Molecular Saddles. 4.[1] Redox-Active Cyclophanes by Bridging the 9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene System: Synthesis, Electrochemistry, and X-ray Crystal Structures of Neutral Species and a Dication Salt

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We report the synthesis of a new series of cyclophanes **11a**−**d** by ester-forming macrocyclization reactions of diol **9** with the dicarbonyl chloride derivatives of benzene, thiophene, ferrocene, and diphenyl ether, **10a**−**d**, respectively. Compounds **11a**−**d** display a two-electron, quasireversible oxidation wave in the cyclic voltammogram to yield the dication species at $E^{ox}{}_{pa} = 0.70-0.72$ V (for **11a**−**c**) and 0.47 V (for **11d**) (vs Ag/AgCl in acetonitrile). The raised oxidation potentials for **11a**−**c** reflect the reduced stability of the twisted dication structure within the steric constraints of the smaller cyclophanes. Consistent with this, the value of ΔE (defined as $E^{ox}{}_{pa} - E^{ox}{}_{pc}$) decreases (i.e., reversibility of the oxidation process increases) in the sequence **11d** > **11c** > **11a** > **11b** as the bridging chain becomes shorter. X-ray crystal structures are reported for compounds **11a**−**d** and the dication salt **11d**$^{2+}(I_3^-)_2 \cdot (CH_2Cl_2)_{2.25}$. For **11a**−**d** the typical saddle-shaped conformation of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene moiety is observed, with the strain imposed by the cyclophane ring being accommodated in the structure of the bridging unit. In the dication **11d**$^{2+}$ both dithiolium rings are planar and the anthracene unit is essentially aromatic, with the conformation of the bridge basically the same as in neutral **11d**.

Introduction

In the context of organic systems which adopt concave cleft structures,[2] we are developing the chemistry of 9,10-bis(methylene)-9,10-dihydroanthracene derivatives. Crystallographic and theoretical studies have shown that peri interactions with a range of substituents attached to the methylene sites[3] cause the central anthracenediylidene ring to fold into a boat conformation, and thereby the molecule adopts a saddle shape.[4] Bis(1,3-dithiole) substituents are especially interesting in this context[5−24] as they enhance the folding and impart strong π-electron donor properties to the system, e.g., compounds **1**[13] and **2**[24] which display a single, two-electron, quasireversible redox wave to yield a thermodynamically stable dication at E^{ox} = ca. +0.40 V (vs Ag/AgCl) in the cyclic voltammogram (CV).

We have recently synthesized the first cyclophane structures **3** and **4** which incorporate this framework using a 2-fold Horner−Wadsworth Emmons olefination reaction of anthraquinone and the corresponding bis(1,3-dithiole-2-phosphonate) reagents.[25] The oxidation poten-

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Chart 1

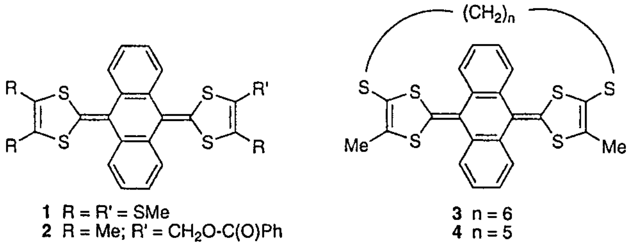
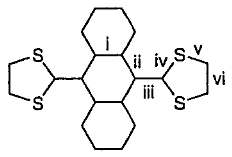


Chart 2

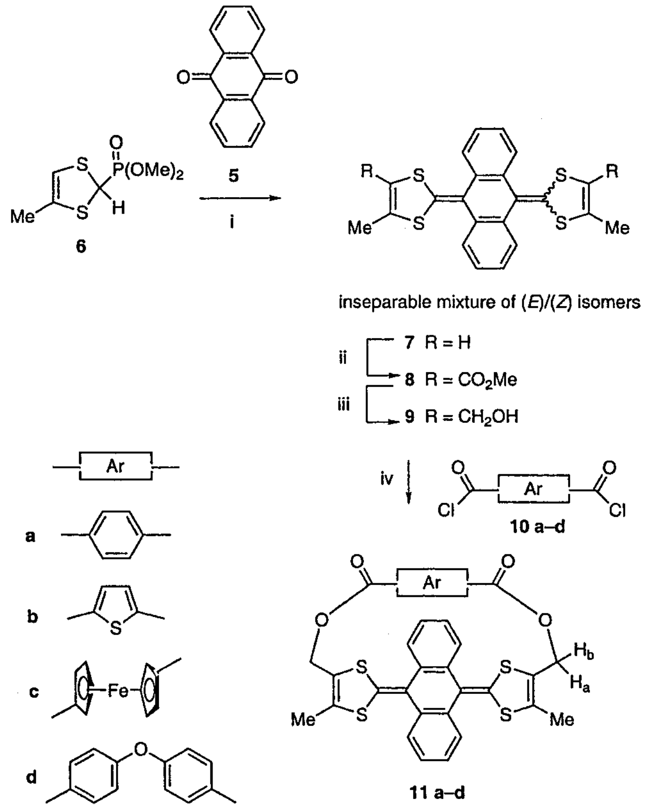


tials of **3** and **4** are raised by ca. 300 mV compared with nonbridged analogues, and in acetonitrile the redox waves are irreversible.[26] We now present a conceptually different and considerably more versatile approach to this class of cyclophanes by bridging the preformed 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system **9** in ester-forming macrocyclization reactions to yield **11a**–**d**. This strategy utilizes the fact that the precursor compound **9** is already in a saddle conformation favorable for intramolecular bridging.[27]

