The first bridged 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives: strained redox-active cyclophanes

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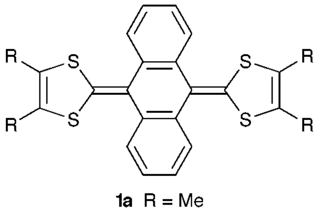
The reaction of anthraquinone and the dianion of bis(1,3-dithiolyl)diphosphonate reagents 2 and 3 afford the cyclophane derivatives 4 and 5, the cyclic voltammetry and X-ray crystal structures of which are reported.

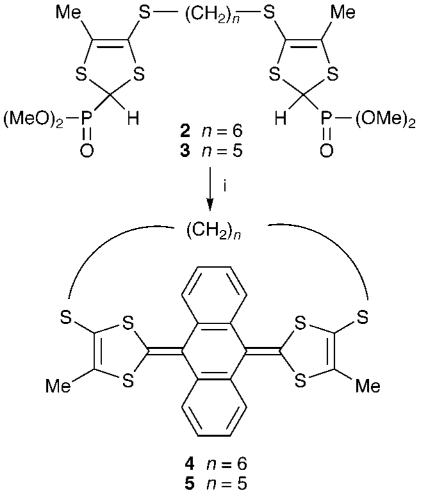
There is considerable current interest in polycyclic ring systems which fold to form concave clefts[1] or saddle-like surfaces.[2] In this context the 9,10-bis(methylene)-9,10-dihydroanthracene building block has received limited attention, although crystallographic and theoretical studies have shown that bulky substituents attached to the methylene sites enforce a folding of the central anthracenediylidene ring into a boat conformation, and, hence, the molecule adopts a saddle shape.[3] Bis(1,3-dithiole) substituents placed at these methylene sites, *e.g.* compound **1**,[3b] provide especially interesting electron donors with extended π-conjugation;[4] they are characterised by a single, two-electron redox wave to yield a thermodynamically stable dication at E^{ox} *ca.* +0.40 V (*vs.* Ag/AgCl) in the cyclic voltammogram (CV).[3a–c,4b,5] Methyl substituents slightly lower the oxidation potential relative to methylsufanyl substituents (*cf.* compounds **1a** and **1b**).



1a R = Me
b R = SMe

We have now incorporated this structural moiety into cyclophane structures,[6] and herein we report the synthesis and characterisation of the first bridged 9,10-bis(methylene)-9,10-dihydroanthracene derivatives, *viz.* compounds **4** and **5**. The synthesis of **4** and **5** was achieved by a two-fold olefination reaction, under high dilution conditions, of anthraquinone using reagents **2** and **3** (Scheme 1),[7] which were deprotonated by LDA at −78 °C, following literature precedents for other 1,3-dithiole phosphonate ester reagents.[8] Compounds **4** and **5**† were isolated as single isomers, and the *cis* configuration was confirmed by X-ray structure analysis.‡

Compound **4** gave a mixture of amber block- and needle-like crystals, which were characterised as monoclinic (α) and orthorhombic (β) polymorphs, respectively, of *cis*-**4**. Two symmetrically independent molecules in the β-**4** structure adopt very similar conformations (Fig. 1), while that of α-**4** is significantly different. In each case, the conformation of the hexamethylene bridge is rather strained and asymmetric: torsion angles around the C–C bonds range from 144 to 180° in β-**4** and from 58 to 176° in α-**4**, where two methylene groups are disordered. The bridge aggravates the U-bend of the bis(dithiolylidene)benzoquinone system: the dihedral angle between the outer S(1)C(16)C(17)S(2) and S(3)C(19)C(20)S(4) moieties is reduced from 77° in non-bridged molecule **1**[3b] to 54° in β-**4** and to only 46° in α-**4**, mostly through increased folding of both dithiole rings along the S(1)···S(2) and S(3)···S(4) vectors (24 and 13° respectively in α-**4**, 24 and 20° in β-**4**, *vs.* 17 and 8° in **1b**). On the other hand, folding of the anthracene system along the C(9)···C(10) vector in**4** (37–40°) remains the same as in **1b** (38°).



