

## Novel Extended $\pi$ -Redox Cage-like Systems and their Conformational Versatility

Philippe Hascoat,<sup>a</sup> Dominique Lorcy,\*<sup>a</sup> Albert Robert,<sup>a</sup> Kamal Boubekeur,<sup>b</sup> Patrick Batail,<sup>b</sup> Robert Carlier<sup>c</sup> and André Tallec<sup>c</sup>

<sup>a</sup> Groupe de Chimie Structurale, Unité Associée au CNRS no. 704, Université de Rennes, Campus de Beaulieu, 35042 Rennes, France

<sup>b</sup> Laboratoire de Physique des Solides, Unité Associée au CNRS no. 2, Université de Paris-Sud, 91405 Orsay, France

<sup>c</sup> Laboratoire d'Electrochimie Organique, Unité Associée au CNRS no. 439, Université de Rennes, Campus de Beaulieu, 35042, Rennes, France

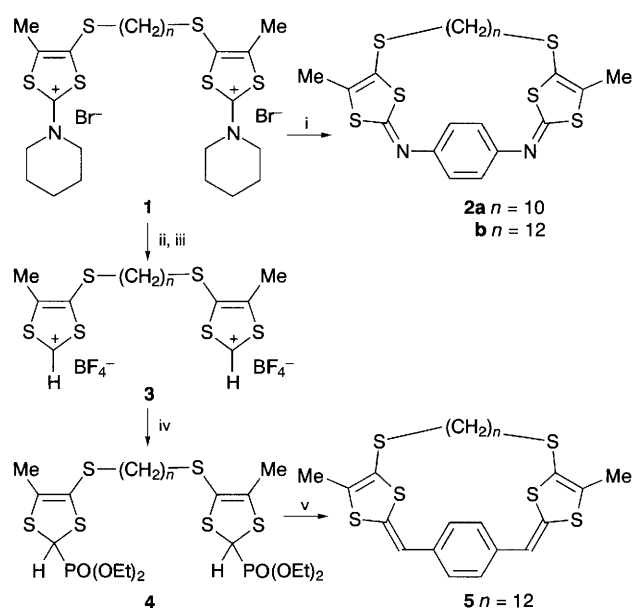
The synthesis and cyclic voltammetry data of cage-like molecules incorporating extended tetrathiafulvalenes are reported together with the demonstration that the two crystal modifications (1.289 and 1.311 g cm<sup>-3</sup>) observed for **2b** correspond to two different *cis* conformers **A** and **B**, the most planar form (**B**) giving the more dense crystal packing.

Macrocycles incorporating one or more tetrathiafulvalene (TTF) units are of special interest when attempting to prepare novel organic materials which could be specific hosts for acceptor molecules, and where strong interactions are expected between two TTF cores or between TTF and the acceptor guest. Several macrocycles incorporating TTF units have been reported,<sup>1</sup> but cyclophanes incorporating extended TTFs have not yet been described. We recently described the reaction of the 2-piperidino-1,3-dithiolium cation with *p*-phenylenediamine for the synthesis of *N,N'*-bis(1,3-dithiol-2-ylidene)benzene-1,4-diamine.<sup>2</sup> Our ongoing interest in the chemistry of cage-like molecules incorporating TTF units<sup>3-5</sup> prompted us to investigate the synthesis and properties of the extended tetrathiafulvalenocyclophanes **2** and **5**.<sup>†</sup>

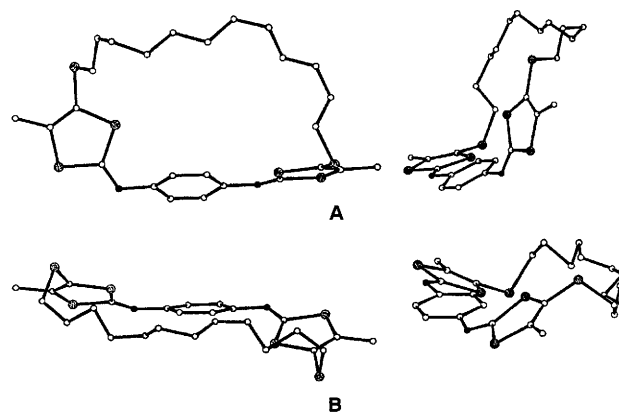
The synthesis of **2** was achieved starting from the bis(2-piperidino-4-alkylthio-1,3-dithiolium) salts **1** in refluxing pyridine with 0.5 equiv. of *p*-phenylenediamine as outlined in Scheme 1.<sup>2</sup> Two different crystal morphologies were observed for **2b** which correspond to two polymorphic modifications as confirmed by the X-ray structure analysis.<sup>‡</sup> These two modifications correspond to two different conformers with the same *cis* configuration as observed previously for the very strained [6]tetrathiafulvalenophane.<sup>3</sup> Note that while the same or slightly longer bridging chains allow for a *trans* configuration in [12]- and [14]-tetrathiafulvalenophanes<sup>5</sup> the presence of the bis(iminobenzene) core and the subsequent increased spatial extension for a given chain length impose the *cis* configuration observed for **2b**. The molecular structures shown in Fig. 1