Results and Discussion

Synthesis. Compound **7** was synthesized (73% yield, as a 50:50 mixture of *E*/*Z* isomers) by 2-fold reaction of anthraquinone **5** with the anion of 4-methyl-1,3-dithiole-2-phosphonate **6**.[21] Deprotonation of **7** using lithium diisopropylamide (LDA) and trapping of the dianion with methylchloroformate afforded diester derivative **8** (*E*/*Z*) (61%) which was reduced with lithium aluminum hydride to give the dialcohol **9** (*E*/*Z*) (82%). Reaction of **9** (*E*/*Z*) with the dicarbonyl chloride derivatives of benzene, thiophene, ferrocene, and diphenyl ether, **10a**–**d**, in the presence of triethylamine under high dilution conditions, afforded products **11a**–**d**, respectively, arising from bridging of the *Z* isomer of **9** (Scheme 1). For these cyclization reactions, higher yields were obtained for the less strained derivatives **11c** and **11d** (14 and 15%, respectively) compared to the more strained analogues **11a** and **11b** (11 and 8%, respectively). In all cases, intractable material (presumably oligomers) was also obtained. On no occasion was the corresponding "trans-bridged" cyclophane observed. Initial evidence to support the cyclophane structures **11a**–**d** came from ^{1}H NMR studies. In particular, the large difference in chemical shift between the two diastereotopic protons H_a and H_b was indicative of conformational rigidity (δ 5.70 (2H) and 4.43 (2H) for compound **11a**; cf. 4.38 (4H) ppm for the precursor **9** in $CDCl_3$). NOESY spectra identified H_a as being closer to the methyl group.

Scheme 1



[a] (i) **6**, LDA, THF, −78 °C, then **5**, −78 °C to 20 °C; (ii) LDA, THF, ClC(O)OMe, −78 °C to 20 °C; (iii) $LiAlH_4$, THF, 20 °C; (iv) **10a**–**d**, Et_3N, CH_2Cl_2, 20 °C.

Addition of a few drops of iodine/CD_3CN solution to the NMR solution of **11a** in CD_3CN resulted in a clean change in the spectrum consistent with complete conversion to the dication salt **11a**$^{2+}(I_3^-)_2$. New peaks were observed at δ 5.86 (4H) and 2.93 (6H, Me), replacing those at 4.70 (2H, H_a), 5.64 (2H, H_b), and 2.07 (6H, Me) for **11a** in CD_3CN. (The sharp signals established that the radical cation species was not present.)

The dication salt **11d**$^{2+}(I_3^-)_2\cdot(CH_2Cl_2)_{2.25}$ was isolated by recrystallization of **11d** from dichloromethane under iodine vapor.

Solution Electrochemistry. Solution electrochemical data, obtained by cyclic voltammetry (CV) are collated in Table 1. Comparing the nonbridged systems **7**–**9**, a notable feature is that the electron-withdrawing ester substituents of compound **8** result in a significant (250 mV) positive shift of the quasireversible two-electron redox wave (neutral → dication species), which is consistent with mesomeric conjugation, as observed previously in ester[28] and thioamide[29] derivatives of tetrathiafulvalene (TTF). A comparison of the cyclophanes **11a**–**d**, with the model nonbridged compound **2**,[24] reveals some very interesting trends. The CVs of **2**, **11a**, and **11d** are shown in Figure 1. The oxidation potential (E^{ox}_{pa}) is raised significantly (by ca. 300 mV) for **11a**–**c** but only

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Table 1. Cyclic Voltammetric Data[a]

compound	E^{ox}_{pa}/V	E^{ox}_{pc}/V	$\Delta E/V^b$
1	0.45 (2e)	0.16	0.29
2	0.41 (2e)	0.12	0.29
3	0.66 (irreversible); 0.85 (2e)[c]	0.71	0.14
4	0.70 (irreversible); 0.84 (2e)[c]	0.75	0.09
7	0.36 (2e)	0.13	0.23
8	0.61 (2e)	0.26	0.35
9	0.36 (2e)	0.08	0.28
11a	0.70 (2e)	0.63	0.07
11b	0.70 (2e)	0.66	0.04
11c	0.72 (2e); 1.08 (1e)	0.60; 0.96	0.12; 0.12
11d	0.47 (2e)	0.28	0.19

[a] Compound ca. 2 × 10^{-3} M, vs Ag/AgCl, electrolyte $Bu_4N^+PF_6^-$, acetonitrile, 20 °C, scan rate 100 mV s^{-1}. Data obtained on a BAS CV50W voltammetric analyzer with *iR* compensation. [b] $\Delta E = E^{ox}_{pa} - E^{ox}_{pc}$ (E^{ox}_{pa} is the oxidation peak potential on the first anodic scan; E^{ox}_{pc} is the coupled reduction peak potential on the cathodic scan). [c] Data obtained in dichloromethane.