Scheme 1 *Reagents and conditions*: i, LDA (2.2 equiv.), anthraquinone, THF, −78 °C, 30 min, then raise to 20 °C.

The structure of **5** contains two independent molecules, one of which shows disorder that can be rationalised as either a varying degree of molecular bending or a rocking of the molecule as a whole. In the other (ordered) molecule (Fig. 2) the pentamethylene bridge adopts a nearly all-*trans* conformation (C–C–C–C torsion angles 164–177°) and enhances the folding of the anthracene moiety (by 43.4°) and both dithiole rings (by 29.4 and 22.6°), thus narrowing the dihedral angle between the S(1)C(16)C(17)S(2) and S(3)C(19)C(20)S(4) planes to 34.7°. The cavity is essentially empty in the solid state structures of both **4** and **5**.

The solution electrochemistry of compounds **4** and **5** was studied by cyclic voltammetry and differential pulse voltammetry. Both compounds display an irreversible two-electron oxidation wave at E^{ox} +0.69 V (compound **4**) and +0.74 V (compound **5**) [*vs.* Ag/AgCl, electrolyte $Bu_4N^+ClO_4^-$ (0.1 M),

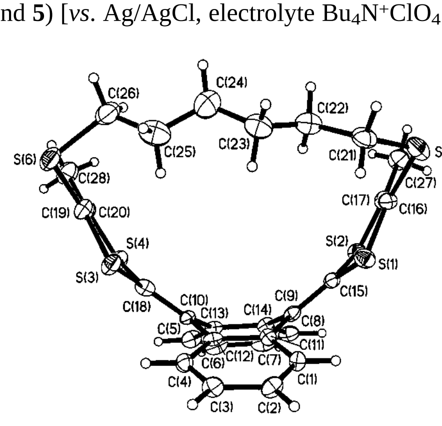


Fig. 1 Molecular structure of **4** in the β-polymorph (30% displacement ellipsoids).

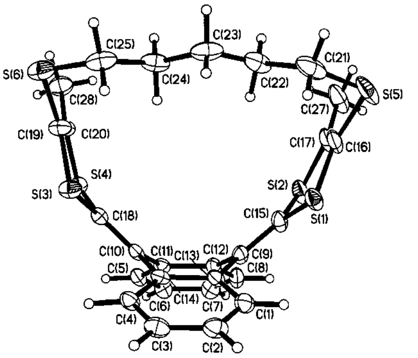


Fig. 2 Molecular structure of **5** (50% displacement ellipsoids).

MeCN, room temperature, scan rate 100 mV s^{-1}], *i.e.* the oxidation wave of the bridged systems **4** and **5** shows a significant positive shift (ΔE^{ox} *ca.* 300 mV) compared to the non-bridged analogues, *e.g.* **1**,[3b] recorded under the same conditions. This is explained by the rigidity of **4** and **5** (imparted by the bridge) restricting the conformational change which is known to accompany oxidation of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system.[3a] The slightly higher oxidation potential of **5** compared to **4** (ΔE^{ox} 50 mV) is also consistent with oxidation becoming progressively harder as the strain in the system increases, as observed previously for strained tetrathiafulvalenes.[9] A second oxidation wave is observed at E^{ox} +1.0 V. Simulation of the data suggest an ECE process where dication formation is followed by a chemical reaction to form a new electroactive species, which gives rise to the oxidation wave at more positive potentials. The UV-Vis absorption spectra of **4** and **5** display a significant blue shift in the two longest wavelength bands compared to the non-bridged analogues [λ_{max} (MeCN) **1a**:[3b,8] 235, 369, 433 nm; **4**: 264, 356, 416 nm; **5**: 264, 352, 412 nm]. The further small blue shift (4 nm) for these two bands in compound **5** compared to **4** is again consistent with the more folded structure of **5**.

