# Syntheses and X-ray Crystal Structures of Functionalised 9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene Derivatives

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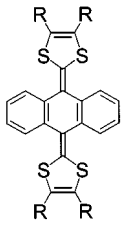
The synthesis of new derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene has been achieved by two different routes. Deprotonation of **8** using LDA in THF at –78 °C, followed by in situ quenching of the lithiated intermediate **9** with *N,N*-dimethylformamide, *N*-methyl isothiocyanate and methyl chloroformate gave aldehyde, thioamide and methyl ester derivatives **10–12**, respectively. Sulfur insertion into the lithiated species **9** followed by reaction of the transient thiolate anion with benzoyl chloride gave the thioester derivative **13** which served as a convenient shelf-stable precursor of other mono-functionalised derivatives of **8**. Debenzoylation of **13** and trapping of the transient thiolate anion with iodomethane and 6-bromohexan-1-ol yielded **14** and **15**, respectively. Reaction of cation salt **17** with the anion of anthrone **18** gave compound **20**, the thiolate anion of which reacted with 6-bromohexan-1-ol to afford the alcohol derivative **21**. Subsequent reactions gave alcohol derivative **25** of the title system. The unexpected product **29** was obtained from reaction of **28** with triethyl phosphite. The X-ray crystal structures of compounds **12**, **14**, **28**, and **29** are reported. The molecules adopt a saddle-like conformation; 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.

## Introduction

In the context of new π-electron donor molecules related to tetrathiafulvalene, bis(1,3-dithiole) systems with extended π-conjugation have received considerable attention in the last few years, with emphasis on their use as components of electronically conductive charge-transfer materials. Representative structural modifications include derivatives with the incorporation of vinylogous conjugation between the two dithiole rings,[1] or those with quinonoid[2] or heteroaromatic[3] spacer units. The molecules which are planar (or nearly planar) have been the most widely studied, with the aim of obtaining face-to-face π dimers or stacks in the solid state which generally favour highly conducting properties. In contrast to the planar extended π systems of this type, 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, viz. 9,10-bis(benzo-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene, was synthesised by Akiba et al.[4] We first reported the saddle-shaped structure of the neutral system in an X-ray crystallographic study of the tetramethyl derivative **2**,[5] and theoretical calculations by other workers have established that steric hindrance introduced by benzoannulation of the quinonoidal unit determines this loss of planarity.[6] Compounds **1** and **2** undergo a single, two-electron, oxidation wave to yield a thermodynamically stable dication at $E^{ox}$ ca. +0.3 V (*vs* Ag/AgCl) in the cyclic voltammogram.[2b,6,7] A dramatic structural change accompanies oxidation to the dication: the central anthracene ring becomes aromatic and planar, with the 1,3-dithiolium cations almost orthogonal to this plane (X-ray crystallographic evidence for $\mathbf{2}^{2+}$).[5]



**1** R = H
**2** R = Me

Herein we report our work on two different approaches to a versatile range of derivatives of **1** which contain a reactive functional group attached to one of the 1,3-dithiole rings.[8] These derivatives are designed to enable system **1** to be exploited as a functionalised building block in the fields of supramolecular and materials chemistry. This is a new direction for studies on system **1**. The known derivatives of **1** are restricted to those with simple alkyl,[2b,5] thioalkyl,[9] or aryl/thioaryl[4,10] substituents on the dithiole rings, which are not suitable for further functionalisation. Heterocyclic analogues,[11] and a few derivatives with substituents attached to the anthracenediylidene spacer[12] have been reported. We also report the formation of an unexpected ring opened product obtained from derivative **28** during the course of this work.

