

Extreme Conformational Constraints in π -Extended Tetrathiafulvalenes: Unusual Topologies and Redox Behavior of Doubly and Triply Bridged Cyclophanes

Christian A. Christensen, Andrei S. Batsanov, and Martin R. Bryce*

Contribution from the Department of Chemistry, University of Durham, Durham DH1 3LE, U.K.

Received April 13, 2006; E-mail: m.r.bryce@durham.ac.uk

Abstract: Doubly and triply bridged 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (ex-TTF) derivatives have been synthesized. Key steps are the generation and macrocyclization reactions of ex-TTFdithiolate reagents. The X-ray crystal structures of the doubly bridged cyclophanes **15** and **16** and the triply bridged system **23** show that the saddle-like conformation of the ex-TTF framework is enhanced by the short bridges between the dithiole rings. Unlike all previous ex-TTF derivatives (which display a single quasi-reversible two-electron oxidation wave, $D^0 \rightarrow D^{2+}$), cyclic voltammetry of the cyclophanes reveals two reversible, one-electron oxidation steps ($D^0 \rightarrow D^{++} \rightarrow D^{2+}$), with differences between the half-wave potentials ($E_2^{1/2} - E_1^{1/2}$) of 0.22–0.26 V. The conformational changes and gain in aromaticity which drive the second oxidation process in unrestricted ex-TTF systems (including singly bridged cyclophanes) have been prevented by multiple bridging. The radical cation species gives rise to a very broad, low-energy band ($\lambda_{max} = 2175$ and 2040 nm for **15** and **21**, respectively), assigned to an *intra*molecular interaction. The steric constraints imposed by multiple bridging have become so extreme that the π -framework of **15**, **16**, **21**, and **23** exhibits remarkable optical and redox behavior which is not characteristic of ex-TTF systems.

Introduction

Tetrathiafulvalene (TTF) derivatives with extended π -electron conjugation are versatile building blocks in supramolecular and materials chemistry.¹ Of particular interest are derivatives which incorporate a central *p*-quinodimethane spacer.² For example, the π -electron donor unit 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (**1**, Chart 1; herein abbreviated "ex-TTF") offers a unique combination of redox, charge delocalization, and structural properties which are very different from those of the parent TTF. Solution electrochemical studies have established that, whereas TTF undergoes two reversible, one-electron oxidation waves, ex-TTF system **1** undergoes the unusual phenomenon of inverted potentials ($E_1^{\text{ox}} > E_2^{\text{ox}}$).^{3,4} Solution



⁽¹⁾ Frère, P.; Skabara, P. J. Chem. Soc. Rev. 2005, 34, 69-98.

⁽¹⁾ Fiele, L., Skadada, J. S. Chen, Sole, Rev. 2005, 54, 67 (2007), 56.
(2) (a) Martín, N.; Ortí, E. In Handbook of Advanced Electronic Photonic Materials and Devices; Nalwa, H. S., Ed., Academic Press: San Diego, 2001; Vol. 3, Chapter 6, pp 245–265. (b) Bendikov, M.; Wudl, F.; Perepichka, D. F. Chem. Rev. 2004, 104, 4891–4945. (c) Yamashita, Y. In Tetrathiafulvalene Chemistry, Fundamentals and Applications of Tetrathiafulvalene; Yamada, J., Sugimoto, T., Eds.; Springer-Verlag: Berlin, 2004; Chapter 12, pp 287–310. (d) Yamashita, Y.; Tanaka, S.; Imaeda, K.; Inokuchi, H.; Sano, M. J. Chem. Soc., Chem. Commun. 1991, 1132–1133.

^{(3) (}a) Hu, K.; Evans, D. H. J. Phys. Chem. 1996, 100, 3030-3036. (b) Evans, D. H.; Hu, K. J. Chem. Soc., Faraday Trans. 1996, 92, 3983-3990. (c) Kraiya, C.; Evans, D. H. J. Electroanal. Chem. 2004, 565, 29-35. (d) Gruhn, N. E.; Macías-Ruvalcaba, N. A.; Evans, D. H. J. Phys. Chem. A 2006, 110, 5650-5655. (e) Macías-Ruvalcaba, N. A.; Evans, D. H. J. Phys. Chem. B 2006, 110, 5155-5160. References 3c-e refer to 9,10-disubstituted anthracenes and emphasize that the changes in geometry which accompany the redox process are crucial in causing inverted potentials.

