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New π -Electron Rich Donors and Cavities and their Supramolecular Assemblies: Synthesis, Electrochemistry and Crystal Structures

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The synthesis, solution redox properties and X-ray crystal structures of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives are described.

Keywords: anthracene; macrocycles; cyclophanes; supramolecular

INTRODUCTION

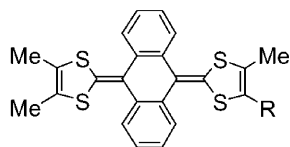
The studies of Hünig *et al.* on multi-stage redox systems^[1] together with work on tetrathiafulvalene (TTF)^[2] has led to interest in bis(1,3-dithiole) derivatives with quinonoid π -conjugation between the dithiole rings^[3]. Our attention has been focussed on 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives which undergo a single, quasi-reversible, two-electron oxidation wave to yield a thermodynamically stable dication at E^{ox} ca. +0.3 V (in MeCN *vs* Ag/AgCl) in the cyclic voltammogram (CV)^[4-7]. X-Ray crystal structures have shown that a major structural change accompanies oxidation to the dication: the central anthracenediylidene ring which is boat shaped in the neutral

molecule, becomes a planar anthracene system, with the heteroaromatic 1,3-dithiolium cations almost orthogonal to this plane^[8-11].

RESULTS AND DISCUSSION

We report the synthesis of new derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene with enhanced supramolecular order in the solid state, and cyclophanes in which the redox properties are tuned by the nature of the bridge.

Compound **1**^[5] was converted into the carboxymethyl derivative **2** (lithiation and reaction with methyl chloroformate) which was reduced to hydroxymethyl derivative **3** (LiAlH₄). Esterification of **3** (NEt₃, acyl chloride) afforded benzoyl and 2-naphthaloyl ester derivatives **4** and **5**, respectively^[12].



- 1**: R = H
- 2**: R = CO₂Me
- 3**: R = CH₂OH
- 4**: R = CH₂OC(O)Ph
- 5**: R = CH₂OC(O)2-naphthyl

The X-ray crystal structures of **3**, **4** and **5**·CH₂Cl₂, show that each molecule adopts a usual^[5] saddle-like conformation, with the anthracenediylidene unit folded along the C(9)...C(10) vector by 37 – 41°. The packing motifs (Figures 1-3) comprise pseudo-dimers of molecules, engulfing each other with their U-shaped bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene moieties.

Molecule **3** (Figure 1) is disordered between three possible positions, so that methyl and hydroxymethyl substituents are statistically mixed. Such kind of disorder is unusual, although the steric demands of the two groups are similar: normally the ordered structure is

stabilised by hydrogen bonds. It would seem *a priori* possible for the molecules **3** to be linked by a chain of hydrogen bonds. However, such a chain is incompatible with the pseudo-dimeric packing motif and so its non-realisation is evidence of the high stability of this motif.



FIGURE 1 Crystal packing of **3**

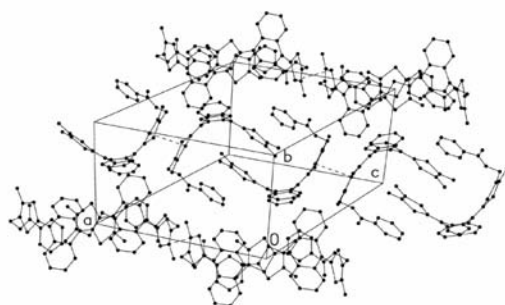


FIGURE 2 Crystal packing of **4**

The dimeric motif is most pronounced for **4** and **5**·CH₂Cl₂. In the former structure, the dimers form chains which are arranged in a herringbone motif (Figure 2). The pseudo-dimers of **5** form a close-packing layer (Figure 3). In the dimer of **4**, the electron-rich dithiole moiety lies in proximity to the electron-poor benzoyl group of the other

molecule. However, although the donor (D) and acceptor (A) moieties are nearly parallel (interplanar angle 10°) the π -overlap is very limited. In **5** each naphthoyl group is sandwiched between two dithiole groups and the contacting π -conjugated systems are practically parallel (interplanar angles 0.4 to 3.6°). Both structures contain 'oligomeric' stacks: 4-layer ADDA in **4** and 6-layer DADDAD in **5**.

