

New redox materials based on functionalised 9,10-anthracenediylidenes*

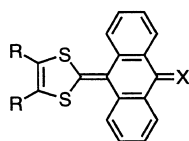
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Abstract: The syntheses, electronic, optical and structural properties of a range of derivatives of 9,10-anthracenediylidene are described. The first family of compounds are π -electron donors based on 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene. Recent synthetic developments are reviewed, including the functionalisation, *via* lithiation and subsequent *in situ* quenching with electrophiles, of the trimethyl derivative **8**. X-Ray crystal structures of selected derivatives reveal that the molecules adopt a saddle-shaped conformation. The second family of compounds are novel single-component donor– π -acceptor species which possess intramolecular charge transfer, notably 10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9-(2,2-dicyanomethylene)anthracene **19**. Cyclic voltammetric data, UV/visible spectra, ultrafast time-resolved spectroscopy and X-ray structural data are reported.

INTRODUCTION

Conjugated π -electron systems containing two or more redox centres within the same molecule continue to receive much attention, due to their interesting unconventional electronic and optoelectronic properties [1]. This article concerns 9,10-anthracenediylidene derivatives bearing a 1,3-dithiole group as a π -donor, together with either a second 1,3-dithiole group (a D– π -D system) or an acceptor substituent (a D– π -A system), i.e. general structures **A** and **B**, respectively (Scheme 1). In the context of new π -electron donor molecules, bis(1,3-dithiole) systems with extended π -conjugation have been studied as D– π -D tetrathiafulvalene (TTF) analogues, with emphasis on their use as components of electronically conductive charge transfer materials [2].



A X = π -donor, e.g. 1,3-dithiole
B X = π -acceptor, e.g. C(CN)₂

Scheme 1

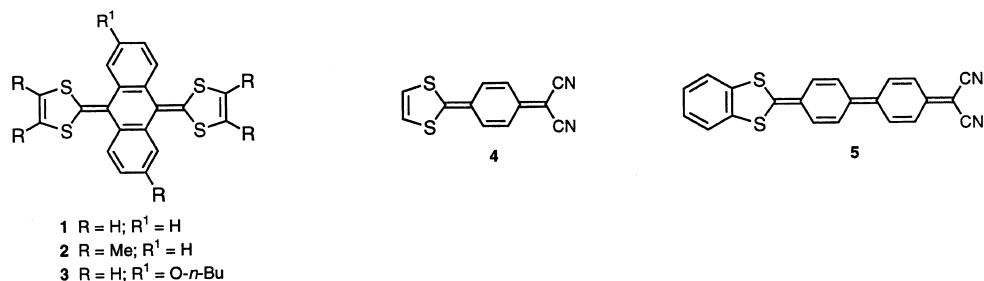
Representative structural modifications include derivatives with the incorporation of vinylogous conjugation between the two dithiole rings [3], or those with quinonoid [4] or heteroaromatic [5] spacer units. The molecules which are planar have attracted the most attention, with the aim of obtaining face-to-face π -dimers or stacks in the solid state which generally favour highly conducting properties. We have a continuing interest in the saddle-shaped 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system **1**, the first derivative of which, namely the 9,10-bis(benzo-1,3-dithiol-2-ylidene) analogue, was

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synthesised by Akiba *et al.* [6]. We first reported the saddle-shaped structure of the neutral system in an X-ray crystallographic study of the tetramethyl derivative **2** [7], and theoretical calculations have established that steric hindrance introduced by benzoannulation of the quinonoidal unit determines this loss of planarity [8]. Compounds **1** and **2** undergo a single, two-electron, oxidation wave to yield a thermodynamically stable dication at $E^{\text{ox}} \approx +0.3$ V (vs. Ag/AgCl) in the cyclic voltammogram [8,9]. A fascinating structural change accompanies oxidation to the dication: the central anthraquinonoid system becomes aromatic and planar, with the 1,3-dithiolium cations almost orthogonal to this plane (X-ray crystallographic evidence for 2^{2+}) [7]. New derivatives of system **1** are reported herein.