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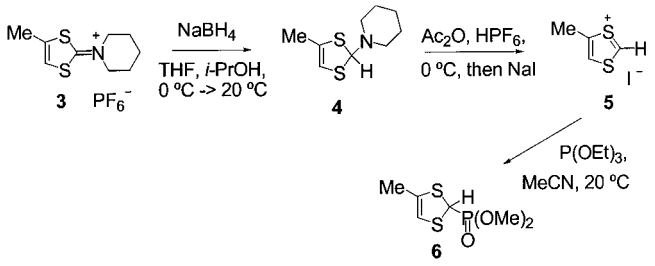
## Results and Discussion

### Synthesis

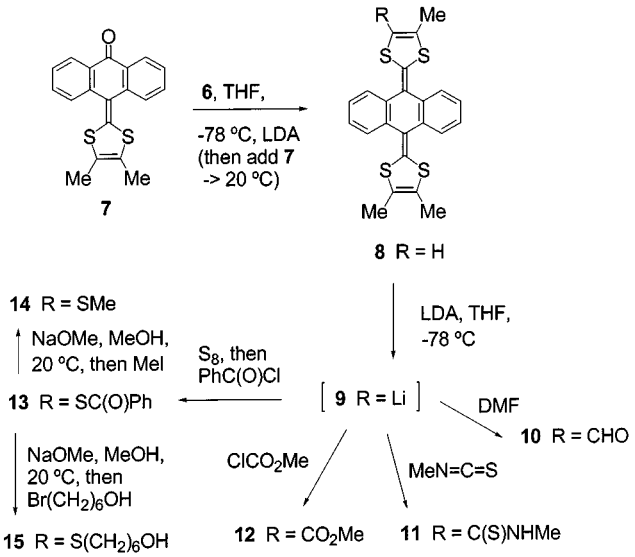
Our attempts to functionalise **1** via reaction of its monolithio derivative with electrophiles were thwarted by the low solubility of **1** in suitable solvents at low temperature. To circumvent this problem, and to ensure that only monolithiation occurred, we synthesised the new trimethyl derivative **8**. For this we required the phosphonate ester reagent **6**, which was synthesised from the known iminium salt **3** (81% overall yield) as shown in Scheme 1, using procedures we have recently optimised for the dimethyl analogue.[13]




Scheme 1. Synthesis of reagent **6**

Reaction of compound **7** (readily obtained in multi-gram quantities from anthrone)[2b] with the phosphonate anion obtained by deprotonation of reagent **6** using lithium diisopropylamide (LDA) in THF at −78°C afforded compound **8** in 55% yield (Scheme 2). Deprotonation of **8** using LDA in THF at −78°C, followed by quenching with an excess of $D_2O$ gave a quantitative yield of the monodeuterio derivative of **8** ($^1$H-NMR evidence) confirming the very efficient generation of lithiated species **9**. The results of trapping species **9** with a selection of electrophiles are shown in Scheme 2. The yields of the substituted products **10** and **11** were consistently lower than those for analogous trimethyl-TTF derivatives[13] (TTF = tetrathiafulvalene): the majority of unchanged compound **8** was easily recovered. Aldehyde and thioamide derivatives **10** and **11** were obtained repeatedly in only 13−17% yields, with *N,N*-dimethylformamide and *N*-methyl isocyanate as the electrophiles. For the synthesis of **10**, dimethylformamide was preferable to *N*-methylformanilide as the formylating reagent, in contrast to the analogous reaction with TTF[14] or trimethyl-TTF.[13] A considerably more efficient trapping of intermediate **9** occurred with methylchloroformate to yield the methyl ester derivative **12** (83% yield). Sulfur insertion into the lithiated species **9** followed by reaction of the transient thiolate anion with benzoyl chloride gave the thioester derivative **13** (53% yield). Compound **13** is a convenient shelf-stable precursor of other monofunctionalised derivatives of **8**. Debenzoylation of **13** was readily achieved (sodium methoxide, room temperature) and the transient thiolate anion thereby generated was trapped efficiently with iodomethane and 6-bromohexanol to yield **14** and **15**, respectively (80−93% yields). The X-ray crystal structures of compounds **12** and **14** are discussed below.