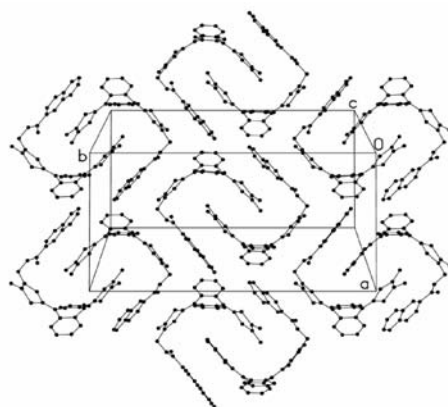


FIGURE 3 Crystal packing of **5**

We have studied two series of cyclophane derivatives: one formed by bridging across the two dithiole rings^[13], and the other by bridging the 2,6-positions of the anthracene system^[14]. The interest here is to see how the solid state structures and redox properties vary with the different linker units. The synthetic methodology involves reactions of **6** with a dicarbonyl chloride under high dilution conditions. Representative derivatives are the phenyl and diphenyl ether bridged systems **7** and **8**.

The CVs (Figure 4) show that the oxidation potential ($E^{\text{ox}}_{\text{pa}}$) is raised significantly (by *ca.* 300 mV) for **7**, but only slightly (by 60 mV) for **8**, compared to the non-bridged compound **4**. This is consistent with the shorter bridge of **7** hindering the conformational change which

accompanies oxidation to the dication. The value of ΔE is reduced as the bridge is shortened, with ΔE reduced to only 70 mV for compound **7**. This reflects the reduced stability of the twisted dication structure within the steric constraints of the smaller cyclophane.

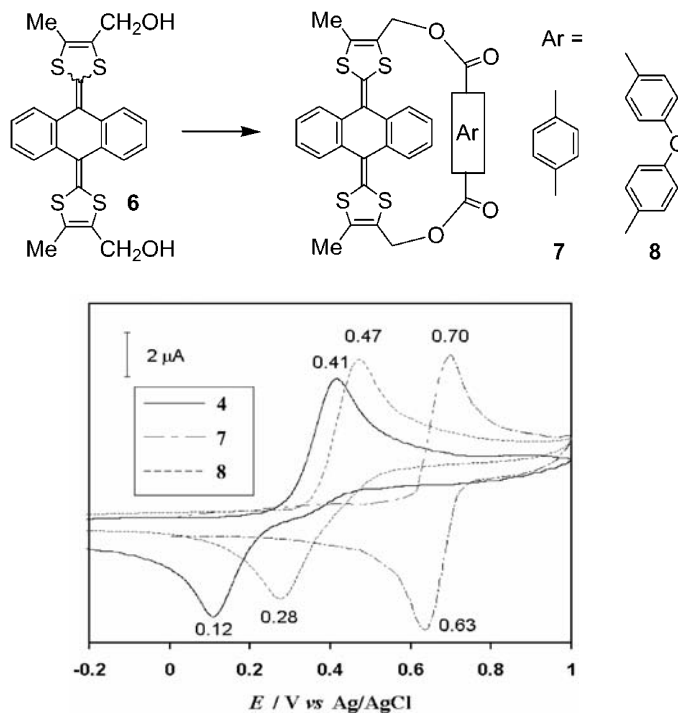


FIGURE 4 Cyclic voltammograms of compounds **4**, **7** and **8** (vs. Ag/AgCl, electrolyte $\text{Bu}_4\text{N}^+\text{PF}_6^-$, MeCN, 20 °C, scan rate 100 mV s⁻¹).