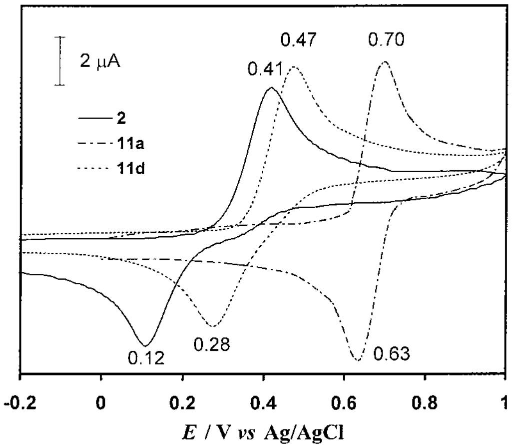

Figure 1. Cyclic voltammograms of **2**, **11a**, and **11d** (under the conditions stated in Table 1).

slightly (by 60 mV) for **11d**. This is consistent with the shorter bridges of **11a**−**c** hindering the marked conformational change which accompanies oxidation to the dication (see the crystal structure of **11d**$^{2+}$, below). Another striking feature of these data is a sequential reduction in the value of Δ*E* (i.e., increased reversibility of the oxidation process) as the bridge is progressively shortened with Δ*E* reduced to only 70 and 40 mV for compounds **11a** and **11b**, respectively, compared to the typical values in the range 230−350 mV for nonbridged derivatives (Table 1). This reflects the reduced stability of the twisted dication structure within the steric constraints of the smaller cyclophanes. The oxidation potentials of compounds **3** (E^{ox}_{pa} 0.69 V) and **4** (0.74 V in MeCN, $Bu_4N^+ClO_4^-$), reported previously,[25] were also raised significantly by the conformational rigidity imposed by the bridge, but for **3** and **4** under these conditions the CV wave was irreversible, with electrochemical and chemical oxidation leading to decomposition of the compounds. However, we have now found a marked solvent effect on this redox chemistry: in CH_2Cl_2, $Bu_4N^+PF_6^-$ the waves are quasireversible, and the oxidation potentials are further raised to E^{ox}_{pa} 0.85 and 0.84 V for **3** and **4**, respectively. The CV of compound **11c** reveals an additional, quasireversible, one-electron oxidation wave at E^{ox}_{pa} 1.08 V, corresponding to the ferrocene/ferrocenium redox couple, i.e., formation of the **11c**$^{3+}$ species. The smaller current associated with this second wave is also consistent with the primary oxidation wave of these cyclophanes being a two-electron process, which has been firmly established for nonbridged systems.[7,15,22] The positive shift for the ferrocene oxidation wave in **11c**, compared to standard diester derivatives of ferrocene (e.g., $Fc(CO_2C_{17}H_{35})_2$ $E^{1/2}$ 0.972 V vs Ag/AgCl in CH_2Cl_2),[30] is explained by intramolecular Coulombic repulsion between the ferrocenium and dithiolium cations, together with steric constraints of the bridge.

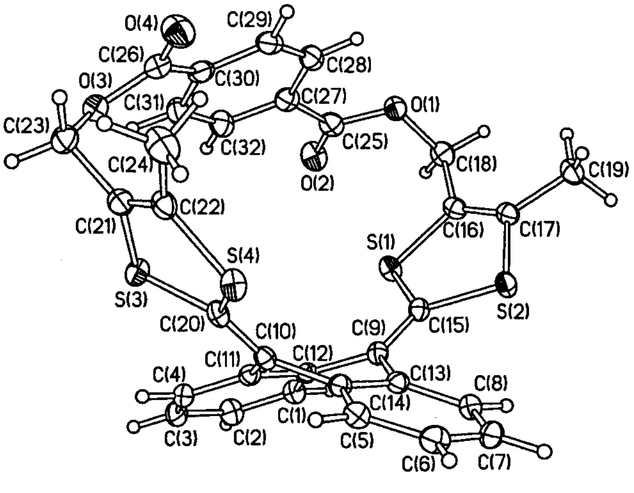

Figure 2. Molecular structure of **11a**. Henceforth thermal ellipsoids are drawn at the 50% probability level.

Crystal Structures. The asymmetric unit of **11a** comprises two molecules of slightly different conformations, forming pseudodimers wherein a methyl group of each molecule is inserted into the intramolecular cavity of another. In both molecules the bridging benzene ring suffers a boatlike distortion: the C(28)C(29)C(31)C(32) plane forms dihedral angles of ca. 3° with the C(27)C(28)C(32) and C(29)C(30)C(31) planes, while the C(25)−C(27) and C(26)−C(30) bonds are further tilted out of the latter planes by ca. 7.5° (Figure 2). This distortion clearly indicates the steric strain which, however, is not relieved in the most obvious way: by rotation around the C(25)−C(27) and C(26)−C(30) bonds. The carboxy groups remain conjugated with the benzene ring in what would be, but for the bending, a perfectly in-plane conformation with the C═O bonds of the carboxy groups in trans orientations.

Compound **11b** crystallizes as a 1:1 solvate with CH_2Cl_2; the solvent molecule is disordered equally between two positions. The bridging thiophene ring is planar (Figure 3); the carboxy groups bonded to C(27) and C(30) are inclined to its plane by 6° and 8°, respectively. The O(1) and O(3) atoms adopt syn orientations with respect to each other and to S(5), resulting in intramolecular noncovalent distances of S(5)···O(1) = 2.774(7) Å and S(5)···O(3) = 2.753(7) Å.