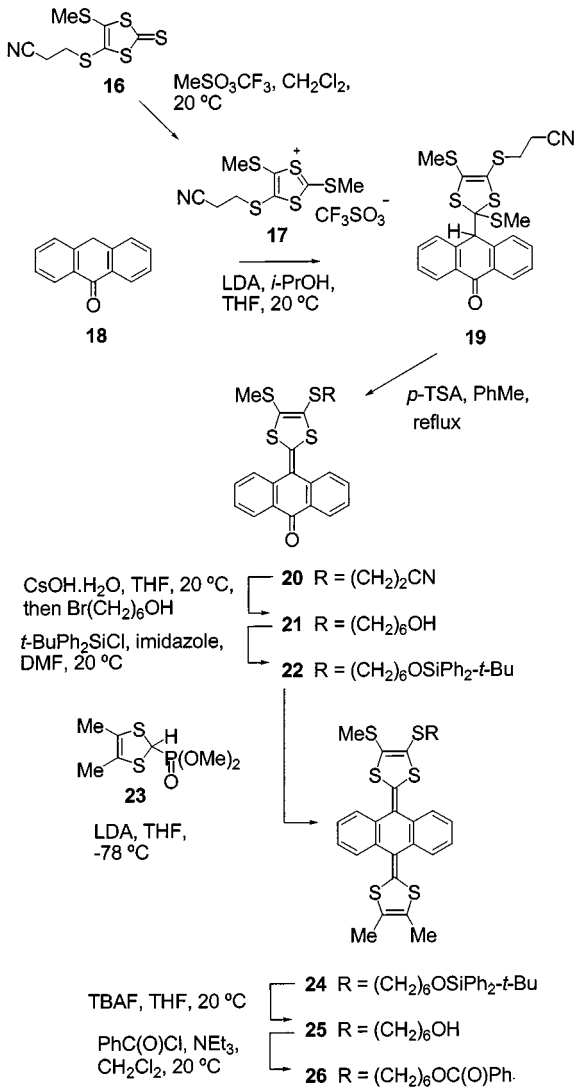
An alternative approach which has yielded a different series of derivatives of **1** is shown in Scheme 3. This route



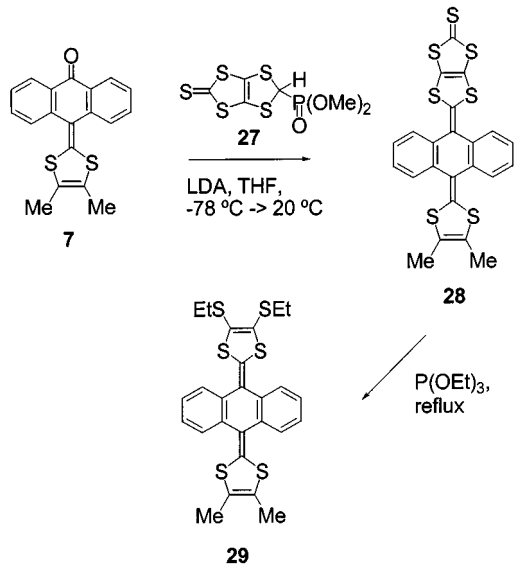

Scheme 2. Generation and trapping of species **9**

utilises the cyanoethyl protecting group protocol developed by Becher et al. in the 1,3-dithiole and TTF series.[15] Methylation of thione **16**[15a] with methyl triflate gave cation salt **17** which was reacted, without purification, with the anion of anthrone **18** (generated using LDA at room temperature) to afford initially compound **19** ($^1$H-NMR evidence) which was converted into the desired compound **20** by treatment with *p*-toluenesulfonic acid (18% yield, based on thione **16**). The low yield of this reaction was due to the competing deprotection of the cyanoethylthio group of **17** and/or **19** under these basic conditions. The thiolate anion derived from **20** was liberated cleanly using Becher's conditions (cesium hydroxide at room temperature)[15] and trapped in situ with 6-bromohexan-1-ol to afford the alcohol derivative **21** in 89% yield. Conversion of **21** into its *tert*-butyldiphenylsilyl ether derivative **22** (90% yield) and subsequent reaction with the anion derived from reagent **23**[2b] gave compound **24** (70% yield) desilylation of which (tetrabutylammonium fluoride) gave alcohol derivative **25** (79% yield). The suitability of compound **25** for further elaboration was established by reaction with benzoyl chloride in the presence of triethylamine which gave the benzoyl ester derivative **26** in 50% yield. Thus both routes (Schemes 2 and 3) afford derivatives of the parent system **1** which contain one reactive substituent suitable for further functionalisation.

