Tetrathiafulvalenoparacyclophanes and Tetrathiafulvalenophanes

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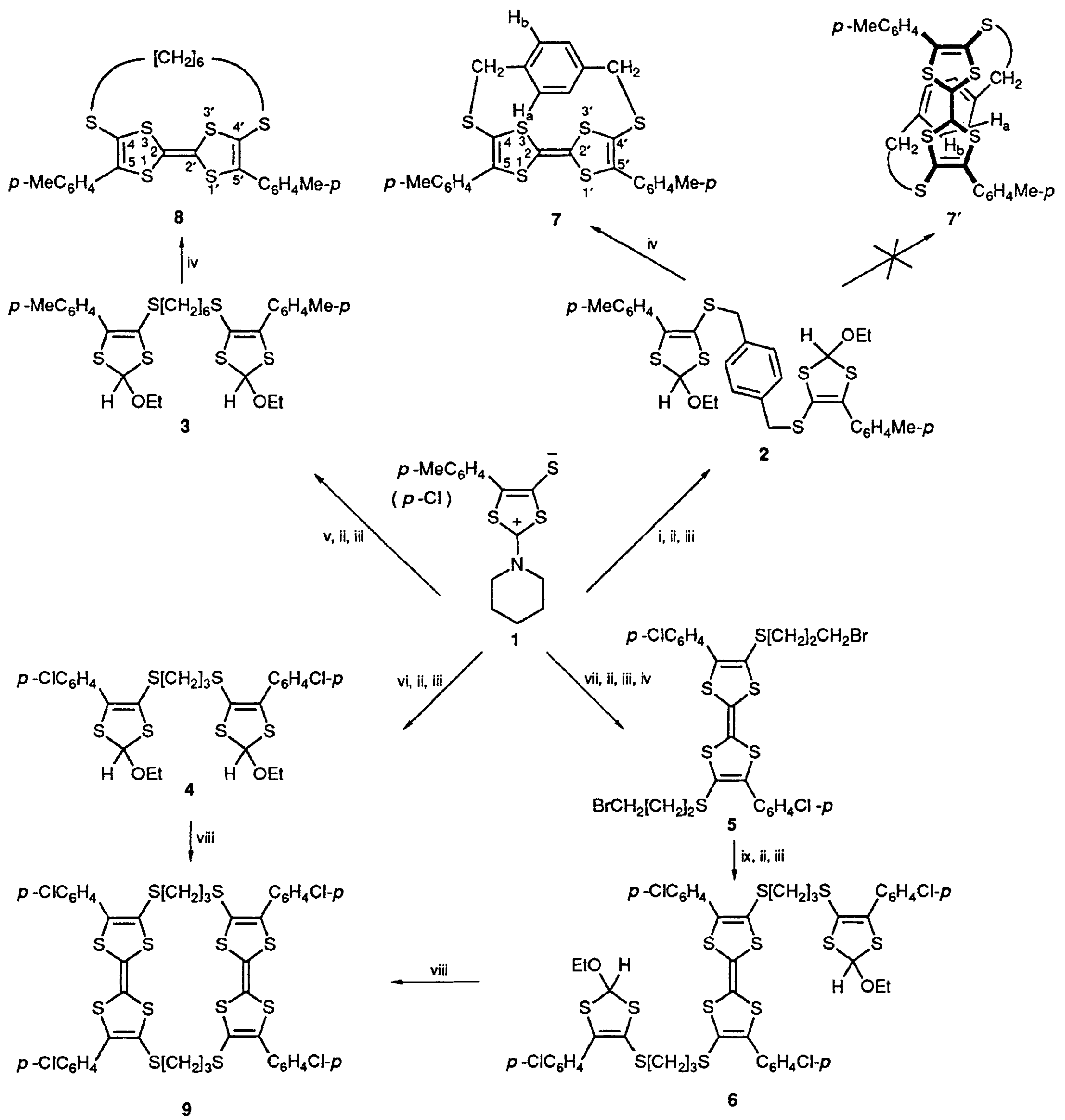
cis-Cyclophane-like tetrathiafulvalenes (TTF) **7** or **8** with two sulphur atoms linked at the 4 and 4′ positions of the two dithiole moities of the TTF are efficiently obtained from 4-thioxo-mesoionic dithioles; if the linking bridge is too small (less than 8 atoms) a cage-like bis-TTF **9** is obtained.

We have described a synthetic route to tetrathiafulvalenes (TTF) using mesoionic dithioles as starting materials[1,2] and we have shown that this reaction enabled us to synthesize many substituted TTF derivatives, particularly amphiphilic ones, which were used to prepare Langmuir–Blodgett films.[3–4] Owing to the noteworthy electrical properties of some charge-transfer complexes obtained from TTF and acceptor molecules, these compounds have been extensively studied.[5] As early as 1980, Staab *et al.* had described the first tetrathiafulvalenoparacyclophanes and tetrathiafulvalenophanes.[6] Since then, a number of interesting macrocyclic and cage-like molecules incorporating TTF units have been reported.[7,8] We show here that mesoionic dithioles are good starting materials for the synthesis of cage-like TTF derivatives. The reaction sequences we have used are presented in Scheme 1.

The reactions proceeded analogously to those described for the synthesis of simpler TTF compounds:[1,2] alkylation of **1** followed by reduction of the dithiolium cation intermediate, displacement of the piperidinium unit by EtOH under acidic conditions *via* a carbene intermediate,[1] and intramolecular cyclisation of the bis-ethoxydithiole. The bis-ethoxydithioles **2**, **3**, **4** and **6** were isolated and characterized (^{1}H and ^{13}C NMR, high-resolution mass spectrometry; yield *ca.* 90%).



