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Formation of Attractive π-Redox Cyclophanes

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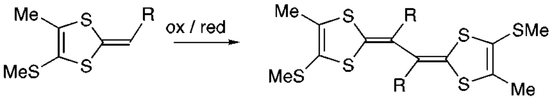
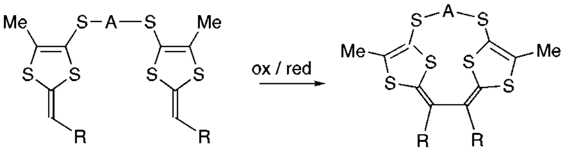
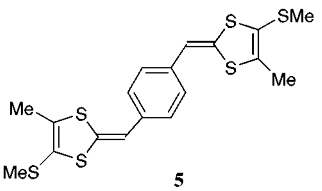
The use of cage molecules incorporating one or more TTF units as host molecules seems very attractive in order to prepare novel organic materials.[1] Due to the presence of TTF cores within these macrocycles, it would be interesting to study their organization in the solid state particularly when long chains are substituting the TTF core allowing some discotic organization. Moreover, the other interest of these compounds is their cavities, which could encage specific acceptors. In an earlier study we examined the electrochemical synthesis of TTF vinylogues starting from 1,4-dithiafulvenes **1**.[2] This oxidative dimerization of dithiafulvenes appears to be very general[3] and we have extended it to the synthesis of cage molecules using this time bis(1,4-dithiafulvenes) **3** as starting materials. We also report our preliminary investigation on the electrochemical oxidation of 1,4-bis(1,4-dithiafulven-6-yl) benzene **5**.



1 **2**

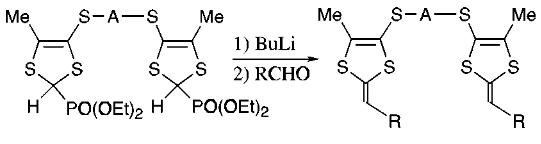


3 **4** **(1)**



5

Scheme 1



6 **3**

A = $(CH_2)_3$, $(CH_2)_4$, $(CH_2)_{12}$

The synthesis of bis(dithiafulvenes) **3** was achieved starting from bis(phosphonates) **6**[4] in basic medium (Scheme 1). Wittig−Horner reaction between different aldehydes and bis(dithiolyl) phosphonate anion afforded bis(dithiafulvenes) **3**.[5] Different molecules **3** where the two dithiafulvenes are linked together with a bis(thioalkyl) chain of various length were synthesized.

Bis(dithiafulvenes) **3** undergo the same redox behavior as 1,4-dithiafulvenes **1**.[2,6] On the first anodic scan, an irreversible oxidation peak (a) is observed corresponding to the oxidation of **3** into the bis(cation radical) $\mathbf{3}^{2(\bullet+)}$. Then the new redox (b/c) system which appears upon successive scans, at less positive potentials, is associated with the redox behavior of the formed cage **4**. The data are summarized in Table 1 together with the oxidation potentials of noncyclic analogues **2** for comparison. As previously observed for **2**, formation of **4** occurs according to an ECE mechanism. It is noteworthy that even with a short bridging chain the shape of the voltammogram remains unchanged.

Preparative electrolyses were performed under the experimental conditions already described for **1** in a one-pot procedure by a two-step electrochemical synthesis: first an oxidation and then a reduction; after the electrolyses, workup of the solution leads to dimer **4**. Cyclic voltammetry of dimers **4** have been recorded in the same conditions as for **3**. There again, one reversible electrochemical system is observed corresponding to peaks (b/c) of the cyclic voltammogram of **3**. All the bis(dithiafulvenes) **3** undergo intramolecular coupling under oxidation even when the bridging chain is short. Crystals were obtained for **4b**, and the structure has been determined by X-ray analysis.[7] Like their noncyclic analogues **2**, cagelike molecules **4**, due to steric hindrance, are nonplanar (Figure 1). However, due to the bis(thioalkyl) link, steric strain could restrain conformational modifications upon oxidation of **4** as compared to the noncyclic analogue **2**.[6]

We also extended our research to 1,4-bis(1,4-dithiafulven-6-yl)benzene. Intramolecular cyclization of 1,2-bis(1,4-dithiafulven-6-yl)benzene was already described in the litterature.[8] Besides, polymerization of 1,2-bis(1,4-