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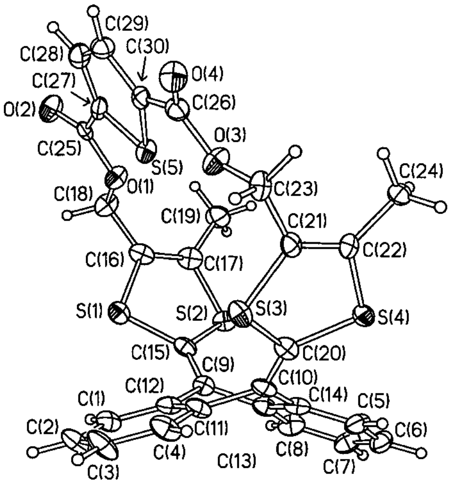

Figure 3. Molecular structure of **11b**.

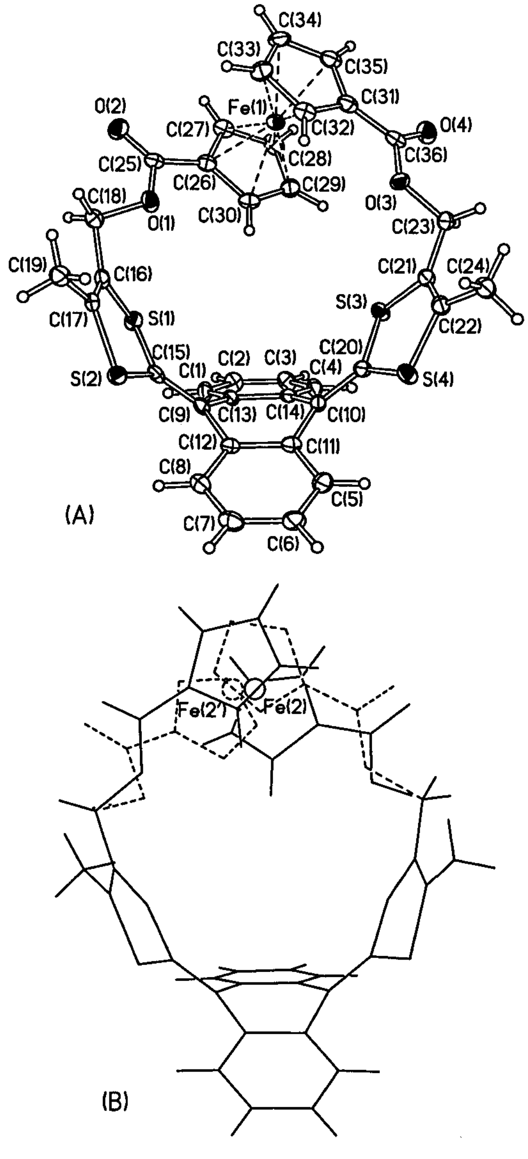

Figure 4. Molecules A and B (showing the disorder) in the structure of **11c**.

The asymmetric unit of **11c** comprises two molecules, A and B (Figure 4). Molecule A shows no disorder, while in B the entire $Fe(C_5H_5CO_2)_2$ moiety is disordered (in a 86.1(2) to 13.9(2)% ratio) between two conformations, related by turning the ferrocene moiety upside-down and a concerted rotation around both C(Cp)−C(carboxyl) bonds, so that the C═O bonds remain pointing in the same direction. Thus, the two conformations are (roughly) mirror images of each other, and either can be identified with the conformation of molecule A or its inversion equivalent (the crystal being centrosymmetric). In all cases, the carboxy groups are coplanar with the cyclopentadienyl rings within ≤7°.

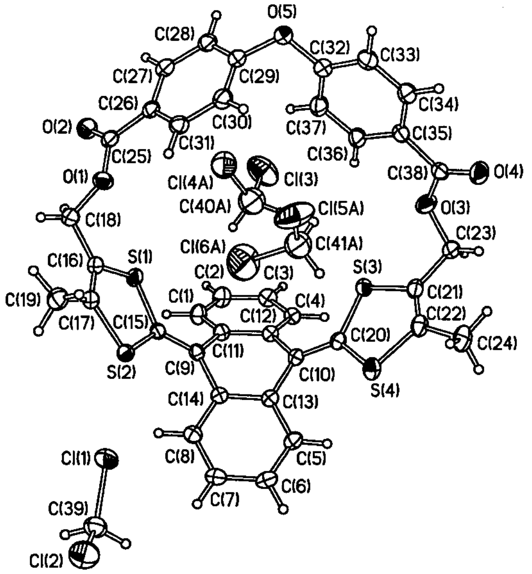

Figure 5. Molecular structure of **11d**·$3CH_2Cl_2$, showing the ordered solvent molecule.