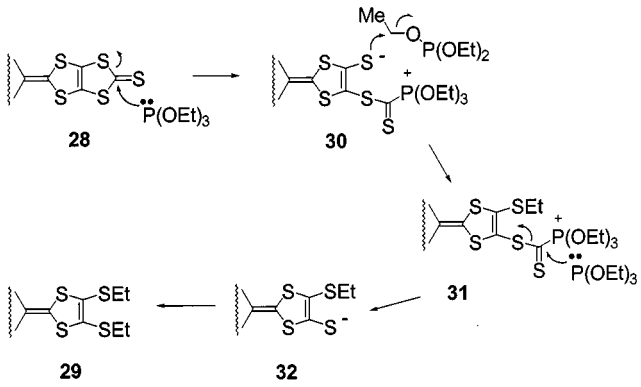
During the course of this work we have explored a different functional modification to system **1**, namely, the attachment of a bicyclic 1,3-dithiole moiety. Reaction of compound **7** with the anion generated from phosphonate ester reagent **27**[16] gave the expected product **28** (60% yield). With the aim of synthesising a bis[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthraceno]TTF derivative by a standard phosphite-induced coupling reaction,[17] compound **28** was heated in neat triethyl phosphite. However, no coupled product was obtained; the only isolated product was the unexpected compound **29** (50% yield) in which the 1,3-dithiole-2-thione ring has been transformed into two ethylsul-




Scheme 3. Synthesis of compounds **24**–**26**




Scheme 4. Synthesis of compound **29**




Scheme 5. Postulated mechanism for the conversion of **28** into **29**

fanyl substituents (Scheme 4). The structures of both compounds **28** and **29** were established unequivocally by single crystal X-ray analysis (see below). The conversion of **28** into **29** under these reaction conditions appears to be an unprecedented reaction of a 1,3-dithiole-2-thione derivative. Reactions of trialkylphosphite reagents with cyclic trithiocarbonates are generally assumed to proceed *via* an initial thiophilic addition,[17–19] although a carbophilic mechanism has been considered.[17a,b] It is not readily apparent how a thiophilic addition can explain the formation of **29**; we, therefore, propose initial opening of the 1,3-dithiole-2-thione ring of **28** induced by carbophilic addition of triethyl phosphite, to form the zwitterionic intermediate **30** (Scheme 5). Ethylation of **30** then occurs by an O,S transfer of an ethyl group from triethyl phosphite[19] to yield **31**. This is more likely to be an intermolecular transfer (as shown) than an intramolecular process. Generation of a second thiolate anion, and ethylation then gives product **29**.

Solution electrochemical and UV/Vis spectroscopic data for the new derivatives of the parent system **1** are entirely in accord with their structures. Cyclic voltammetric data obtained in acetonitrile establish that the redox properties are only slightly modified by the presence of the substituents: a predictable[13] trend is that the two-electron oxidation wave[7] 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 **12** (0.425 V). The lowest energy absorption in the UV/Vis spectra is observed at $\lambda_{max}$ = 420–430 nm, and is essentially unaffected by the substituents. Comparable data for the parent system **1** and benzo-annulated analogues have been discussed recently by Martín, Ortí et al. on the basis of theoretical calculations.[6]

## X-ray Crystal Structures of Compounds 12, 14, 28, and 29

The asymmetric unit of **12** comprises one title molecule (Figure 1a) and one $CDCl_3$ molecule of crystallisation. Molecule **12** adopts a saddle-like conformation, relieving steric repulsion between sulfur atoms and hydrogen atoms in *peri* positions of the anthracene moiety. The latter is