⁽⁴⁾ For pioneering work on the electrochemistry of two-electron redox systems, see: (a) Fritsch, J. M.; Weingarten, H.; Wilson, J. D. J. Am. Chem. Soc. 1970, 92, 4038–4046. (b) Deuchert, K.; Hünig, S. Angew. Chem., Int. Ed. Engl. 1978, 17, 875–886.

solvent and the substituents).⁵ This redox process, which is electrochemically quasi-reversible and chemically reversible, is accompanied by a remarkable conformational change,⁶ as shown by X-ray crystallographic studies.⁷ The neutral molecules 1 possess a saddle-shaped structure comprising a concave cavity and a strongly folded anthracenediylidene unit, imposed by steric hindrance from the benzoannulated quinoid moiety. In contrast, in the dications 1^{2+} , the anthracene ring system becomes planar and aromatic, with bond lengths similar to those of anthracene itself, and the heteroaromatic 1,3-dithiolium cations are almost orthogonal to this plane. Theoretical studies support the experimental evidence that the two, one-electron oxidations of 1 coalesce under the same oxidation wave, with the dication possessing decreased intramolecular on-site Coulombic repulsion compared to TTF.8 The radical cation of system 1 is a transient species which has been generated by flash photolysis⁹ and pulse radiolysis.¹⁰ This remarkable interplay of redox and conformational properties has led to derivatives of 1 being employed as components of charge-transfer salts,7,11 nonlinear optical materials,12 multi-stage redox assemblies,13 dimeric ex-TTFs,14 highly charged dendrimers,15 and donor-acceptor systems for studies of charge-separated excited states.¹⁶

The structures and properties of aromatic molecules can be manipulated by applying steric constraints, e.g., by incorporation into cyclophane structures.¹⁷ The electron donor properties of the ex-TTF system 1 have been modified in cyclophane derivatives where the linkers are short enough to restrict the conformational change which accompanies the oxidation to the dication. Thus, for systems 2a,b¹⁸ and 3a,¹⁹ the characteristic $D^0 \rightarrow D^{2+}$ oxidation wave in the cyclic voltammogram was

- (6) For other molecular systems where significant conformational changes are triggered by electron transfer, see: (a) Boubekeur, K.; Lenoir, C.; Batail, P.; Carlier, R.; Tallec, A.; Le Paillard, M.-P.; Lorcy, D.; Robert, A. Angew. Chem., Int. Ed. Engl. 1994, 33, 1379-1381. (b) Guerro, M.; Carlier, R.; Boubekeur, K.; Lorcy, D.; Hapiot, P. J. Am. Chem. Soc. 2003, 125, 3159-3167 and references therein. (c) Nygaard, S.; Laursen, B. W.; Flood, A. H.; Hansen, C. N.; Jeppesen, J. O.; Stoddart, J. F. Chem. Commun. 2006, 144 - 146.
- (7) Bryce, M. R.; Moore, A. J.; Hasan, M.; Ashwell, G. J.; Fraser, A. T.; Clegg, W.; Hursthouse, M. B.; Karaulov, A. I. Angew. Chem., Int. Ed. Engl. 1990, 29, 1450-1452
- (8) Martín, N.; Sánchez, L.; Seoane, C.; Ortí, E.; Viruela, P. M.; Viruela, R.
- (9) Jones, A. E.; Christensen, C. A.; Perepichka, D. F.; Batsanov, A. S.; Beeby, A.; Low, P. J.; Bryce, M. R.; Parker, A. W. *Chem. Eur. J.* 2001, *7*, 973-978.
- (10) (a) Martín, N.; Sánchez, L.; Guldi, D. M. Chem. Commun. 2000, 113-114. (b) Guldi, D. M.; Sánchez, L.; Martín, N. J. Phys. Chem. B 2001, 105.7139-7144
- (11) (a) Triki, S.; Ouahab, L.; Lorcy, D.; Robert, A. Acta Crystallogr. 1993, C49, 1189–1192. (b) Batsanov, A. S.; Bryce, M. R.; Lyubchik, S. B.; Perepichka, I. F. Acta Crystallogr. 2002, E58, o1106–o1110.
- (12) (a) Otero, M.; Herranz, M. A.; Seoane, C.; Martín, N.; Garín, J.; Orduna, .; Alacalá, R.; Villacampa, B. Tetrahedron 2002, 58, 7463-7475. (b)
- J.; Alacala, R.; Villacampa, B. *Tetrahedron* 2002, 58, 7465–7475. (b) Insuasti, B.; Atienza, C.; Seoane, C.; Martín, N.; Garín, J.; Orduna, J.; Alacalá, R.; Villacampa, B. J. Org. Chem. 2004, 69, 6986–6995.
 (13) (a) Cerrada, E.; Bryce, M. R.; Moore, A. J. J. Chem. Soc., Perkin Trans. *I* 1993, 537–538. (b) Marshallsay, G. J.; Bryce, M. R. J. Org. Chem. 1994, 59, 6847–6850. (c) Gautier, N.; Mercier, N.; Riou, A.; Gorgues, A. Hudhomme, P. Tetrahedron Lett. 1998, 40, 5997–6000.
 (14) (a) Martín, N.; Párez, L.; Seone, C. L. Org. Chem. 1997, 62
- (14) (a) Martín, N.; Pérez, I.; Sánchez, L.; Seoane, C. J. Org. Chem. 1997, 62, 870–877. (b) Christensen, C. A.; Bryce, M. R.; Batsanov, A. S.; Becher, J. Org. Biomol. Chem. 2003, 1, 511–522. (c) Díaz, M. C.; Illescas, B. M.; Scoane, C.; Martín, N. J. Org. Chem. 2004, 69, 4492–4499. (d) Díaz, M. C.; Illescas, B. M.; Martín, N.; Perepichka, I. F.; Bryce, M. R.; Levillain, C., Incoca, D. M., Martin, N., Felepicina, I. F., Bryce, M. K., Levillatin, E.; Viruela, R.; Ortí, E. *Chem. Eur. J.* 2006, *12*, 2709–2712. (e) Díaz, M. C.; Illescas, B. M.; Martín, N.; Stoddart, J. F.; Canales, M. A.; Jiménez-Barbero, J.; Sarova, G.; Guldi, D. M. *Tetrahedron* 2006, *62*, 1998–2002.
 Godbert, N.; Bryce, M. R. *J. Mater. Chem.* 2002, *12*, 27–36.