Organic compounds of the push-pull D- π -A type are relevant to the development of non-linear optics [10], molecular electronics [11] and physical organic chemistry [12]. Systems containing a quinonoid ring connecting both donor and acceptor moieties are particularly interesting, since the push-pull stabilisation is promoted by the aromatisation of the quinonoid ring. Thus, compound **4** (Scheme 2) was reported by Gompper *et al.* [13] more than 30 years ago to be a blue compound, and the π -extended analogue **5** (Scheme 2) has recently been reported by Otsubo *et al.* [14] to show strong absorption bands in the near-infrared region [λ_{max} (CH₂Cl₂) 957, 1045 nm]. The observed large negative solvatochromism with increasing solvent polarity indicates that zwitterionic forms contribute greatly to the push-pull quinonoid system in compound **5** [14]. We report studies on the single-component donor- π -acceptor species **19** which contains a 9,10-anthraquinonoid spacer group.

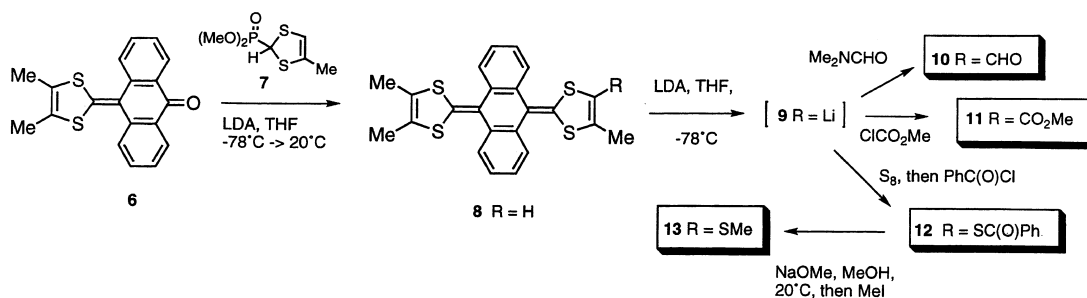


Scheme 2

9,10-BIS(1,3-DITHIOL-2-YLIDENE)-9,10-DIHYDROANTHRACENE DERIVATIVES

Our aim was to functionalise system **1** with substituent groups which would enable this ring system to be exploited more widely as a building block in materials and supramolecular chemistry. Our attempts to generate and trap the monolithio derivative of **1** were thwarted by the low solubility of **1** in suitable solvents at low temperature. The more soluble 2,6-dibutoxy derivative **3** gave complex product mixtures of di- and multi-lithiated products [15]. To circumvent this problem, and to ensure that only monolithiation occurred, we synthesised the new trimethyl derivative **8** [15,16]. Reaction of compound **6** (readily obtained in multi-gram quantities from anthrone [4b]) with the phosphonate anion, obtained by deprotonation of reagent **7** using lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at -78 °C, afforded compound **8** in 55% yield (Scheme 3). Deprotonation of **8** using LDA in THF at -78 °C, followed by quenching with an excess of D₂O, gave a quantitative yield of the mono-deuterio derivative of **8** [¹H nuclear magnetic resonance (NMR) evidence] confirming the very efficient generation of lithiated species **9**. The results of trapping species **9** with selected electrophiles are shown in Scheme 3. Aldehyde derivative **10** was obtained in only 13% yield; however, efficient trapping of intermediate **9** occurred with methylchloroformate to yield the methylester derivative **11** (83% yield). Sulfur insertion into the lithiated species **9**, followed by reaction of the transient thiolate anion with benzoyl chloride, gave the thioester derivative **12** (53% yield). By analogy with a related tetrathiafulvalene derivative [17], compound **12** is a convenient shelf-stable precursor of other mono-functionalised derivatives of **8**. Debenzoylation of **12** was readily achieved (sodium methoxide, room temperature) and the transient thiolate anion thereby generated was trapped efficiently with iodomethane to yield **13** (80% yield). Thus this route (Scheme 3) opens up the way to a range of new derivatives of the parent system **1**.