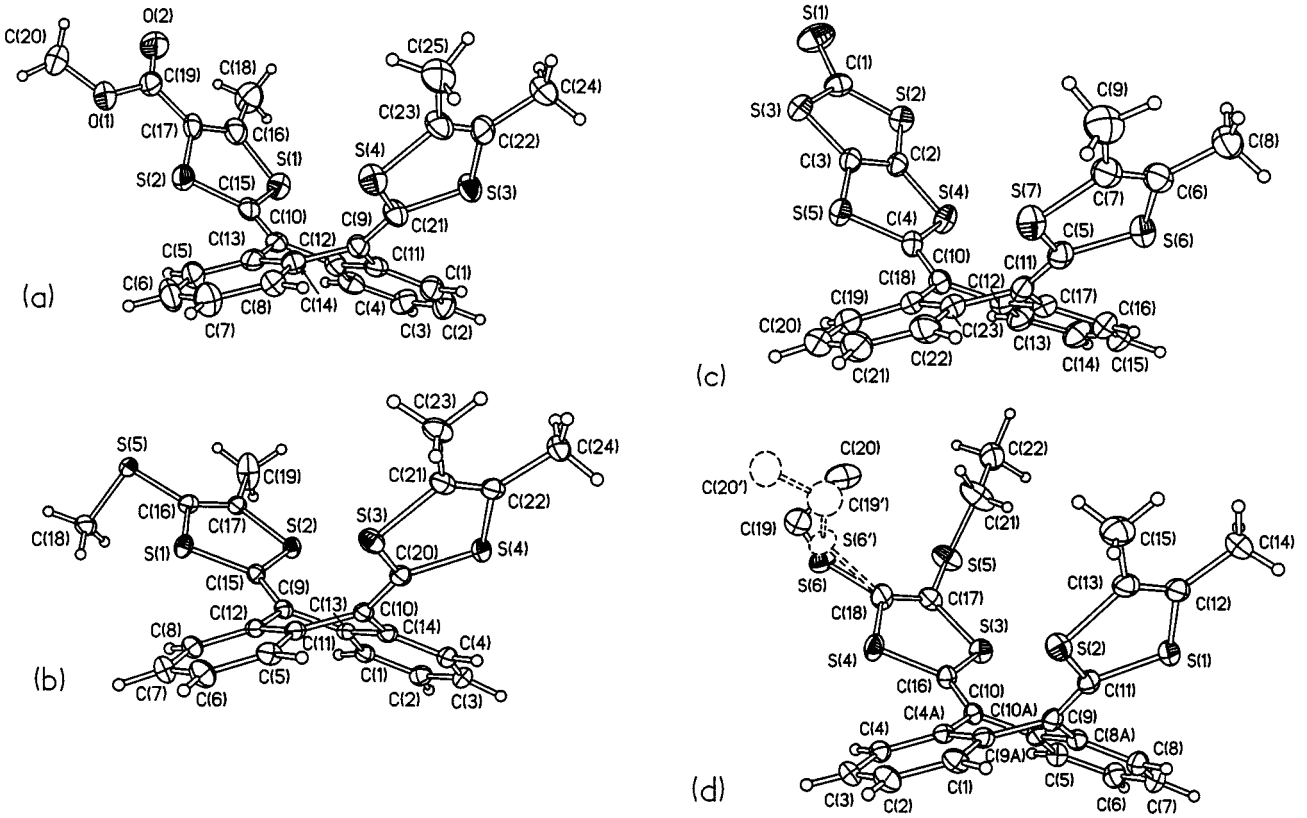



Figure 1. Molecular structures of **12** (a), **14**(b), **28** (c) (Molecule A), and **29** (d)**,** showing the disorder in **29**. Atomic displacement ellipsoids at the 50% probability level.