Table 2. Dihedral Angles and Intramolecular Distances

	11a		**11b**	**11c**		**11d**	**11d**$(I_3)_2$
φ [deg][a]	39.2	35.3	39.4	33.8	36.2	37.5	6
δ_1 [deg]	15.6	16.0	23.8	23.0	23.9	11.3	0
δ_2 [deg]	15.0	16.1	19.4	12.3	17.4	3.1	0
θ [deg]	71.4	67.0	46.7	58.9	44.3	95.0	163
d_1 [Å]	7.13	7.11	5.41	6.03	5.67 (5.49[b])	8.98	9.55
d_2 [Å]	9.34	9.32	8.01	8.40	7.91	10.60	11.35

[a] φ is the folding along the C(9)···C(10) vector; $\delta_1$is the folding along the S(1)···S(2) vector; $\delta_2$is the folding along the S(3)···S(4) vector; θ is the dihedral angle between the S(1)C(16)C(17)S(2) and S(3)C(21)C(22)S(4) planes; $d_1$is the intramolecular O(1)···O(3) distance; $d_2$is the intramolecular C(18)···C(23) distance. [b] Minor disordered position.

The asymmetric unit of **11d** (Figure 5) comprises one title molecule and three CH_2Cl_2 molecules. Two of the latter lie inside the molecular cavity of **11d** and are intensely disordered, the third one is situated in an *inter*molecular space and is ordered. The two bridging benzene rings in **11d** form a dihedral angle of 73°, while the carboxy substituents at each ring deviate slightly (by 8° and 5°) from the ring plane, by an out-of-plane tilting of the C(benzene)−C(carboxy) bond, rather than by a twist around this bond.

The molecular conformations of **11a**−**d** are similar to the previously reported analogues, both with[25] and without[6,13,21,22] bridges. The anthracenediylidene moiety is folded along the C(9)···C(10) vector by an angle φ (see Table 2). The bis(dithiolene)quinone system is U-shaped, through folding of both dithiole rings along the S(1)··· S(2) and S(3)···S(4) vectors (folding angles δ_1 and δ_2 respectively, Table 2), the boat conformation of the central quinonoid ring, and pyramidalization of the key

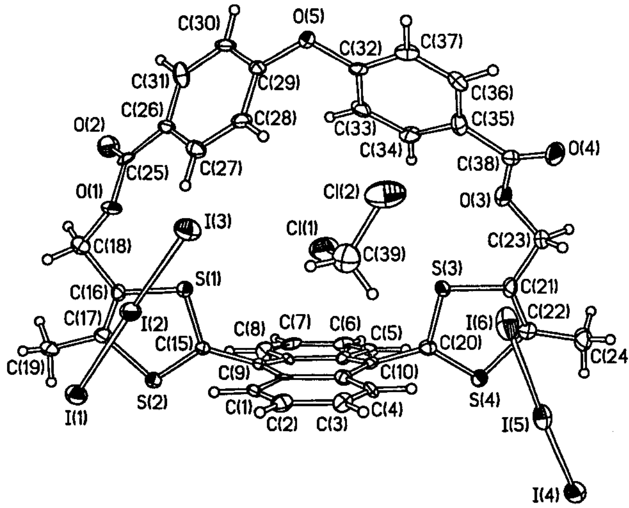

Figure 6. Molecular structure of $\mathbf{11d}^{2+}(I_3^-)_2\cdot(CH_2Cl_2)_{2.25}$, showing the major positions of the disordered solvent molecules.

C(sp^2) atoms. A measure of the overall bending is given by the dihedral angle θ between the S(1)C(16)C(17)S(2) and S(3)C(21)C(22)S(4) planes, which shows a direct linear correlation with the length of the bridge, as defined by the intramolecular distances O(1)···O(3) (d_1) and C(18)···C(23) (d_2). The structures of **3** (in two polymorph modifications) and **4** follow the same trend, having $\theta =$ 54.5° (β-**3**), 46.4° (α-**3**), and 34.7° (**4**) with the bridge lengths (the S···S distance) of 9.08, 8.59, and 8.09 Å, respectively.[25] However, the bridges in all the compounds are flexible, so the actual molecular conformation is a compromise between steric demands of the bridge and the saddle moiety, strongly influenced by the crystal packing. The flexibility is manifest in the crystal structures: **11a** has two independent molecules with the same bridge length but the θ and φ angles differing by ca. 4°; **11c** also has two independent molecules (one of them with the disordered bridge) with the actual bridge length differing by 0.5 Å and the θ angle by ca. 15°; **3** formed two polymorphs in the same crystallization, one of which (monoclinic α) with the bridge disordered and the other (orthorhombic β) with two independent molecules in the asymmetric unit. The average bridge length in β-**3** is 0.5 Å longer and the θ angle is 8° wider than in α-**3**. Nonbridged saddle molecules display a θ of 73−101°, hence only the bridges with $d_2 < 9.5$ Å can be said to actually increase the U-bend. These facts help to explain why the bridge does not prevent the saddle molecule **11d** from undergoing a drastic structural rearrangement on oxidation: d_2 of neutral **11d** is at least 1 Å longer than the threshold and is extended by 0.75 Å in the $\mathbf{11d}^{2+}$ dication—a variation of the same order as between independent molecules in **11d** or between modifications of **3**. It is also noteworthy that the anthraquinone system folding (φ) is not affected by the bridges in any systematic way. The dithiole ring folding (δ) generally increases with the shortening of the bridge, but the correlation is poor, as other degrees of conformational freedom also contribute to the accumulated U-bend.