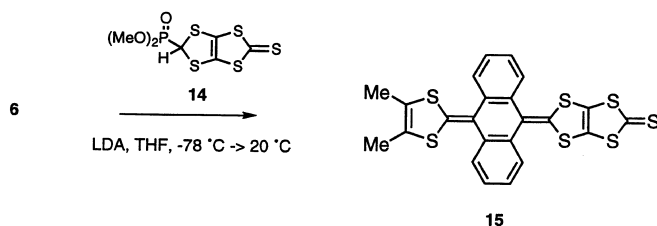
Cyclic voltammetric data for the new derivatives of **1**, obtained in acetonitrile solution, establish that



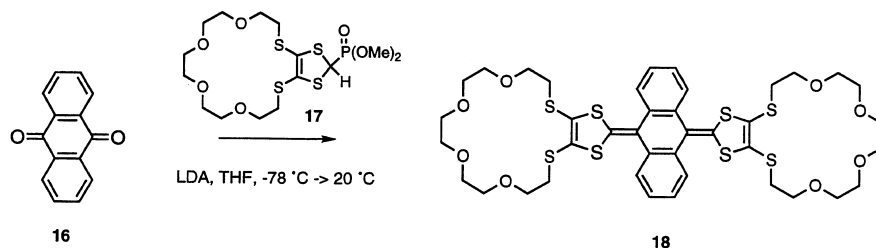
Scheme 3

the redox properties are only slightly modified by the presence of the substituents on the dithiole rings: a predictable trend is that the two-electron oxidation wave is anodically shifted by an electron-withdrawing substituent on the 1,3-dithiole ring: cf. E^{ox} values for compound **8** (0.320 V), compound **10** (0.450 V) and compound **11** (0.425 V). The lowest energy absorption band in the UV visible spectrum is observed at $\lambda_{\text{max}} = 420\text{--}430\text{ nm}$, and is essentially unaffected by the substituents.

We have explored different functional modifications to system **1**, *via* reactions of more elaborate phosphonate reagents **14** [18] and **17** [19]. Reaction of compound **6** with the anion generated from reagent **14** gave product **15** (60% yield) (Scheme 4) exhibiting an interesting solid state structure, as discussed below. The bis(crown-annulated) derivative **18**, obtained from anthraquinone **16** and reagent **17** (Scheme 5) was designed as a sensor for voltammetric recognition of cation binding: preliminary studies show that the first oxidation potential of **18** in organic solvents is shifted to more positive potentials in the presence of Ag^+ salts. These data are consistent with reversible metal binding within the S_2O_4 crown cavities [19].



Scheme 4



Scheme 5

X-Ray analysis reveals that molecule **11** adopts a saddle-like conformation, relieving steric repulsion between sulfur atoms and hydrogen atoms in *peri* positions of the anthracene moiety (Fig. 1). The latter is folded along the C(9) ... C(10) axis by a dihedral angle (ϕ) of 40.5° . The bis(1,3-dithiole)benzoquinone system is U-shaped through an ‘accumulating bend’ comprising the boat conformation of the central (quinonoid) ring, folding of both 1,3-dithiole rings along S ... S vectors, and out-of-plane tilting of the exocyclic C=C bonds, all in the same (inward) direction. Thus the S(1)C(16)C(17)S(2) and S(3)C(22)C(23)S(4) moieties form an acute dihedral angle (θ) of 75.6° . It is interesting to note that the C—S bonds in the methoxycarbonyl-substituted dithiole ring of **11** (but not in the other dithiole ring) are asymmetrical, S(1)—C(16) shortened to 1.743(11) Å and S(1)—C(15) lengthened to 1.785(11) Å [cf.