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[7] The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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Table 1. Cyclic Voltammetry Data of Dithiafulvenes 1, Bis(dithiafulvenes) 3, and TTF Vinylogues 2 and 4 (*E* in V vs SCE, Pt working electrode with 0.1 M n-Bu$_4$NPF$_6$, 100 mV/s)

			E_p **3**		E_0 **4**		$E_p^a - E_p^c$ (mV/s)	
	R	A	CH_3CN	CH_2Cl_2	CH_3CN	CH_2Cl_2	CH_3CN	CH_2Cl_2
a	C_6H_4CN	$(CH_2)_3$	0.79	0.88	0.48	0.71	40	40
b	C_6H_4CN	$(CH_2)_4$	0.77	0.80	0.54	0.63	40	30
c	C_6H_4CN	$(CH_2)_{12}$	0.71	0.82	0.49	0.60	30	50
d	$MeOC_6H_4$	$(CH_2)_4$	0.50	0.61	0.42	0.46	30	40
			E_p **1**		E_0 **2**			
	C_6H_4CN		0.69		0.44	0.54	30	40
	C_6H_4OMe		0.47		0.32	0.32/0.42	30	60/60

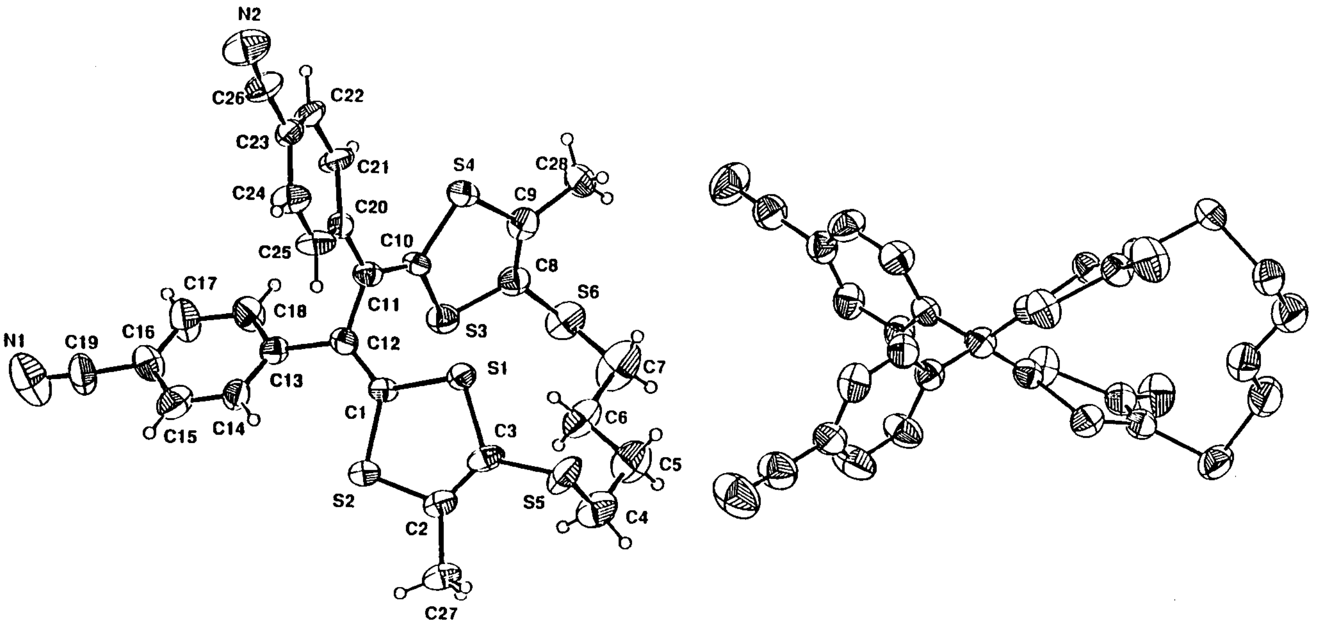

Figure 1. Crystal structure of compound **4b**. Sideway view showing the nonplanarity of the molecule.