observed at significantly higher potentials (+200-300 mV) compared to their nonbridged precursors, unlike 3b, where the longer bridge had essentially no effect on the oxidation potential. Bridging the anthracene unit had less effect (4a, +50 mV; 4b,unchanged) compared to their nonbridged precursors.²⁰

The aim of the present work was to synthesize ex-TTF derivatives which would be sterically constrained to such an extent that they could not undergo any significant conformational change upon oxidation. We were fascinated by the possibility that, if the central anthracenediylidene ring was forced to retain the strongly folded (neutral) geometry upon oxidation, and hence could not aromatize, then the single, two-electron oxidation process $(D^0 \rightarrow D^{2+})$ might be replaced by two sequential, one-electron steps $(D^0 \rightarrow D^{\bullet +} \rightarrow D^{2+})$ with an observable (or even stable) radical cation. We now report the synthesis of the first doubly and triply bridged ex-TTF cyclophanes and describe the fascinating structural and electronic consequences of this unprecedented rigidification of the π -framework.

Results and Discussion

Synthesis. Our initial targets were analogues of 2 doubly bridged across the two dithiole rings. The previous synthesis of 2a and 2b had been achieved in low yields (22% and 10%, respectively) by a two-fold Horner-Wadsworth-Emmons reaction of the corresponding bis(1,3-dithiol-2-yl)phosphonate reagent with anthraquinone.¹⁸ Cyclophanes 3¹⁹ and 4²⁰ had been obtained by a different and more efficient strategy, viz., bridging a preformed ex-TTF system in macrolactonization reactions. For precursors to doubly bridged analogues, we chose ex-TTF derivatives bearing suitable functionality to undergo two intramolecular cyclization reactions. Compounds 13 and 14, with two protected thiolates and two alkyl iodide chains, seemed ideal candidates: the short pentamethylenedithio and tetramethylenedithio bridges which would form by intramolecular nucleophilic displacement of the iodides should ensure that only the cis/cis isomer would form in each case; the "criss-cross" trans/ trans isomers would be too strained.

However, since no methodology existed for the synthesis of ex-TTF derivatives bearing cyanoethyl-protected thiolates, we modified the protocol for phosphite-mediated coupling of 1,3dithiole-2-chalcogenones commonly used for the synthesis of cyanoethyl-protected TTF thiolates.²¹ Although the crosscoupling reactions of anthraquinone or anthrone derivatives with

- (17) (a) Diederich, F. Cyclophanes; Royal Society of Chemistry: Cambridge, 1991. (b) Vögtle, F. Cyclophane Chemistry; Wiley: Chichester, 1993. (c) For a series of multiply bridged and sterically constrained cyclophanes, see: Song, Q.; Ho, D. M.; Pascal, R. A., Jr. J. Am. Chem. Soc. 2005, 127, 11246-11247.
- (18) Finn, T.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K. Chem. Commun. 1999, 1835-1836.
- Godbert, N.; Batsanov, A. S.; Bryce, M. R.; Howard, J. A. K. J. Org. Chem. (19)2001. 66, 713-719.
- (2007, 00, 113, 113, 113)
 (20) Christensen, C. A.; Batsanov, A. S.; Bryce, M. R.; Howard, J. A. K. J. Org. Chem. 2001, 66, 3313–3320.