S(2)—C(15) 1.757(10) and S(2)—C(17) 1.756(10) Å]. Such distortion was observed earlier in thiocarbamoyl-TTF and thiocarbamoyl-Me₃TTF [20] and can be attributed to a mesomeric effect. Crystal packing (Fig. 1) shows the motif reported earlier for the tetra(methylsulfanyl) analogue [21]: pairs of inversion-related molecules engulf each other's dimethyl-substituted dithiole moiety. These moieties contact face-to-face, but the interplanar separation of approximately 3.7 Å is rather long. CDCl₃ molecules occupy cavities between these pairs and are disordered.

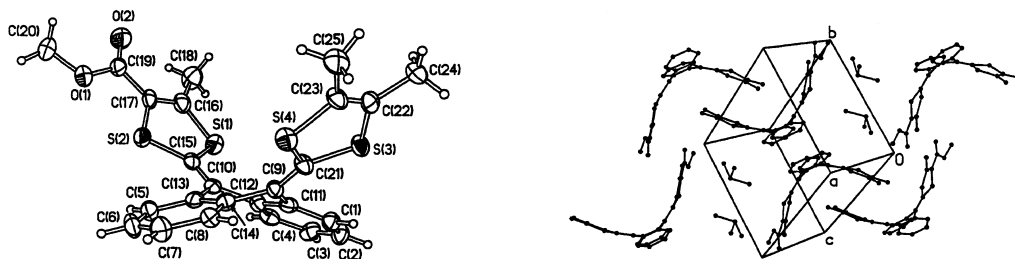


Fig. 1 X-Ray molecular structure of **11** (left) and crystal packing of **11** (right).

The asymmetric unit of **15** comprises two molecules (A and B) and one severely disordered molecule of CDCl₃. The crystal packing of **15** (Fig. 2) is rather dissimilar from that of **11**. Molecule A and its inversion equivalent engulf each other's dimethyldithiole ends, as does molecule B and its inversion equivalent. In each dimer, the dithiole rings overlap in an antiparallel fashion, with interplanar separations of 3.64 Å (A–A') and 3.55 Å (B–B') and shortest C...S contacts of 3.66 Å in either case. These two dimers are oriented in mutually perpendicular planes and give rise to an unusual three-dimensional network of intermolecular contacts comparable to (or shorter than) the standard van der Waals' distances [22] S...S 3.60 and C...S 3.61 Å.

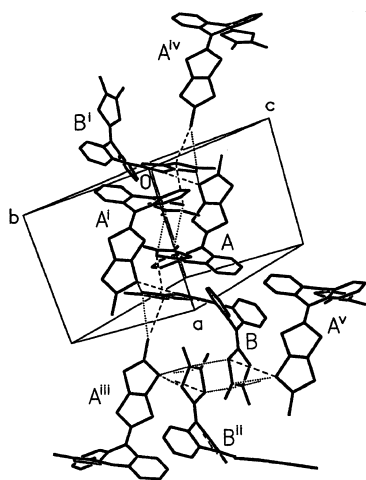
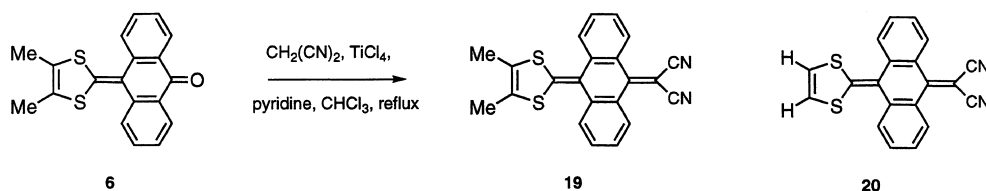


Fig. 2 Crystal packing of **15**.