folded along the C(9)···C(10) axis by a dihedral angle ($\phi$) 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 ($\theta$) of 75.6°. The C−S bonds in the methoxycarbonyl-substituted dithiole ring of **12** are rather 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−-$Me_3$TTF[20] and can be attributed to a mesomeric effect [*i.e.* a contribution from a canonical form with double S(1)=C(16) and C(17)=C(19) bonds]. In the other (dimethyl-substituted) dithiole ring of **12**, the C(21)−S(3) and C(21)−S(4) bonds are equivalent [1.767(9) Å] as are the S(3)−C(22) and S(4)−C(23) bonds [1.749(10) Å]. Crystal packing (Figure 2a) shows the motif reported earlier for the tetra(methylsulfanyl) analogue:[9c] pairs of inversion-related molecules engulf each other′s dimethyl-substituted dithiole moiety. These moieties contact face-to-face, but the interplanar separation of ca. 3.7 Å is rather long. $CDCl_3$ molecules occupy cavities between these pairs and are disordered.

Compound **14** exhibits a wider $\theta$ angle (86.9°) due to the more planar dithiole rings, and in spite of more pronounced folding of the anthracene moiety ($\phi$ = 45.1°). It has the same packing motif as **12**, but without any solvent of crystallisation. The SMe group is disordered over three positions, at C(16), C(17), and C(21), with occupancies of 80%, 15%, and 5%, respectively. For the former two, the nearly-overlapping positions of the sulfur and the methyl carbon atoms, S(5) and C(19), could not be resolved and were refined as a single atom; for the latter, the methyl group bound to sulfur was not located. The major position only is shown in Figure 1b.

In compound **29** (Figure 1d), one of the ethylthio substituents is disordered over two positions, S(6)C(19)C(20) and S(6′)C(19′)C(20′); their occupancies were refined to 61.2 and 38.8(2)%, respectively. The conformation ($\phi$ = 40.6, $\theta$ = 79.1°) is practically identical with that of **12**. The packing motif is similar to that of **12** and **14**, but here the ethylthio (rather than the methyl) groups enter the intramolecular cavity of the opposing molecule (Figure 2b).

The asymmetric unit of **28** comprises two title molecules (A and B) and one severely disordered molecule of $CDCl_3$. Both molecules A and B have essentially planar S(1)C(1)S(2)S(3)C(2)C(3) systems, which form dihedral angles of 90.4° (A) and 94.1° (B) with the S(6)C(6)C(7)S(7) moieties. Folding of the anthracene system along the C(10)···C(11) axis is unequal (35.9° in A *vs.* 45.2° in B),

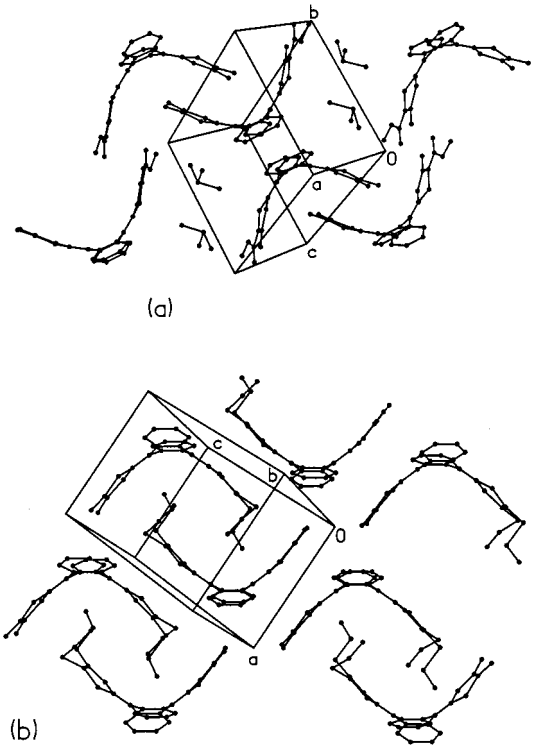



Figure 2. Crystal packing of **12** (a) and **29** (b); the disorder and H atoms are not shown.