^{(5) (}a) Yamashita, Y.; Kobayashi, Y.; Miyashi, T. Angew. Chem., Int. Ed. Engl. **1989**, *28*, 1052–1053. (b) Moore, A. J.; Bryce, M. R. J. Chem. Soc., Perkin Trans. 1 **1991**, 157–168. (c) Bryce, M. R.; Coffin, M. A.; Hursthouse, M. B.; Karaulov, A. I.; Müllen, K.; Scheich, H. *Tetrahedron Lett.* **1991**, *32*, 6029-6032. (d) Liu, S.-G.; Pérez, I.; Martín, N.; Echegoyen, L. J. Org. Chem. 2000, 65, 9092-9102. (e) Liu, S.-G.; Pérez, I.; Martín, N.; Echegoyen, L. J. Org. Chem. 2000, 65, 9092-9102.

^{(16) (}a) Herranz, M. A.; Martín, N.; Ramey, J.; Guldi, D. M. Chem. Commun. 2002, 2968–2968. (b) Kodis, G.; Liddell, P. A.; de la Garza, L.; Moore, A. L.; Moore, T. A.; Gust, D. J. Mater. Chem. 2002, 12, 2100-2108. (c) K. L., Molec, I. A., Gust, D. J. *Mater. Chem.* 2004, *12*, 2160 (19)
 González, S.; Martín, N.; Swartz, A.; Guldi, D. M. *Org. Lett.* 2003, *5*, 557–560. (d) Díaz, M. C.; Herranz, M. A.; Illescas, B. M.; Martín, N.; Godbert, N.; Bryce, M. R.; Luo, Ch.; Swartz, A.; Anderson, G.; Guldi, D. M. *J. Org. Chem.* 2003, *68*, 7711–7721. (e) Perepichka, D. F.; Bryce, M. R.; Perepichka, I. F.; Lyubchik, S. B.; Christensen, C. A.; Godbert, N.; Batsanov, A. S.; Levillain, E.; McInnes, E. J. L.; Zhao, J. P. J. Am. Chem. *Soc.* **2002**, *124*, 14227–14238. (f) Giacalone, F.; Segura, J. L.; Martín, N.; Guldi, D. M. J. Am. Chem. Soc. **2004**, *126*, 5340–5341. (g) Giacalone, F.; Segura, J. L.; Martín, N.; Ramey, G.; Guldi, D. M. Chem. Eur. J. 2005, 11, 4819-4834.



1,3-dithiole-2-thione derivatives were sluggish compared to the self-coupling of the 1,3-dithiole-2-thiones, we found that crosscoupling, which provided a new route to highly functionalized ex-TTF derivatives,²² was possible by slow addition of the 1,3dithiole-2-thione to the anthraquinone/anthrone. Thus, slow addition of 6^{23} and 7^{23} to an excess of anthraquinone 5 in triethyl phosphite at 125 °C gave the anthrone derivatives 8 and 9 in 44% and 46% yields, respectively (Scheme 1). The second phosphite coupling using reagent 10^{24} furnished the ex-TTF derivatives 11 and 12 in 77% and 81% yields, respectively. Halogen exchange using sodium iodide in refluxing 2-butanone afforded the diiodide derivatives 13 and 14 in high yields. The slow addition of compound 13 to cesium hydroxide monohydrate in dimethylformamide (DMF) at room temperature under high dilution conditions²¹ gave the desired product **15** in 92% yield, which is remarkably efficient for a double macrocyclization reaction. The analogous cyclization of 14 gave 16 in only 16% yield; the major product was an insoluble powder, most likely a polymer, suggesting that the shorter tetramethylenedithio linkers and increased ring strain in 16 disfavored the intramolecular reactions. The yield of 16 was increased to 27% by adding a solution of 14 in DMF and a solution of NaOMe in common organic solvents was considerably reduced compared to that of their precursors, they were unambiguously characterized by ¹H NMR, ¹³C NMR, HRMS, and elemental analysis. Especially the high symmetry of the ¹³C NMR spectra of 15

and 16 established that cis/cis bridging had occurred, and hence only one isomer was formed in each case (Figure S1 in the Supporting Information).

MeOH and DMF simultaneously to DMF under very high

Although the solubility of the cyclophanes 15 and 16 in

dilution conditions.