establish that within conformer **A**, located in a general position in the cell, the  $\pi$  systems of the two dithiole rings are twisted away relative to those of the central bis(iminobenzene) fragment by 14.9(4) and 52.8(2)°. The large latter value suggests tendency towards a *trans* configuration and explains the more important strain of the alkyl side chain. The twist angle is only 28.3(4)° for the independent dithiole ring within conformer **B**, located on a twofold crystallographic axis. Therefore, the flexible character along the chain is more pronounced in the second modification of **2b**, hence the high thermal motion and/or disorder observed for the chain carbon atoms. Note that the flattening of the molecules in conformer **B** (the side chain being approximately coplanar with the dithiole rings) is responsible for the more compact structure in the solid state as exemplified by its significantly larger density (1.289 and 1.311 g cm<sup>-3</sup> for the modifications **A** and **B**, respectively).

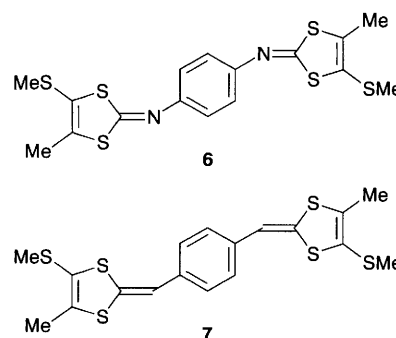
Reduction of bis(dithiolium) salt **1** with sodium borohydride followed by the reaction of the bis(aminodithiole) intermediate with tetrafluoroboric acid afforded **3**. Bisdithiolylium tetrafluoroborate **3** reacted with triethylphosphite in the presence of



**Scheme 1** Reagents and conditions: i, *p*-phenylenediamine (0.5 equiv.); ii, NaBH<sub>4</sub>-EtOH; iii, HBF<sub>4</sub> (48% solution in water), Ac<sub>2</sub>O; iv, NaI, P(OEt)<sub>3</sub>, MeCN; v, BuLi in THF, -78 °C, terephthalaldehyde (0.5 equiv.)



**Fig. 1** Views perpendicular (left) and parallel (right) to the central N...N axis of the molecular structures of the two conformers (**A** and **B**) of **2b** (S dotted, N black, C open atoms)



**Table 1** Cyclic voltammetry data of extended tetrathiafulvalenocyclophanes and analogues

Compound	$E_{ox}^1/V^a$	$E_{ox}^2/V^a$
DMDMT-TTF <sup>b</sup>	0.38	0.77
<b>2a</b>		1.01
<b>2b</b>		1.02
<b>5</b>	0.21	0.55
<b>6</b>		1.03
<b>7</b>	0.49	0.80

<sup>a</sup> vs. SCE, Pt working electrode with 0.1 mol dm<sup>-3</sup> Bu<sub>4</sub>NPF<sub>6</sub>, 100 mV s<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> In MeCN.

sodium iodide to give the corresponding bis(phosphonate) **4** in quantitative yield. The synthesis of the extended TTF **5** was performed by a Wittig–Horner reaction between terephthalaldehyde and bis(dithioly)phosphonate anion, the reaction proceeded analogously to those described for simpler extended TTFs.<sup>6</sup>

The redox behaviour of these new cages **2** and **5** were studied by cyclic voltammetry. The results are collected in Table 1 together with the oxidation potentials of related examples for comparison. As previously observed for non-cyclic analogues **6** and **7** substitution of the CH linking group for an N group significantly decreases the donor ability of these compounds.<sup>2</sup> The molecules **2** present the same behaviour as their analogue **6**, they seem to undergo a two-electron redox reaction at approximately the same potential.<sup>2</sup> Compounds **5** and **7** exhibit, during the first anodic scan, two successive irreversible peaks, but other systems appear during the following scans. It is noteworthy that the oxidation potential of **5** is much lower than that of its non-cyclic analogue.

The first extended tetrathiafulvalenocyclophanes have been prepared and electrochemically characterized. The cyclic voltammetry behaviour for compounds **2** display less donor character than their analogue **5** with a CH bridge instead of an imino one. The low oxidation potential for **5** indicates strong electron-donating properties and it will be of interest to investigate the formation of charge-transfer complexes from this new donor. Moreover, complications observed during cyclic voltammetry of this compound and the non-cyclic analogue **7** suggest that coupling reactions can take place during oxidation of these substrates.<sup>7</sup>

Received, 20th March 1995; Com. 5101735A

## Footnotes

† All new compounds gave satisfactory analytical values. Selected data for **2b**: yellow crystals, yield 40%; mp 133 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ

1.33 (m, 16H), 1.61 (m, 4H), 2.27 (s, 6H) 2.68 (t, 4H) 7.09 (s, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.87, 28.31, 28.90, 29.19, 29.57, 36.16, 118.17, 121.39, 133.17, 147.35, 163.94; HRMS Calc. for C<sub>26</sub>H<sub>34</sub>N<sub>2</sub>S<sub>6</sub>, 566.1046. Found, 566.1030. For **5**: yellow crystals, yield 31%; mp 158 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.30 (m, 16H), 1.69 (m, 4H), 2.12 (s, 6H), 2.27 (t, 4H), 6.39 (s, 2H), 7.21 (s, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 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 Calc. for C<sub>28</sub>H<sub>36</sub>S<sub>6</sub>, 564.1141. Found, 564.1131.

‡ Crystal data for **2b**: C<sub>26</sub>H<sub>34</sub>N<sub>2</sub>S<sub>6</sub>; Form A [Form B]: yellow plate-like crystals [yellow needle-like crystals], *a* = 11.981(3), *b* = 9.376(4), *c* = 26.586(3) Å, β = 101.74(1)°, *V* = 2924(1) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.289 g cm<sup>-3</sup>, μ = 4.67 cm<sup>-1</sup>, monoclinic, space group *P*2<sub>1</sub>/*n* [*a* = 16.161(2), *b* = 19.892(3), *c* = 10.364(3) Å, β = 120.41(1)°, *V* = 2873(1) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.311 g cm<sup>-3</sup>, μ = 4.67 cm<sup>-1</sup>, monoclinic, space group *C*2/*c*]. Among the 5859 measured reflections with 1 < θ < 26°, 5736 were independent of which 2964 were used {*I* > 3σ(*I*)} [among the 2899 measured reflections with 1 < θ < 26°, 2744 were independent of which 931 were used {*I* > 3σ(*I*)}]. Structure solution by direct methods and difference Fourier techniques (SDP<sup>8</sup> and Xtal3.2<sup>9</sup> systems of programs). Refinements (on *F*<sup>2</sup>) by full-matrix least-squares methods: *R* = 0.047, *R<sub>w</sub>* = 0.061 for 307 parameters, *w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*) + 0.025*F<sub>o</sub>*<sup>2</sup>], GOF = 1.685 [*R* = 0.067, *R<sub>w</sub>* = 0.088 for 172 parameters and 19 restraints, *w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*) + 0.016*F<sub>o</sub>*<sup>2</sup>], GOF = 1.758]. Residual electron density -0.28, +0.78 e Å<sup>-3</sup> [-0.54, +0.69 e Å<sup>-3</sup>], largest shift/error = 0.00 [0.12]. All S, N and C atoms were refined anisotropically and H atoms simply introduced in structure factor calculations with an overall isotropic temperature factor [All S, N and C atoms were refined anisotropically except C<sub>9</sub> to C<sub>13</sub> (along the side alkyl chain) which were found with high thermal motion or disordered and consequently refined isotropically. H atoms carried by the non disordered C atoms were simply introduced in structure factor calculations with an overall isotropic temperature factor]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

## References

- Reviews: M. Adam and K. Mullen, *Adv. Mater.*, 1994, **6**, 439; T. Jørgensen, T. K. Hansen and J. Becher, *Chem. Soc. Rev.*, 1994, **23**, 41, and references therein; J. Becher, J. Lau, P. Leriche, P. Mork and N. Svenstrup, *J. Chem. Soc., Chem. Commun.*, 1994, 2715.
- D. Lorcy, A. Robert, R. Carlier and A. Tallec, *Bull. Soc. Chim. Fr.*, 1994, **7**, 774.
- K. Boubekeur, P. Batail, F. Bertho and A. Robert, *Acta Crystallogr., Sect. C*, 1991, **47**, 1109.
- F. Bertho-Thoroval, A. Tallec, A. Souizi, K. Boubekeur and P. Batail, *J. Chem. Soc., Chem. Commun.*, 1991, 843.
- K. Boubekeur, C. Lenoir, P. Batail, R. Carlier, A. Robert, M. P. Le Paillard, D. Lorcy and A. Robert, *Angew. Chem., Int. Ed. Engl.*, 1994, **3**, 1379.
- M. Salle, A. Belyasmine, A. Gorgues, M. Jubault and N. Soyer, *Tetrahedron Lett.*, 1991, **32**, 2897.
- M. Fourmigué, I. Johannsen, K. Boubekeur, C. Nelson and P. Batail, *J. Am. Chem. Soc.*, 1993, **115**, 3752.
- B. A. Frenz, Enraf–Nonius Structure Determination Package, SDP Users Guide, Delft, The Netherlands, 1983.
- S. R. Hall, H. D. Flack, J. M. Stewart, XTAL3.2 Reference Manual, Universities of Western Australia, Geneva and Maryland, 1992.