while folding along the S(4)···S(5) vector is of the opposite sense (13.7° outward in A, *vs.* 7.6° inward in B). The crystal packing of **28** (Figure 3) is rather dissimilar from that of the other compounds studied herein. 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 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[21] S···S 3.60 and C···S 3.61 Å. Thus, 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(2A)···S(2B) 3.66 Å and S(2A)···S(4B) 3.49 Å. However, no *continuous* stacks exist in the structure, and the aforementioned BAA′B′ stack is 'underpinned' at either end by the thione C(1A)=S(1A) bond of another A molecule. This bond is aligned perpendicular to the stacked planes and points towards the midpoint of the C(1B)−S(3B) bond [S(1A)···S(3B) 3.52 Å, S(1A)···C(1B) 3.45 Å]. On the other hand, 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. Thereby, S(3A) forms extremely short contacts with C(6B) and C(7B)

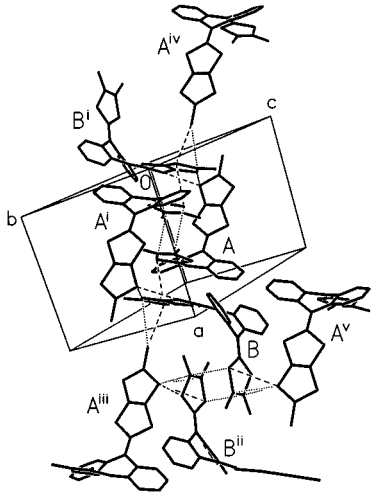



Figure 3. Crystal packing of **28**, showing intermolecular contacts S···S (dashes) and S···C (dots) shorter than 3.7 Å. The molecules shown are related to the parent ones (A and B) by symmetry operations: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $3 - x$, $-y$, $-z$; (iii) $x + 1$, $y$, $z - 1$; (iv) $-x$, $1-y$, $2-z$; (v) $2 - x$, $-y$, $1 - z$. Disordered $CDCl_3$ molecules are omitted.

(3.29 Å each), as well as rather close ones with S(6B) and S(7B) (3.61 and 3.62 Å respectively).

In all four compounds, the two outer rings of the anthracene moiety retain their aromatic character. The exocyclic C=C bond lengths [average 1.35(1), 1.366(3), 1.358(6), and 1.361(3), for **12**, **14**, **28**, and **29**, respectively] are common for dithiolene groups.

## Conclusion

Two routes have been developed to gain access to derivatives of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system which contain a "reactive handle" suitable for further chemical elaboration. The availability of these new derivatives in synthetically-useful quantities paves the way for the development of this very interesting strained ring system as a redox-active building block in supramolecular and materials chemistry.

## Experimental Section

$^1$H- and $^{13}$C-NMR spectra were obtained on Oxford 200, Varian Unity 300 and Varian VXR 400S spectrometers operating at 199.992 ($^1$H) and 50.293 ($^{13}$C), 299.908 ($^1$H) and 75.420 ($^{13}$C), and 400.0 ($^1$H) and 100.6 ($^{13}$C) MHz, respectively. − Mass spectra were recorded on a Micromass Autospec spectrometer operating at 70 eV. − Infrared spectra were recorded using a golden gate on a Paragon 1000 FTIR spectrometer operated from a Grams Analyst 1600. − Electronic absorption spectra were obtained using a Perkin−Elmer II UV/Vis spectrophotometer operating with 1 mL quartz cells. − Melting points were obtained on a Philip Harris melting point apparatus and are uncorrected. − All reagents were of commercial quality; solvents were dried using standard procedures. − All reactions were performed under an inert atmosphere of argon in pre-dried glassware. − Cyclic voltammetric data were measured

with iR compensation using a BAS CV50 electrochemical analyser. The experiments were carried out with 5 mL of a ca. $10^{-4}$ M solution of the compound in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, puriss, electrochemical grade) as the supporting electrolyte, at scan rate 100 mV $s^{-1}$. The oxidation potentials (which represent a two-electron process) were measured *versus* a platinum wire quasi-reference electrode and corrected *versus* decamethylferrocene/decamethylferrocenium$^+$ by adding decamethylferrocene to the studied solution after the experiment, and referenced *versus* Ag/AgCl.[22]