The high-yielding synthesis of 15 opened a way to triply bridging the ex-TTF system by combining the methodology in Scheme 1 with that used to synthesize 4.20 For this goal, we needed an analogue of 15 with substituents at the 2- and 6-positions of the anthracenediylidene unit which would be suitable for a macrolactonization reaction. Coupling of anthraquinone derivative 17^{20} with thione 6, under the same conditions used for 8, gave anthrone derivative 18 in only 34% yield. It was apparent that 17 is less reactive than anthraquinone itself. This was confirmed in the second phosphite coupling: as much as 9 equiv of the thione 10 was required to give the ex-TTF derivative 19 in 57% yield (Scheme 2; cf. Scheme 1). This lower reactivity of 17 and 18 could arise from the electrondonating effect of the alkoxy substituents and/or a steric effect of the bulky tert-butyldiphenylsilyl (TBDPS) protecting groups. Halogen exchange gave the highly functionalized compound 20 in 88% yield. Treatment of 20 with cesium hydroxide monohydrate (6 equiv, 20 °C, 24 h) induced the desired double cyclization and cleaved the TBDPS protecting groups²⁵ to afford product 21 in 78% yield. (The 2-hydroxyethoxy substituents of 21 imparted good solubility in organic solvents, in contrast to 15.) In the final step, 21 reacted with 1,4-benzenedicarbonyl chloride 22 in the presence of pyridine to yield the triply bridged cyclophane 23 in 42% yield (cf. 39% for the comparable reaction to form 4a).²⁰

The structure of 23 was confirmed by ¹H NMR, ¹³C NMR, HRMS, and elemental analysis. Due to C_2 symmetry, the ¹³C NMR spectrum was very simple and the ¹H NMR spectrum was similar to that of 15 combined with the high-frequency part of the spectrum for 4a. Most diagnostic for the phenyl bridge is the upfield shift of the phenyl protons [δ 6.91 ppm (4H), s] due to the ring current of the dihydroanthracene ring system (cf. 4a δ 6.89 ppm).²⁰

X-ray Crystal Structures of 15, 16, and 23. The fascinating architectures of 15, 16, and 23 were revealed in their X-ray molecular structures. For 15, the structures of both unsolvated crystals (Figure 1) and a toluene solvate (Figure S2, Supporting Information) were solved. In the former, the ex-TTF moiety has local C_{2v} symmetry and both pentamethylene bridges adopt practically planar all-trans conformations (Figure S3, Supporting Information), but their planes are inclined differently (by 18° and 76°) to the ex-TTF (local) mirror plane, which passes through the C(9), C(10), C(15), and C(18) atoms, and are nearly perpendicular to one another (dihedral angle 86°). In 15 \cdot C₇H₈, the molecule has crystallographic C_2 symmetry. The entire $-S(CH_2)_5S$ – moiety of both bridges is disordered between two orientations. In both cases, it also adopts trans conformations

⁽²¹⁾ For a review of the synthesis and reactivity of cyanoethyl-protected TTF thiolates, see: Simomsen, K. B.; Becher, J. Synlett **1997**, 1211–1220.

⁽²²⁾ The development of this methodology for the synthesis of a series of new and versatile ex-TTF building blocks will be reported elsewhere.

⁽²³⁾ Takimiya, K.; Imamura, K.; Shibata, Y.; Aso, Y.; Ogura, F.; Otsubo, T. J. Org. Chem. 1997, 62, 5567–5574.

Svenstrup, N.; Rasmussen, K. M.; Hansen, T. K.; Becher, J. Synthesis **1994**, 809–812. (24)

⁽²⁵⁾ It is known that cesium hydroxide monohydrate can cleave silyl protecting groups during the deprotection of cyanoethylthio groups: Christensen, C. A.; Bryce, M. R.; Becher, J. *Synthesis* **2000**, 1695–1704.



around all C–C bonds and gauche conformations around C–S bonds, the mean C₅ planes being inclined to the ex-TTF mirror plane by 76° and 88°. Thus, the whole molecule conforms approximately to the C_{2v} symmetry. The change of conformation from **15** to **15**·C₇H₈ is a consequence of the contact with the planar toluene molecule, and it results in a substantial increase of molecular bending. This shows that the ex-TTF unit in **15** still possesses sufficient flexibility that its conformation can be affected by the demands of crystal packing. In **16**, both bridges have more strained conformations, and the approximate molecular symmetry is reduced to C_2 , with an appreciable (chiral) twist of the ex-TTF moiety itself.



Figure 1. X-ray molecular structure of 15.

For **15** and **16** (Figure 2), the usual saddle-like conformation of the ex-TTF framework is aggravated by the short bridges between the dithiole rings. A good measure of the overall bending is the angle (θ , Table 1) between the planar SC=CS moieties of the dithiole rings, e.g., S(1)C(16)C(17)S(2) and S(5)C(19)C(20)S(6) in Figure 1. In nonbridged systems, θ ranges from 73° to 101°;²⁶ one hexamethylenedithio bridge (**2a**)¹⁸ reduces it to 46–54°, and one pentamethylenedithio



Figure 2. X-ray molecular structure of 16.