Dimethyldithiole rings of the A–A' dimer are sandwiched between dithiolethione systems of two adjacent B molecules (interplanar angle 7°, shortest S...S contacts 3.63 Å). This tetramer is additionally strengthened by interactions between molecules A and B (S...S contacts 3.66 Å and 3.49 Å). However, no continuous stacks exist in the structure, and the aforementioned BAA'B' stack is 'underpinned' at either end by the exocyclic thione bond of another A molecule; this bond is aligned perpendicular to the stacked planes (S...S contacts 3.45–3.52 Å). The dimethyldithiole rings of the B–B' dimer are contacted on the outer sides by dithiolethione moieties of adjacent A molecules, in an edge-to-face fashion, with the shortest contacts S...C 3.29 and S...S 3.61 Å.

10-(4,5-DIMETHYL-1,3-DITHIOL-2-YLIDENE)-9-(2,2-DICYANOMETHYLENE) ANTHRACENE **19**

For studies on D- π -A systems of type **B**, we focused our attention on the strong dimethyl-substituted donor and the strong dicyanomethylene acceptor moieties, to maximise intramolecular charge transfer (ICT) behaviour. Compound **19** was synthesised in 66% yield from **6**, as shown in Scheme 6 [21]. Solution electrochemistry of compound **19** shows a reversible oxidation wave that can be attributed to formation of the radical cation of the 1,3-dithiole moiety ($E^{\text{ox}} = +0.95$ V) and a reduction wave forming the radical anion ($E_1^{\text{red}} = -0.96$ V, CH_2Cl_2 , versus saturated calomel electrode, SCE) for which the negative charge is presumably located on the acceptor group, as discussed for related dicyanomethylene species [3c,23].



Scheme 6

The electronic absorption and emission spectra of compound **19** in solution were recorded in different solvents (Fig. 3). The low energy band in the 556–600 nm region is assigned to an ICT band. [The precursor ketone **6**, with a weaker acceptor moiety, shows an ICT band at shorter wavelength (481 nm)]. Compound **19** exhibits solvatochromism: the UV absorption bands show little dependence on the solvent, whereas the ICT band exhibits a bathochromic shift and an increase in band width with increasing solvent polarity (although the peak positions for CHCl_3 and MeCN are reversed from this general trend). The emission band from **19** is also solvent dependent, being weak in cyclohexane, very weak in CHCl_3 and unobserved in MeCN or aqueous solution. This band shows both a bathochromic shift and a larger Stokes shift from the absorption band with increasing solvent polarity.

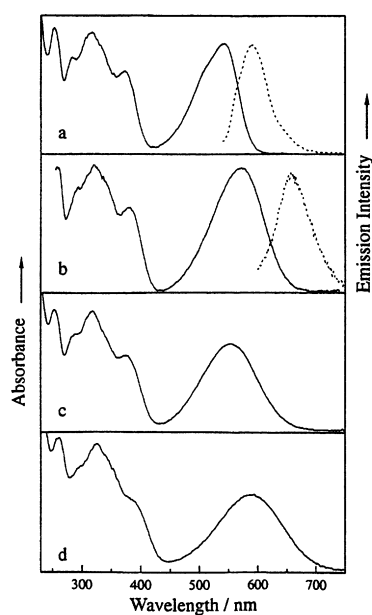


Fig. 3 UV/visible absorption (full line) and emission (broken line) spectra of **19** in cyclohexane (a), chloroform (b), acetonitrile (c) and aqueous solution (d).

The photophysics of compound **19** has been studied by ultrafast time-resolved UV/visible spectroscopy. The key feature of the time-resolved difference spectrum is a photoinduced absorption at 400–580 nm (Fig. 4). The kinetics of the transient signals obtained on UV photolysis of **19** fit a single-exponential decay corresponding to a lifetime for the excited state species of $\tau_{\text{obs}} \approx 170$ ps in MeCN and ≈ 400 ps in CHCl_3 [21]. These observations agree with data reported for other D- π -A excited states [24] and are consistent with the excited state being a twisted ICT (TICT) state.

