> for crystallographic files in .cif format.

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