Table 1. Selected Angles (Deg) in the Molecular Structures in the Cyclophanes As Determined by X-ray Crystallographic Analysis^a

	15	15·C ₇ H ₈	16	23 •(CH ₂ Cl ₂) ₂
φ	40.2	40.8	43.4	40.6
δ_1	18.4	30.2	30.6	31.9
δ_2	18.3	30.9	28.7	32.4
θ	42.9	33.0	4.8	31.7

^a The angles are defined in the text.

bridge (2b) reduces it to 35°. The second pentamethylenedithio bridge in **15** adds little extra strain, but the two tetramethylenedithio bridges in **16** make these peripheral moieties of the ex-TTF unit nearly parallel. On the other hand, the folding (φ) of the anthracene system along the C(9)···C(10) vector does not exceed the range observed in unconstrained ex-TTF derivatives (35–45°),²⁶ and the overall bending (θ) in **16** is enhanced mainly by stronger folding of both dithiole rings (Table 1), as defined by angles between planes S(1)C(15)S(2) and S(1)-C(16)C(17)S(2) (δ_1), or S(5)C(18)S(6) and S(5)C(19)C(20)S(6) (δ_2).

^{(26) (}a) Bryce, M. R.; Finn, T.; Moore, A. J.; Batsanov, A. S.; Howard, J. A. K. *Eur. J. Org. Chem.* 2000, 51–60. (b) Godbert, N.; Bryce, M. R.; Dahaoui, S.; Batsanov, A. S.; Howard, J. A. K.; Hazendonk, P. *Eur. J. Org. Chem.* 2001, 749–757. (c) Bryce, M. R.; Finn, T.; Batsanov, A. S.; Kataky, R.; Howard, J. A. K.; Lyubchik, S. B. *Eur. J. Org. Chem.* 2002, 1199–1205.



Figure 3. X-ray molecular structure of 23 · (CH₂Cl₂)₂.

Table 2. UV-Vis Absorption Spectra Recorded in Dichloromethane at 20 $^\circ\text{C}$

compound	$\lambda_{max}/nm \ (lg \ \epsilon)$		
11	432 (4.44), 362 (4.20)		
12	431 (4.43), 362 (4.19)		
13	432 (4.44), 362 (4.21)		
14	432 (4.45), 362 (4.20)		
15	414 (4.35), 372 (4.11), 351 (4.15), 269 (4.44)		
16	398 (4.08), 370 (4.08), 340 (4.07), 267 (4.40)		
19	428 (4.44), 361 (4.21)		
20	428 (4.43), 361 (4.20)		
21	411 (4.32), 353 (4.22)		
23	414 (4.26), 353 (4.16)		

The conformation of the ex-TTF moiety in $23 \cdot (CH_2Cl_2)_2$ (Figure 3 and Figure S4, Supporting Information) is very similar to that in $15 \cdot C_7H_8$. The folding is largely unaffected by the bis-(lactone) bridge, as was the case for cyclophane 4a.²⁰

Optical Absorption and Electrochemical Properties. The UV-vis absorption data for the cyclophanes and their precursors are collated in Table 2. Precursors 11-14 showed two bands typical of ex-TTF derivatives⁹ at $\lambda_{max} = 432$ and 362 nm. Incorporation of methylenedithio bridges in cyclophanes 15 and 16 leads to a blue-shift of the longest wavelength absorption band, indicating loss of π -conjugation (see spectra of 13, 15, and 16 in Figure 4). There is a shift from $\lambda_{max} = 432$ nm to 414 nm upon incorporation of the two pentamethylenedithio bridges (cyclophane 15). Shortening of the bridges to tetramethylenedithio (cyclophane 16) has an even greater impact: the extinction coefficient of the longest wavelength band is approximately halved (relative to precursor 14; spectrum similar to that of precursor 13 shown in Figure 4) and shifted to λ_{max} = 398 nm. Thus, the blue-shift and the decrease of the extinction coefficient, especially of the longest wavelength band, are good measures of the folding of the ex-TTF moieties. Qualitatively similar behavior was noted for strained TTF cyclophanes.²⁷ For 2,6-disubstituted doubly bridged cyclophane 21 the trend is the same: the longest wavelength band is blue-shifted by 17 nm relative to that of precursor 20. However, the third bridge in this system [i.e., the bis(lactone) bridge in 23] makes little



Figure 4. UV-vis absorption spectra of **13**, **15**, and **16** in dichloromethane at 20 °C.