dithiafulven-6-yl)benzene[9] and 1,3,5-tris(1,4-dithiafulven-6-yl)benzene was also observed,[10] but to our knowledge nothing was reported on the behavior of 1,4-bis(1,4-dithiafulven-6-yl)benzene **5**. The redox behavior of **5** was first studied by cyclic voltammetry. As can be seen on Figure 2, what occurred with this compound was not as obvious as in the case of dithiafulvene **1** or bis(dithiafulvenes) **3**. On the first anodic scan two irreversible peaks are observed ($E_{ox}^1 = 0.49$ V, $E_{ox}^2 = 0.8$ V), and upon successive scans the second irreversible oxidation peak tends to decrease.[4] However, we performed a preparative electrolyses of **5**. A solution of dichloromethane containing 1.5 mmol of **5** and 1 M of tetrabutylammonium hexafluorophosphate is oxidized under controlled potential (1 V vs SCE). Then, without any treatment, the solution is reduced at −0.2 V vs SCE. After removal of the supporting electrolyte and chromatography on silica gel, we mainly isolated macrocyclophanes **7** and **8** including four and five bis(dithiafulvenyl)benzene units (Scheme 2). Comparison of the ^{1}H NMR spectra of **5** with **7** and **8** mixture provided evidence of the ring closure by disappearance of vinylogous protons. The FAB spectrum also confirmed the existence of these oligomers. Surprisingly in this case cyclooligomerization is favored rather than polymerization, leading to novel macrocyclophane compounds with multi 1,3-dithiole rings. It is worth noting that cyclooligomerization occurs only if the oxidation step of the macroscale elctrolyses is carried out at a potential more positive than the last irreversible oxida-

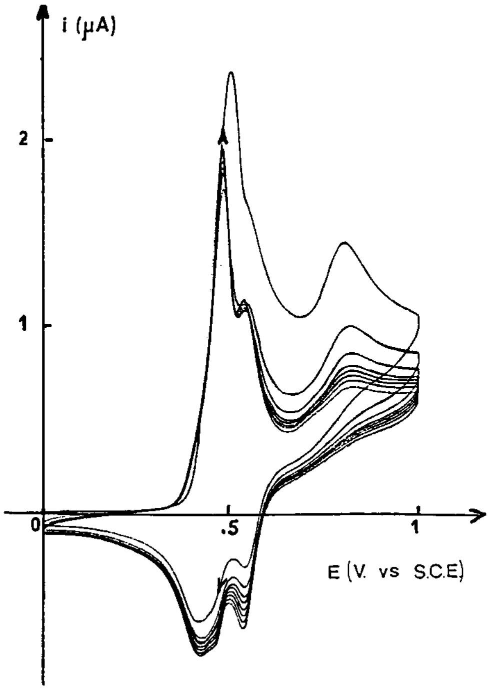

Figure 2. Voltammetric behavior of **5** in CH_2Cl_2, 1 M nBu_4NPF_6, at a platinum anode, scan speed of 0.1 V s^{-1}.

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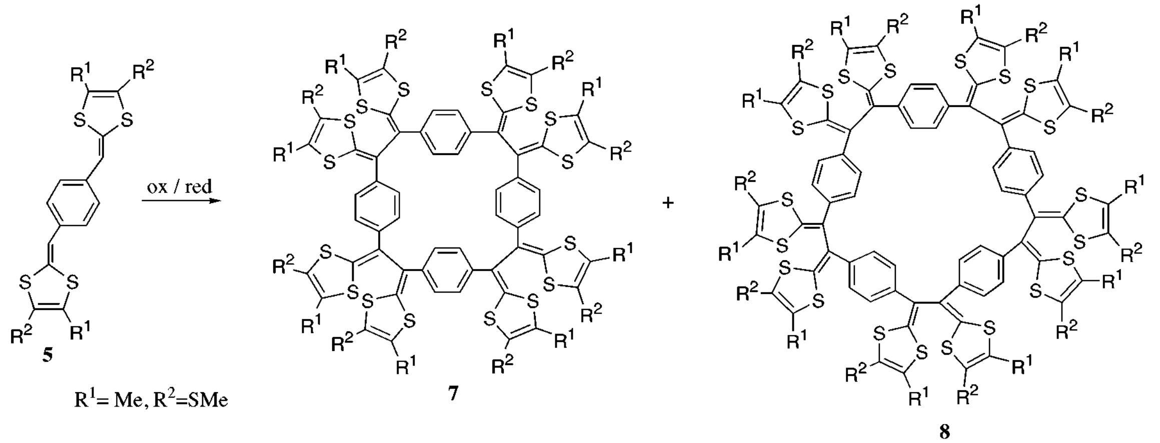
Scheme 2



5

R^1= Me, R^2=SMe

7

8

tion wave observed on the cyclic voltammogram of **5** (0.8 V).