Scheme 1 *Reagents*: i, $CH_2BrC_6H_4CH_2Br$ (0.5 equiv.); 1 h, Me_2CO; ii, $NaBH_4$–EtOH, 10 min; iii, 12 mol dm^{-3} HCl (2 ml) 2 h; iv, CCl_3CO_2H–C_6H_6 reflux, 1 h, filtration over Al_2O_3; v, $CH_2Br(CH_2)_4CH_2Br$ (0.5 equiv.), 1 h, Me_2CO; vi, $CH_2BrCH_2CH_2Br$ (0.5 equiv.), 1 h, Me_2CO; vii, $CH_2BrCH_2CH_2Br$ (3 equiv.), Me_2CO, 4 h; viii, slow addition of the reactant in benzene solution (4×10^{-5} mol l^{-1}) (0.5 ml h^{-1}) into CCl_3CO_2H (1.5 g)–C_6H_6 (250 ml), reflux (1 week), filtration over Al_2O_3; ix, mesoionic derivative **1**; *p*-$Cl_2C_6H_4$ (2 equiv.), $CHCl_3$, reflux (48 h)

Surprisingly the bis-ethoxydithioles **2** and **3** underwent cyclisation of the heterocyclic unit in the presence of CCl_3CO_2H in boiling benzene, cleanly to give *cis*-[2]tetrathiafulvaleno[2]paracyclophane **7** (connected by the 4 and 4′ position of the TTF unit) (yield 91%, purified) and the *cis*-[8]tetrathiafulvalenophane **8** (similarly connected) (yield 72%, purified). The structure of **8** was ascertained by an X-ray analysis.[9] As expected for such a strained TTF-phane the TTF moiety adopts a boat conformation. The ^1H NMR spectrum (300 MHz, $CDCl_3$) of **7** showed hindered rotation in the cyclophane bridge. The two methylene protons appeared as an AB system at δ 3.48 while the aromatic protons appeared as two doublets ($J_{a,b}$ = 1 Hz) at δ 6.56 and 7.47. This coupling constant of 1 Hz is consistent with the two *meta*-protons H_a and H_b in **7** being non-equivalent, and eliminates the isomeric structure *trans*-**7′** with two non-equivalent *ortho* protons ($J_{a,b}$ for this *trans*-structure expected in the range *ca.* 7–8 Hz).

To the best of our knowledge **7** is the first reported example of a [2]tetrathiafulvaleno[2]paracyclophane and it is worth noting that the high yield of the synthesis and the selectivity of the reaction are related more to the [4]tetrathiafulvaleno-[4]paracyclophane structure than to the [3]tetrathiafulvaleno[3]paracyclophane described earlier.[6a] Of course, if the bridge becomes smaller the intramolecular cyclisation does not take place. For instance when the bis-ethoxydithiole **4** was treated under high dilution (very slow addition of **4** in boiling C_6H_6–CCl_3CO_2H) the cage like compound **9** was obtained (yield 81%). The same compound **9** can alternatively be prepared from the TTF **6** synthesized from **5** according to our procedure[1,2] (yield 90%, m.p. 160 °C). It was not possible to characterize **9** by high-resolution mass spectroscopy, but permeation gel chromatography gave $M \approx 1050^{10}$ in agreement only with a bis-TTF structure **9**, making other oligomeric or polymeric structures unlikely. We failed to obtain a suitable crystal of **9** for X-ray analysis. Compound **9** is drawn in Scheme 1 with a *cis–cis*-configuration but we have no reason to eliminate the other possible *trans–trans*- or *cis–trans*-configurations. It must be stressed that even if TTF compounds related to **5**, in the solid state, have a *trans* configuration, trace amounts of acids give rise in solution to an equilibrium between *cis*- and *trans*-isomers.[11] A postulated protonated intermediate has recently been characterized by Müllen *et al.*[8a] The formation of a *cis–cis*-cage-like bis-TTF **9** must be considered even if the starting TTF **5** is *trans*.

Two reversible one-electron oxidation waves were observed during the electrochemical oxidation of a macrocycle incorporating a non-planar TTF moiety,[8b] while a non-reversible oxidation wave was reported for a cage with a bent TTF moiety.[8a] The electrochemical oxidation of **7** and **8** with cyclic voltammetric monitoring (0.1 mol dm^{-3} Et_4NBF_4, Ag working electrode, 500 mV s^{-1}, solvent CH_2Cl_2) showed only one irreversible oxidation wave at 0.46 V (*vs.* Ag/$AgNO_3$ electrode). Under the same conditions the tetrathiafulvalenophane **9** gave two reversible one-electron transfers at 0.18 and 0.45 V.

Work is in progress in order to change the size of the molecular cage, and to investigate the electronic properties of these novel macrocycles.

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9 K. Boubekeur, P. Batail, F. Bertho and A. Robert, *Acta Crystallogr., Sect. 2*, in press. Compound **8** was further characterized by mass spectrometry: calc. for $C_{26}H_{26}S_6$ 530.035; found *m/z* 530.030; ^1H NMR ($CDCl_3$) δ 1.70 (m, 4H), 2.62 (t, 8H) and 7.34 (m, 16H); UV (CH_2Cl_2) λ_{max} 323 nm; ε 24400.

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