Table 3. Cyclic Voltammetry Data^a

compound	E ^{ox} pa/V	E ^{ox} po/V	$\Delta E_{\rm p}/{\rm V}^{b}$
11	0.60	0.51	0.09
12	0.61	0.49	0.12
13	0.60	0.51	0.09
14	0.61	0.49	0.12
15	1.01, 1.25	0.95, 1.19	0.06, 0.06
16 ^c	0.99, 1.26	0.92, 1.18	0.07, 0.08
19	0.63	0.41	0.22
20	0.63	0.41	0.22
21	0.92, 1.13	0.86, 1.08	0.06, 0.05
23	0.98, 1.20	0.92, 1.14	0.06, 0.06

^{*a*} Compound ca. 1 × 10⁻³ M, electrolyte 0.1 M Bu₄NPF₆ in dichloromethane, 20 °C, vs Ag/AgCl, scan rate 100 mV s⁻¹. ^{*b*} $\Delta E_p = E^{xx}_{pa} - E^{xx}_{pc}$ (E^{xx}_{pa} is the oxidation peak potential on the first anodic scan; E^{xx}_{pc} is the coupled reduction peak potential on the cathodic scan). ^{*c*} Scan rate 5000 mV s⁻¹ due to some deposition of oxidized species on the electrode at lower scan rates.



Figure 5. Cyclic voltammograms of 13 and 15 vs Ag/AgCl under the conditions stated in Table 3.

difference to the spectrum, as observed for cyclophane 4a in comparison with its nonbridged precursors.²⁰

Cyclic voltammetric (CV) data recorded in dichloromethane are collated in Table 3. Figure 5 shows the CVs of **13** and **15**. As expected, all the nonbridged precursors show a single, quasireversible, two-electron oxidation wave at 0.60-0.63 V. The oxidation potentials of the doubly and triply bridged cyclophanes **15**, **16**, **21**, and **23** are raised considerably compared to those of their precursors, and surprisingly, **16** is slightly easier to oxidize (by ca. 20 mV) than its less strained (longer-bridged) analogue **15**. However, most remarkably, and in striking contrast to all other ex-TTF cyclophanes (i.e., singly bridged systems),^{18–20}

^{(27) (}a) Lau, J.; Blanchard, P.; Riou, A.; Jubault, M.; Cava, M. P.; Becher, J. J. Org. Chem. 1997, 62, 4936–4942. (b) Wang, C.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K. Chem. Eur. J. 1997, 3, 1679–1690. (c) Otsubo, T.; Aso, Y.; Takimiya, K. Adv. Mater. 1996, 8, 203–211.



Figure 6. Spectroelectrochemistry of 21 in dichloromethane at 20 °C, showing oxidation of the neutral species to the radical cation.

the oxidation occurs in two reversible,28 one-electron oxidation waves $(D^0 \rightarrow D^{\bullet+} \rightarrow D^{2+})$. Hence, these are the first ex-TTF derivatives in which the formation of the radical cation species is observable by CV (the differences between the half-wave potentials²⁹ of the first and second oxidation processes, $E_2^{1/2}$ – $E_1^{1/2}$, are 0.22–0.26 V). The reason must be that little or no conformational change can accompany the oxidation of the doubly or triply bridged cyclophanes, due to their very rigid structures. This conformational change, with twisting of the dithiolium rings to relieve peri-interactions and concomitant gain in aromaticity and anthracene planarity which drives the second oxidation process in unrestricted analogues, is prevented; thus, in 15, 16, 21, and 23, the radical cation is stabilized with respect to the dication. Indeed, these molecules effectively cease to behave as ex-TTFs; the two 1,3-dithiol-2-ylidene systems have lost much of their conjugation because of the steric constraints in the system. The oxidation potentials of 21 are lowered by 90-120 mV compared to those of the unsubstituted analogue 15, presumably due to the electron-donating alkoxy groups. The third bridge in 23 increases the oxidation potentials by 60-70mV, an increase similar to that seen for 4a compared to 1 (R = SMe).20

Spectroelectrochemical studies on 15 (Figure S5, Supporting Information) and **21** (Figure 6) gave similar results, with the increased solubility of 21 facilitating these studies. Upon oxidation of 21, the strong bands of the neutral species at λ_{max} = 353 and 411 nm were replaced by a sharp band at λ_{max} = 423 nm, two broad bands at $\lambda_{max} = 580$ and 760 nm, and a very broad band at ca. 1300–2700 nm, with $\lambda_{\text{max}} = 2040$ nm, making the spectrum of the radical cation species 21^{++} most unusual. The bands at $\lambda_{max} = 580$ and 760 nm are similar to those of the radical cation of alkylthio-TTF derivatives.³⁰ The very broad low-energy band is reminiscent of a similar absorption ($\lambda_{max} = 2300$ nm) of a partly oxidized dimeric TTF cyclophane, which was unambiguously assigned to a mixedvalence band, resulting from *inter*molecular interaction.³¹ For cyclophanes 15 and 21, we assign the low-energy band to a

mixed-valence interaction between the neutral and the oxidized dithiole rings: the ratio of the low-energy band to the other bands in the spectrum was unaffected by the concentration of the solution, consistent with an *intra*molecular interaction. The extent of delocalization of the radical cations 15^{•+} and 21^{•+} cannot be deduced from these data. Low solubility prevented spectroelectrochemical studies on 16.