In summary, we have extended the scope of the electrochemical synthesis of TTF vinylogues to the preparation of related cage molecules as well as macrocyclophanes. The cyclic voltammetry of **4** clearly indicates the same redox behavior than their noncyclic analogues **2**. Moreover, we have discovered that 1,4-bis(1,4-dithiafulven-6-yl)benzene **5** undergoes the same coupling reaction upon oxidation. Up to now single crystals of **7** and **8** were not obtained for a more complete structure determination of these cyclophanes. Cyclooligomerization of **5** and related compounds is under investigation in our laboratory as well as the possibility of these macrocycles to be specific hosts for acceptor molecules.

Experimental Section

^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz with $CDCl_3$ as solvent and tetramethylsilane as internal reference. Mass spectra were carried out at Centre de Mesures Physiques de l'Ouest, Rennes. Elemental analysis results were obtained from the Laboratoire Central de Microanalyse du CNRS (Lyon).

General Experimental Details for Bis(1,4-dithiafulvenes) 3. As observed for the dithiafulvenes **1** we published earlier,[2] all the molecules **3** synthesized and described below are present as three isomers (*ZZ*/*EE*/*EZ*) in solution which were observed by ^{1}H NMR but not separated.

n-BuLi (3.25 mmol from a 1.6 M solution in hexane) was added to a solution of bis(phosphonates) **6** (1.6 mmol) in dry THF (70 mL) at −78 °C under nitrogen. After 15 min a solution of the aldehyde (3.2 mmol) was added to the solution. The reaction mixture was stirred at low temperature during 1 h and then allowed to reach room temperature. After 3 h, THF was removed in vacuo, the reaction mixture was extracted with methylene chloride, and the extract was washed with water, dried over Na_2SO_4, and evaporated. Chromatography of the residue, on a silica gel column using methylene chloride/petroleum ether (8/2) as the eluent, gave the corresponding bis(dithiafulvenes), **3a**−**c** crystallized in presence of methanol.

3a: yellow powder; yield 35%; mp 60 °C; ^{1}H NMR δ 1.97 (m, 2H), 2.18 (s, 6H), 2.84 (m, 4H), 6.40 (s, 2H), 7.23 (d, 4H, J = 8.4 Hz), 7.57 (d, 4H, J = 8.4 Hz). Anal. Calcd for $C_{27}H_{22}N_2S_6$·$0.5CH_3OH$: C, 56.66; H, 4.15; N, 4.80. Found: C, 56.63; H, 3.89; N. 4.60. HRMS calcd for $C_{27}H_{22}N_2S_6$ 566.0099, found 566.0107.

3b: yellow powder; yield 40%; mp 110 °C; ^{1}H NMR δ 1.74 (m, 4H), 2.17 (s, 6H), 2.75 (m, 4H), 6.42 (s, 2H), 7.25 (d, 4H, J = 8.15 Hz), 7.58 (d, 4H, J = 8.15 Hz). Anal. Calcd for $C_{28}H_{24}N_2S_6$: C, 57.89; H, 4.16; N, 4.82; S, 33.11. Found: C, 57.35; H, 4.28; N. 4.45; S, 33.59. HRMS calcd for $C_{28}H_{22}N_2S_6$ 580,0167, found 580,0263.

3c: yellow powder; yield 40%; mp 60 °C; ^{1}H NMR δ 1.23 (m, 16H), 1.58 (m, 4H), 2.16 (s, 6H), 2.70 (m, 4H), 6.41 (s, 2H), 7.23 (d, 4H, J = 8.4 Hz), 7.56 (d, 4H, J = 8.4 Hz). Anal. Calcd for $C_{36}H_{40}N_2S_6$·$1.5CH_3OH$: C, 60.76; H, 6.25; N, 3.78. Found: C, 60.71; H, 5.47; N. 3.96. HRMS calcd for $C_{36}H_{40}N_2S_6$ 692.1548, found 692.1515.

3d: yellow oil; yield 40%; ^{1}H NMR δ 1.68 (m, 4H), 2.09 (s, 6H), 2.68 (m, 4H), 3.76 (s, 6H), 6.36 (s, 2H), 6.86 (d, 4H, J = 8 Hz), 7.13 (d, 4H, J = 8 Hz). HRMS calcd for $C_{28}H_{30}O_2S_6$ 590.0543, found 590.0570.