The asymmetric unit of the triiodide salt of **11d** comprises one $\mathbf{11d}^{2+}$ dication, two I_3^- anions, and CH_2Cl_2 of crystallization (Figure 6). One independent CH_2Cl_2 molecule fits into the intramolecular cavity and is ordered, one occupies an intermolecular cavity and displays a chaotic disorder (approximated by three orientations), and another is disordered around an inversion center and has a nonstoichiometric occupancy (estimated as 0.25 per asymmetric unit). The $\mathbf{11d}^{2+}$ dication shows a drastic change of conformation and bond lengths compared to the neutral molecule, similar to those observed for nonbridged systems.[6,9,22] Both dithiolium rings are planar with the bonding pattern indicative of a +1 charge on each, while the anthracene system is essentially aromatic. However, the bridge imposes significant distortions. Thus, all three nonbridged dications studied[6,9,22] have (crystallographic) C_i symmetry, with rigorously planar anthracene moieties and the dithiolium rings coplanar to each other and nearly perpendicular to the latter. In $\mathbf{11d}^{2+}$ the anthracene unit has a similar, but much smaller, folding than the anthracenediylidene in the neutral molecules. Its central ring thus adopts a boat conformation, the C(9)C(12)C(13) and C(10)C(11)C(14) planes form a dihedral angle of 162°, and the C(9)−C(15) and C(10)−C(20) bonds are tilted further out of these planes by 8° and 6° and form an angle of 149° between them. Both dithiolium rings deviate by ca. 20° from the normality to the anthracene system and form a dihedral angle of 163° between them. The conformation of the bridge is basically the same as in the neutral **11d**; the benzene rings form a dihedral angle of 74°, the carboxy groups are tilted out of the ring planes slightly more than in **11d** (by 12 and 8°), and the overall length of the bridge increases by 6% or 7%.

The linear triiodide anions in $\mathbf{11d}(I_3)_2$ are entirely surrounded by cations and solvent molecules and form no noncovalent I···I contacts. Most I···S and I···C distances correspond to normal van der Waals interactions. The contacts of the terminal I(1) atom with C(16) and C(17) (3.62 and 3.53 Å) are significantly shorter than the standard van der Waals distance (3.82 Å)[31] and may indicate a specific interaction. Note that the I(1)−I(2) bond of 2.952(1) Å is considerably longer than the I(2)−I(3) bond, 2.912(1) Å, while in the other anion, which forms its only shortened contact, I(5)···S(4) = 3.64 Å (cf. the standard 3.97 Å), by its central iodine atom, the I(4)−I(5) and I(5)−I(6) bond lengths are equal (2.924(1) and 2.923(1) Å).

Conclusions

New chemistry of the saddle-shaped 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system comprising macrocyclization reactions of the versatile building block **9** to yield a new series of cyclophane derivatives **11a**−**d** has been developed. The solution electrochemical properties and the molecular conformations, determined by X-ray crystal analyses, have been correlated with the steric constraints of the bridging unit. The first salt of a cyclophane of this family has been structurally characterized. Further studies aimed at tuning the redox and structural properties of the title system by different modes of intramolecular bridging and molecular recognition studies within related cyclophane cavities are in progress.

Experimental Section

General Procedures. All solvents were dried and distilled before use. All reactions were performed under an atmosphere of dry nitrogen.

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Table 3. Average Bond Distances (See Chart 2)

bond	11a	11b	11c	11d	[11d]$^{2+}$
i	1.417(3)	1.405(8)	1.413(5)	1.420(3)	1.44(1)
ii	1.481(3)	1.487(8)	1.481(5)	1.482(3)	1.41(1)
iii	1.362(3)	1.343(8)	1.360(5)	1.366(3)	1.48(1)
iv	1.766(2)	1.769(6)	1.767(4)	1.768(2)	1.683(8)
v	1.766(2)	1.765(6)	1.768(4)	1.760(2)	1.728(8)
vi	1.338(3)	1.347(8)	1.334(6)	1.338(3)	1.34(1)

***(E,Z)*-9,10-Bis(4-methyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (7).** Compound **6**[21] (5.11 g, 22.3 mmol) was dissolved in tetrahydrofuran (100 mL) at −78 °C and a solution of LDA (1.5 M, 16.4 mL, 24.6 mmol) was added dropwise. The mixture was stirred at −78 °C for 1 h, then anthraquinone **5** (2.32 g, 11.0 mmol) was added, and the mixture was left to warm to 20 °C overnight. After evaporation of the solvent in vacuo, the residue was chromatographed on a silica column (eluent: dichloromethane/hexanes (1:1 v/v)) to afford **7** (3.34 g, 73%) as a yellow solid, mp 239−240 °C. ^{1}H NMR ($CDCl_3$): δ 7.70−7.64 (4H, m), 7.30−7.23 (4H, m), 5.82 (2H, dd, $J = 1.3$ Hz), 2.05 (6H, dd, $J = 1.3$ Hz). UV−vis (CH_2Cl_2): λ_{max} (lg ϵ) 432 (4.29), 368 (4.05) nm. MS (EI) m/z (%) 408 (100, M^+). Anal. Calcd for $C_{22}H_{16}S_4$: C, 64.66; H, 3.95. Found: C, 64.83; H, 4.02.