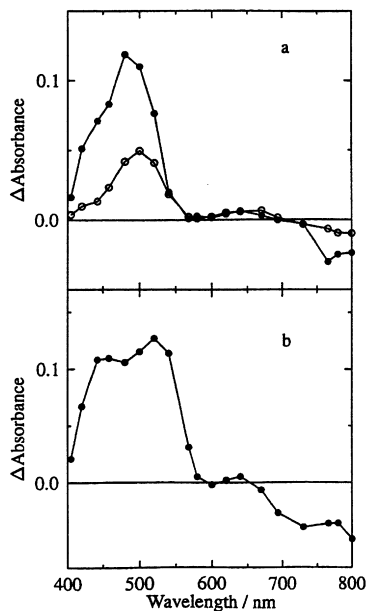


Fig. 4 Time-resolved UV/visible difference spectra of **19** in acetonitrile at 4 ps (a) and in chloroform at 5 ps (b) after photolysis at 606 nm (filled circles) or 303 nm (open circles).

The single-crystal X-ray analysis of **19** (Fig. 5) reveals a saddle shaped structure similar to that of the bis(1,3-dithiole) compounds **11** and **15**, discussed above, with the central ring of the anthraquinonoid unit in a boat conformation. The folding in the structure of **19** is less than that in compounds **11** and **15**, and is smaller along the C(4a)—C(10a) vector than along the C(8a)—C(9a) vector (23° versus 29°), reflecting the reduced steric demands of the dicyanomethylene substituent.

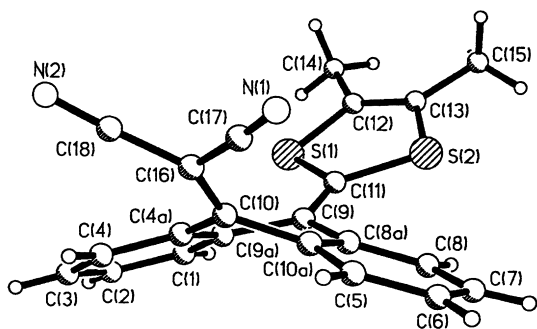


Fig. 5 X-Ray molecular structure of **19**.

Theoretical calculations have been performed on compound **20** [21]. The energies and topologies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) explain the redox properties and support the ICT nature of the lowest energy absorption band observed experimentally for **19**. The oxidation and reduction processes have been studied in detail by optimising the molecular structure of the radical cation, radical anion and dianion. It is interesting to note that, for the

dianion species 20^{2-} , the $C(CN)_2$ unit rotates, thereby removing interactions on the acceptor site of the molecule; nonetheless, the anthracene moiety remains significantly distorted from planarity, due to the $S-H_{peri}$ contacts at the donor site. This contrasts with the planar anthracene moiety of the dication of **2** (X-ray crystal structure [7] and theoretical calculations [8]) and the dianion of 11,11,12,12-tetracyano-9,10-anthraquinodimethane (theoretical calculations [25]).

CONCLUSIONS AND FUTURE DIRECTIONS

We have discussed new multi-functional π -electron systems of general structures **A** and **B** which are readily available with a variety of substitution patterns starting from anthraquinone or anthrone. The reactivity of 1,3-dithiole-2-phosphonate reagents has been successfully exploited, and the anion chemistry of compound **8** has been developed. We have shown that the 9,10-anthracenediylidene spacer group imparts interesting electronic and structural properties when incorporated into D- π -D and D- π -A systems which possess folded, saddle-shaped structures by virtue of the boat conformation of the central ring. A special feature of these materials is the interplay of redox states and conformational change. This family of compounds provides redox-active cavities, optically active and fluorescent molecules. They are emerging as versatile building blocks in materials and supramolecular chemistry. Future directions for our work include:

- (a) the synthesis of theoretically interesting bridged derivatives and cyclophanes;
- (b) derivatives with extended supramolecular order in the solid state;
- (c) redox-active dendrimers incorporating these moieties;
- (d) studies on charge transfer and host-guest interactions;
- (e) electrochemically controlled optical and fluorescent switches and sensors.

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