General Experimental Details for Cages 4. Macroscale electrolyses were performed in a divided cell, the working electrode being a platinum grid. A solution containing 1 mmol of the bis(1,4-dithiafulvene) **3** in acetonitrile and 1 M of tetrabutylammonium hexafluorophosphate is introduced in the working compartment. The solution is oxidized under controlled potential (0.6 V to 0.8 V vs aqueous SCE, depending on R) and, without any treatment, reduced at −0.2 V. After the electrolyses, the solvent was removed in vacuo, and toluene (50 mL) was added to the residue. Tetrabutylammonium hexafluorophosphate precipitated and was filtered off. The organic phase was evaporated, and the residue was chromatographed on silica gel column using methylene chloride for R = C_6H_4CN and methylene chloride/petroleum ether (7/3) as eluent for R = C_6H_4OMe. The vinylogous TTF **4** crystallized in methylene chloride/methanol.

4a: orange crystals; yield 15%; mp 196 °C; ^{1}H NMR δ 2.17 (s, 6H), 2.27 (m, 2H), 2.68 (m, 4H), 7.35 (d, 4H, J = 8.9 Hz), 7.51 (d, 4H, J = 8.9 Hz); ^{13}C NMR δ 15.33, 30.57, 36.25, 109.97, 118.36, 118.85, 124.45, 126.90, 132.45, 135.32, 141.49, 142.30; HRMS calcd for $C_{27}H_{20}N_2S_6$ 563.9951, found 563.9958. Anal. Calcd for $C_{27}H_{20}N_2S_6$·CH_2Cl_2: C, 51.75; H, 3.41; N, 4.31; Cl, 10.91. Found: C, 52.09; H, 3.47; N. 4.35; Cl, 10.40.

4b: orange crystals; yield 30%; mp > 270 °C; ^{1}H NMR δ 1.72 (m, 4H), 2.16 (s, 6H), 2.70 (m, 4H), 7.40 (d, 4H, J = 8.9 Hz), 7.52 (d, 4H, J = 8.9 Hz); ^{13}C NMR δ 15.35, 30.02, 35.51, 109.56, 118.85, 118.92, 122.31, 126.51, 132.49, 134.01, 141.30, 142.67; HRMS calcd for $C_{28}H_{22}N_2S_6$ 578,0173, found 578,0101. Anal. Calcd for $C_{28}H_{22}N_2S_6$·$1.5CH_2Cl_2$: C, 50.16; H, 3.56; N, 3.96. Found: C, 50.10; H, 3.36; N. 4.12.

4c: yellow powder; yield 30%; mp 167°C; ^{1}H NMR δ 1.20 (m, 16H), 1.52 (m, 4H), 2.06 (s, 6H), 2.98 (m, 4H), 7.40 (d, 4H, J = 8.9 Hz), 7.50 (d, 4H, J = 8.9 Hz); ^{13}C NMR δ 15.43, 26.43, 27.30, 27.96, 28.23, 29.58, 36.23, 108.78, 119.54, 120.48, 126.24, 132.63, 133.74, 136.18, 140.91, 144.19; HRMS calcd for $C_{36}H_{38}N_2S_6$ 690.1248 found 690.1359. Anal. Calcd for $C_{36}H_{38}N_2S_6$: C, 62.56; H, 5.54; N, 4.05. Found: C, 62.36; H, 5.54; N. 4.10.

4d: yellow powder; yield 37%; mp > 260 °C; ^{1}H NMR δ 1.68 (m, 4H), 2.02 (s, 6H), 2.50/2.72 (m, 4H), 3.74 (s, 6H), 6.72 (d, 4H, J = 8.9 Hz), 7.22 (d, 4H, J = 8.9 Hz). ^{13}C NMR δ 15.29, 29.74, 35.01, 55.24, 113.83, 117.52, 125.64, 128.02, 130.35, 132.67, 133.23, 158.36; HRMS calcd for $C_{28}H_{28}O_2S_6$ 588.0413, found 588.0413. Anal. Calcd for $C_{28}H_{28}O_2S_6$: C, 57.10; H, 4.79. Found: C, 57.00; H, 5.17.

Macrocyclophanes 7 and 8. After the macroscale electrolyses and removal of tetrabutylammonium hexafluorophosphate, the organic phase was evaporated, and the residue was chromatographed on silica gel column using methylene chloride as eluent. The macrocyclophanes **7** and **8** were obtained as an unseparable mixture (ratio 4:6): yellow powder; yield 47%; mp > 260 °C; ^{1}H NMR δ 2.07 (m), 2.22 (m), 7.35 (m).

Supporting Information Available: ^{1}H NMR spectra for compounds **5** and **7**/**8** and mass spectrum for **7**/**8** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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