***(E,Z)*-9,10-Bis(4-methoxycarbonyl-5-methyl)-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (8).** To a stirred solution of **7** (3.0 g, 7.35 mmol) in tetrahydrofuran (250 mL) was added dropwise a solution of LDA (1.5 M, 10.8 mL, 16.2 mmol). The mixture was stirred at −78 °C for 2 h, and then methylchloroformate (3.42 mL, 440 mmol) was added. The mixture was left to warm to 20 °C overnight. After evaporation of the solvent in vacuo, the residue was chromatographed on a silica column (eluent: dichloromethane/hexanes (1:3, then 1:1 v/v)) to afford **8** (2.36 g, 61%) as a yellow solid, mp 152−154 °C. ^{1}H NMR ($CDCl_3$): δ 7.63−7.55 (4H, m), 7.33−7.25 (4H, m), 3.77 (6H, s), 2.38 (6H, s). IR (KBr): ν 1716, 1696 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (lg ϵ) 420 (4.26), 356 (4.04) nm. MS (EI) m/z (%) 524 (100, M^+). Anal. Calcd for $C_{26}H_{20}O_4S_4$: C, 59.52; H, 3.84. Found: C, 59.14; H, 3.87.

***(E,Z)*-9,10-Bis(4-hydroxymethyl-5-methyl)-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (9).** To a stirred solution of **8** (2.0 g, 3.8 mmol) in tetrahydrofuran (100 mL) at 0 °C was added lithium aluminum hydride (1.15 g, 30.4 mmol), and the mixture was stirred for 1 h at 0 °C and then for 2 h at 20 °C. After adding wet sodium sulfate (excess), the mixture was stirred for 1 h, and the color changed from green to orange. The mixture was filtered through Celite; the filtrate was evaporated, and the residue was chromatographed on silica (eluent ethyl acetate) to afford **9** (1.45 g, 82%) as a yellow solid, mp > 250 °C. ^{1}H NMR ($CDCl_3$): δ 7.64−7.57 (4H, m), 7.31−7.28 (4H, m), 4.38 (4H, s), 2.00 (6H, s). IR (KBr): ν 3407 (broad) cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (lg ϵ) 432 (4.31), 368 (4.09) nm. MS (EI) m/z (%) 468 (100, M^+). Anal. Calcd for $C_{24}H_{20}O_2S_4$: C, 61.50; H, 4.30 Found: C, 61.82; H, 4.60.

Compounds 11a−d. General Procedure. To a solution of **9** (300 mg, 0.64 mmol) in dichloromethane (300 mL) was added the appropriate diacid chloride, **10a**, **10b**, **10c,**[32] or **10d,**[33] (0.64 mmol) and triethylamine (0.36 mL, 2.56 mmol), and the mixture was stirred at 20 °C for 2 h. After evaporation in vacuo, the residue was chromatographed on silica with dichloromethane as eluent. The product was recrystallized from dichloromethane/hexanes.

There was obtained **11a** (42 mg, 11%) as yellow crystals, mp >250 °C (dec). ^{1}H NMR ($CDCl_3$): δ 7.88 (4H, s), 7.60−7.59 (2H, m), 7.39−7.36 (2H, m), 7.34−7.32 (2H, m), 7.26−7.20 (2H, s), 5.70 (2H, d, $J = 12.6$ Hz, H_a), 4.43 (2H, $J = 12.8$ Hz, H_b), 2.05 (6H, s). (CD_3CN): δ 7.86 (4H, s), 7.56−7.54 (2H, m), 7.43−7.33 (6H, m), 5.64 (2H, d, $J = 12.8$ Hz, H_a), 4.70 (2H, d, $J = 13.0$ Hz, H_b), 2.07 (6H, s). IR (KBr): ν 1725 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (lg ϵ) 420 (4.41), 356 (4.17) nm. MS (EI) m/z (%) 598 (100, M^+). Anal. Calcd for $C_{32}H_{22}O_4S_4$: C, 64.19; H, 3.70 Found: C, 63.90; H, 3.94.

11a^{2+}. ^{1}H NMR ($CD_3CN + I_2$): δ 8.02−7.98 (4H, m), 7.84 (4H, s), 7.77−7.72 (4H, m), 5.86 (4H, s), 2.93 (6H, s).

11b. Obtained (32 mg, 8%) as yellow crystals, mp ca. 200 °C (dec). ^{1}H NMR ($CDCl_3$): δ 7.65 (2H, s), 7.53−7.49 (2H, m), 7.37−7.28 (6H, m), 5.12 (2H, d, $J = 12.4$ Hz, H_a), 4.61 (2H, $J = 12.6$ Hz, H_b), 2.06 (6H, s). IR (KBr): ν 1719 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (lg ϵ) 420 (4.41), 356 (4.17) nm. MS (EI) m/z (%) 604 (100, M^+). HRMS Calcd for $C_{30}H_{20}O_4S_5$ 604.00497. Found: 604.00487.

11c. Obtained (62 mg, 14%) as yellow crystals, mp ca. 230 °C (dec). ^{1}H NMR ($CDCl_3$): δ 7.50−7.48 (2H, s), 7.39−7.37 (4H, m), 7.29−7.27 (2H, m), 4.87 (2H, d, $J = 12.6$ Hz, H_a), 4.74−4.72 (2H, m), 4.71 (2H, d, $J = 12.4$ Hz, H_b), 4.60−4.58 (2H, m), 4.34−4.28 (4H, m), 2.07 (6H, s). IR (KBr): ν 1713 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (lg ϵ) 420 (4.28), 356 (4.13) nm. MS (EI) m/z (%) 706 (21, M^+), 274 (100). HRMS Calcd for $C_{36}H_{26}FeO_4S_4$ 706.01305. Found: 706.01316.