In summary, double olefination reactions of anthraquinone have afforded novel bridged 9,10-bis(methylene)-9,10-dihydroanthracenes, paving the way for studies on a new family of conformationally strained cyclophanes with interesting redox and structural properties.

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Notes and references

† Both compounds **4** and **5** gave mass spectrometric and elemental analytical data consistent with their structures. *Selected data* for **4**: yellow crystals, 22% yield; mp 286–288 °C (decomp.); $\delta_H(CDCl_3)$ 1.11 (m, 4H), 1.32 (m, 4H), 2.10 (s, 6H), 2.23 (m, 2H), 2.68 (m, 2H), 7.35 (m, 6H), 7.49 (m, 2H). For **5**: yellow crystals, 10% yield; mp 294–296 °C (darkens at 250 °C); $\delta_H(CDCl_3)$ 0.85 (m, 2H), 1.12 (m, 4H) 1.97 (s, 6H), 2.17 (m, 2H), 2.61 (m, 2H), 7.30 (m, 6H), 7.36 (m, 2H).

‡ Crystals of **4** and **5** for X-ray analysis were grown from MeCN–CH_2Cl_2. X-Ray experiments were performed with a SMART CCD area detector (Mo-K_α radiation, λ = 0.71073 Å). Absorption corrections by numerical integration, structure solutions by direct methods and least-squares refinement against F^2 of all data were performed using SHELX-97 programs (G. M. Sheldrick, University of Göttingen, Germany, 1997); CCDC 186/1377. See http://www.rsc.org/suppdata/cc/1999/1835/ for crystallographic data in .cif format.

Crystal data for α-**4**: $C_{28}H_{26}S_6$, M = 554.85, monoclinic, space group $P2_1/c$ (No. 14), T = 295 K, a = 18.139(2), b = 11.041(1), c = 14.406(2) Å, β = 109.05(1)°, U = 2727.1(5) Å^3, Z = 4, D_c = 1.351 g cm^{-3}, μ = 0.52 mm^{-1}, 24278 reflections (6247 unique) with $2\theta \leqslant 55°$, 384 variables, R = 0.035 on 4325 data with $I \geqslant 2\sigma(I)$, $wR(F^2)$ = 0.092, max. residual $\Delta\rho$ = 0.22 e Å^{-3}; C(25) and C(26) are disordered over two positions (A and B) with occupancies 82.3 and 17.7(6)%. For β-**4**: orthorhombic, space group $Pna2_1$ (No. 33), T = 295 K, a = 19.231(2), b = 9.520(1), c = 30.089(3) Å, U = 5509(1) Å^3, Z = 8, D_c = 1.338 g cm^{-3}, μ = 0.51 mm^{-1}, 31379 reflections (9683 unique) with $2\theta \leqslant 50°$, 384 variables, R = 0.049 on 5758 data with $I \geqslant 2\sigma(I)$, $wR(F^2)$ = 0.099, max. residual $\Delta\rho$ = 0.22 e Å^{-3}; absolute polarity determined from anomalous X-ray scattering [Flack parameter –0.15(9)]. For **5**: $C_{27}H_{24}S_6$, M = 540.82, triclinic, space group $P\bar{1}$ (No. 2), T = 120 K, a = 10.944(4), b = 14.591(5), c = 16.924(7) Å, α = 71.18(1), β = 89.65(2), γ = 85.66(1)°, U = 2550(2) Å^3, Z = 4, D_c = 1.409 g cm^{-3}, μ = 0.55 mm^{-1}, 23433 reflections (11538 unique) with $2\theta \leqslant 55°$, 678 variables, R = 0.048 on 7045 data with $I \geqslant 2\sigma(I)$, $wR(F^2)$ = 0.104, max. residual $\Delta\rho$ = 0.46 e Å^{-3}.

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