X-Ray structures show that the molecular conformation of **8** is similar to non-bridged analogs: the two bridging benzene rings in **8** form a dihedral angle of 73°. The asymmetric unit of the triiodide salt of **8** comprises one $\mathbf{8}^{2+}$ dication, two I_3^- anions and CH_2Cl_2 of

crystallization (Figure 5). The dication shows a drastic change of conformation and bond lengths compared to the neutral molecule, similar to those observed for non-bridged systems^[8-10]. 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, whereas non-bridged dications 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 $\mathbf{8}^{2+}$ the anthracene unit has a similar, but much smaller, folding than the anthracenediylidene in the neutral molecules, with its central ring adopting a boat conformation, and 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 **8**.

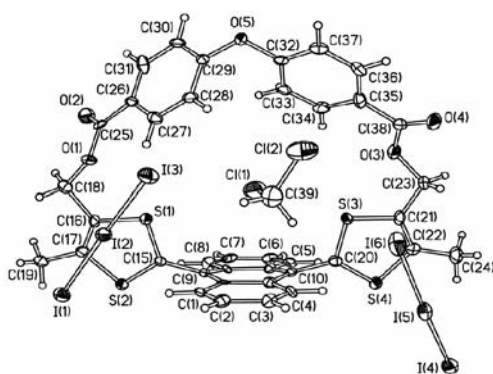
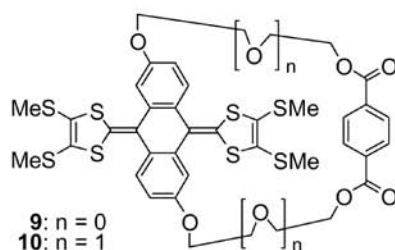


FIGURE 5 Molecular structure of $\mathbf{8}^{2+}(\text{I}_3^-)_2 \cdot (\text{CH}_2\text{Cl}_2)_{2.25}$

Cyclophanes **9** and **10** have also been obtained by macrocyclisation reactions. $E^{\text{ox}}_{\text{pa}}$ is raised by 50 mV for **9** but no increase is seen for **10**, relative to the non-cyclised precursor. Thus the longer bridge of **10** allows free conformational change.



The salt $\mathbf{9}^{2+}(\text{I}_3^-)_2 \cdot (\text{I}_2)_{0.5} \cdot \text{CH}_2\text{Cl}_2$ has an interesting structure (Figure 6). In $\mathbf{9}^{2+}$ the folding of the anthracene unit along the C(9)...C(10) vector is much stronger (22°) than in nonbridged dications and compound $\mathbf{8}^{2+}$ (6°) although the system remains substantially aromatic: bond distances are essentially the same as in anthracene itself. The bridging benzene ring in $\mathbf{9}^{2+}$ is practically parallel and eclipsed with the central anthracene ring.

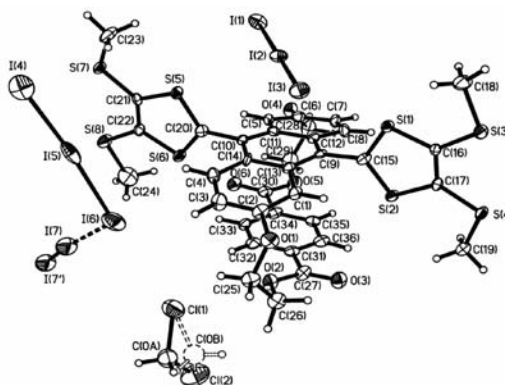


FIGURE 6 Asymmetric unit of $\mathbf{9}^{2+}(\text{I}_3^-)_2 \cdot (\text{I}_2)_{0.5} \cdot \text{CH}_2\text{Cl}_2$

Future studies will concern doubly- and triply-bridged systems which form stable cation radicals and dications. This will enable studies on hitherto inaccessible single-electron transfer processes involving the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system as an

electron donor moiety^[10,15]. There are also interesting prospects for highly-charged dendritic systems based on building block **3**^[16].

Acknowledgments

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