11d. Obtained (66 mg, 15%) as yellow crystals, mp 194−196 °C. ^{1}H NMR ($CDCl_3$): δ 7.90 (4H, d, $J = 9$ Hz), 7.66−7.62 (4H, m), 7.29−7.26 (4H, m), 6.86 (4H, d, $J = 9$ Hz), 5.37 (2H, d, $J = 12.8$ Hz), 4.65 (2H, d, $J = 12.6$ Hz), 2.12 (6H, s). IR (KBr): ν 1720 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (lg ϵ) 440 (4.38), 368 (4.10) nm. HRMS Calcd for $C_{38}H_{26}O_5S_4$ 690.07307. Found: 690.07300.

Table 4. Crystal Data and Experimental Details

compound	**11a**	**11b**	**11c**	**11d**	[**11d**]$(I_3)_2$
formula	$C_{32}H_{22}O_4S_4$	$C_{30}H_{20}O_4S_5 \cdot CH_2Cl_2$	$C_{36}H_{26}FeO_4S_4$	$C_{38}H_{26}O_5S_4 \cdot 3CH_2Cl_2$	$C_{38}H_{26}O_5S_4{}^{2+}\,(I_3{}^-)_2 \cdot 2.25CH_2Cl_2$
mol. mass	598.74	689.69	706.66	945.61	1643.31
T [K]	100	123	123	120	120
crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$ (# 14)	$P2_1/c$ (# 14)	$P2_1/n$ (# 14)	$P\bar{1}$ (# 2)	$P2_1/c$ (# 14)
a [Å]	19.957(4)	11.407(5)	14.739(3)	11.535(3)	15.486(5)
b [Å]	18.278(4)	17.160(8)	16.152(3)	13.215(3)	23.259(7)
c [Å]	16.306(3)	15.607(7)	26.187(9)	14.744(3)	15.957(5)
α [deg]	90	90	90	72.46(1)	90
β [deg]	111.15(1)	99.83(2)	94.94(1)	79.85(1)	117.35(1)
γ [deg]	90	90	90	89.50(1)	90
V [Å$^{3]}$	5547(2)	3010(2)	6211(4)	2107.1(8)	5105(3)
Z	8	4	8	2	4
μ [mm^{-1}]	0.38	0.60	0.80	0.65	4.09
no. of refl total	67857	18028	36823	25443	40267
$2\theta_{max}$ [deg]	58	50	50	58	55
no. of unique refl	14676	5302	10934	10988	11710
Transmission	0.719−0.962	0.762−0.988	0.871−0.959	0.715−0.802	0.285−0.959
$R_{int.}$	0.068	0.151	0.063	0.018	0.113
no of refl $I > 2\sigma(I)$	9818	2901	8145	9748	7844
no. of variables	729	398	846	536	555
$R[F^2 > 2\sigma(F^2)]$	0.045	0.072	0.049	0.051	0.066
$wR(F^2)$, all data	0.110	0.152	0.105	0.134	0.110
$\Delta\rho_{max,min}$ [eÅ^{-3}]	0.48, −0.39	0.62, −0.44	0.54, −0.63	1.48, −0.96	1.42, −1.13

$11d^{2+}(I_3^-)_2\cdot(CH_2Cl_2)_{2.25}$. The salt was obtained as red crystals by storing a solution of **11d** (5 mg) in dichloromethane (3 mL) under iodine vapor in a stoppered vial (20 cm^3) at 20 °C.

Crystal Structure Analyses. X-ray diffraction experiments were carried out on a SMART three-circle diffractometer with a 1K CCD area detector, using graphite-monochromated Mo-K_α radiation ($\bar{\lambda} = 0.71073$ Å) and a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. A hemisphere (**11a**−**c**) or full sphere (**11d** and **11d**$(I_3)_2$) of reciprocal space was covered by a combination of 4 or 5 sets of ω scans, each set at different φ and/or 2θ angles. Reflection intensities were integrated using the SAINT program[34] and corrected for absorption by the numerical integration method based on crystal face indexing for **11c** and **11d**$(I_3)_2$ or by semiempirical method based on the intensities of Laue equivalents (using SADABS software[35]) for **11a**, **11b**, and **11d**. The structures were solved by direct methods and refined by full-matrix least squares against the F^2 of all data, using the SHELXTL software.[36] Crystal data and experimental details are summarized in Table 4; atomic coordinates, thermal parameters, and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.[37]

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Supporting Information Available: Copies of ^1H NMR spectra of **11b**, **11c**, and **11d**; ORTEP diagrams of compound **11a** (molecule A and B, 50% thermal ellipsoids), solvent disorder in **11b**, and compound **11c** (molecule B, major and minor ferrocene position, 50% thermal ellipsoids); full crystallographic data for **11a**−**d** and **11d**$^{2+}(I_3^-)_2\cdot(CH_2Cl_2)_{2.5}$; and a copy of the cyclic voltammogram of **11c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) Supplementary publications nos. CCDC-145254 to 145257 for **11a**−**d** and **11d**$^{2+}(I_3^-)_2\cdot(CH_2Cl_2)_{2.25}$, respectively, can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.