For both 15 and 21, the radical cation species were stable on the spectroelectrochemical time scale (>1 h), and the spectra of the neutral species could be completely recovered upon electrochemical reduction. Furthermore, clean isosbestic points were seen at $\lambda \approx 320$ and 420 nm in the formation of **21**⁺⁺ (Figure 6, inset). However, further oxidation to form 15^{2+} and 21^{2+} caused decomposition, and the spectra of neither the cation radicals nor the neutral species could be recovered upon reduction. In the CV experiments, this decomposition of the dicationic species was not observed due to the much shorter time scale (a few seconds). The cationic species could not be isolated as salts by electrocrystallization.

Conclusions

Extreme steric constraints have manipulated the redox properties of the ex-TTF framework to yield a stabilized radical cation state. The first doubly and triply bridged derivatives of system 1 (viz., compounds 15, 16, 21, and 23) are fundamentally interesting cyclophanes by virtue of their very unusual topology, which is enhanced by multiple bridging, combined with their π -electron donor properties. The optical absorption and solution electrochemical properties establish that the π -framework has become so constrained that 15, 16, 21, and 23 no longer exhibit the characteristic signatures of ex-TTF systems: the two 1,3dithiol-2-ylidene systems have lost much of their conjugation and behave essentially as separate redox centers. Unlike all previous ex-TTF derivatives, the oxidation of 15, 16, 21, and 23 occurs in two reversible, one-electron oxidation waves. The conformational changes and gain in aromaticity which drive the second oxidation process in unrestricted ex-TTF systems (including singly bridged cyclophanes) have been prevented by the conformational constraints; the radical cations and dications of 15, 16, 21, and 23 have been forced to retain the strongly folded geometry of the neutral species, with fascinating consequences.

Control over the redox and structural properties of the ex-TTF system 1 has been taken to a new level. Unprecedented opportunities now exist for utilizing the radical cation in electron-transfer processes. Moreover, this methodology should be versatile for different bridging groups, which will enable limited molecular motion to occur under precise electrochemical conditions, with possible applications in molecular machinery.³² New ex-TTF cage and sensory systems can also be envisaged.

Acknowledgment. We thank EPSRC and The Danish Research Academy for funding to C.A.C. We thank Professor J. A. K. Howard for the use of X-ray facilities and EPSRC for funding the improvement to the X-ray instrumentation.

Supporting Information Available: General experimental methods, synthetic details, and characterization data for all new

⁽²⁸⁾ Electrochemical reversibility in this context is defined as (i) the ratio between the cathodic and anodic peak currents, $I_c/I_a \approx 1.0$; (ii) the peak potentials E_p , which are independent of the scan rate; and (iii) $\Delta E_p \approx (59/2)$ z) mV, where z is the number of electrons involved in the process.

⁽²⁹⁾ For a reversible redox process, the half-wave potential is defined as $E^{1/2} =$

 ⁽E^{ox}_{pa} + E^{ox}_{pc})/2.
 (30) Khodorkovsky, V.; Shapiro, L.; Krief, P.; Shames, A.; Mabon, G.; Gorgues,

A.; Giffard, M. *Chem. Commun.* **2001**, 2736–2737. Spanggaard, H.; Prehn, J.; Nielsen, M. B.; Levillain, E.; Allain, M.; Becher, J. *J. Am. Chem. Soc.* **2000**, *122*, 9486–9494. (31)

^{(32) (}a) Balzani, V.; Venturi, M.; Credi, A. Molecular Devices and Machines: A Journey into the Nanoworld; Wiley-VCH: Weinheim, 2003. (b) Easton, C. J.; Lincoln, S. F.; Barr, L.; Onagi, H. Chem. Eur. J. 2004, 10, 3120-3128

compounds; copy of the ¹³C NMR spectrum of **15**; spectra of cyclophane **15**⁺ obtained in spectroelectrochemical conditions; X-ray crystallographic file for **15**, **15**⁺C₇H₈, **16**, and **23**⁺(CH₂-Cl₂)₂ in CIF format and additional ORTEP drawings of their

structures. This material is available free of charge via the Internet at http://pubs.acs.org.

JA062358M