**4-Methyl-2-piperidino-1,3-dithiole (4):** To a stirred suspension of salt **3**[23] (75.0 g, 217 mmol) in dry tetrahydrofuran/2-propanol (1:1 v/v, 1.0 L) at 0°C, finely-ground sodium borohydride (37.8 g, 1.0 mol) was added in portions over ca. 6 h. The reaction was then maintained at 0°C for a further 2 h, whereupon it was allowed to warm to room temperature and stirred for a further 40 h. After concentrating to ca. 150 mL, water (500 mL) was added cautiously and the mixture extracted with diethyl ether (4 × 125 mL). The combined extracts were washed with water (3 × 125 mL), dried ($MgSO_4$) and evaporated in vacuo to afford compound **4** (40.6 g, 93%) as a yellow oil of high purity ($^1$H-NMR analysis) suitable for use in the next step without further purification. – $^1$H NMR ($CDCl_3$): δ = 1.41 (m, 2 H), 1.53 (m, 4 H), 2.02 (s, 3 H), 2.49 (t, *J* = 5.2 Hz, 4 H), 5.72 (s, 1 H), 6.18 (s, 1 H).

**4-Methyl-1,3-dithiolium Iodide (5):** To an ice-cooled, stirred solution of acetic anhydride (260 mL) was cautiously added hexafluorophosphoric acid (60 wt% in water, 115.0 g, 0.788 mol) over ca. 2 h. (**CAUTION**: vigorous exothermic reaction!). To the ice-cooled solution of anhydrous hexafluorophosphoric acid thus formed, was added dropwise over ca. 0.5 h a solution of compound **4** (38.0 g, 189 mmol) in dry diethyl ether (250 mL), precipitating immediately the salt **5**. The mixture was diluted with dry diethyl ether (250 mL), stirred for a further 0.5 h, and the product was collected by filtration and washed with diethyl ether (125 mL) affording hexafluorophosphate salt **5** as an off-white solid. Purification was achieved by anion exchange to the iodide salt. To a stirred solution of the hexafluorophosphate salt in anhydrous acetone (125 mL) at 20°C was added a solution of sodium iodide (28.3 g, 189 mmol) in anhydrous acetone (50 mL) to precipitate iodide salt **5** as a bright yellow solid, which was collected by filtration and washed initially with cold anhydrous acetone (25 mL) and then anhydrous diethyl ether (100 mL) to afford 40.6 g (88%) of **5**, m.p. 98–101°C. – $^1$H NMR [$(CD_3)_2SO$]: δ = 2.91 (s, 3 H), 9.09 (s, 1 H), 11.47 (s, 1H). – This salt can be stored under argon for 1 month or in a sealed ampule for several months without any observable decomposition.

**Dimethyl (4-Methyl-1,3-dithiol-2-yl)phosphonate (6):** To a stirred suspension of salt **5** (500 mg, 2.05 mmol) in dry acetonitrile (100 mL) at 20°C, was added trimethyl phosphite (0.28 mL, 2.37 mmol) and the mixture was stirred for 1 h. The solvent was evaporated in vacuo to afford compound **6** (460 mg, 99%) as a light brown oil of high purity ($^1$H-NMR analysis) suitable for use in the next step without further purification. – $^1$H NMR ($CDCl_3$): δ = 1.95 (s, 3 H), 3.89 (d, *J* = 10.5 Hz, 6 H), 4.97 (d, *J* = 4.2 Hz, 1 H), 5.53 (s, 1 H ).

**9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-10-(4-methyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (8):** Into a solution of reagent **6** (465 mg, 2.05 mmol) in dry tetrahydrofuran (150 mL) at –78°C, was added lithium diisopropylamide (1.5 mL of 1.5 M solution in cyclohexane, 2.25 mmol) over a period of 15 min. The reaction was stirred for 3 h at –78°C until a pale cloudy solution formed. Then compound **7**[2b] (725 mg, 2.25 mmol) was added portionwise over 15 min. The reaction was stirred overnight at 20°C. The reaction mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as eluent to afford **8** as a yellow solid (474 mg, 55%). M.p. 288–290°C (from hexane/dichloromethane). – $^1$H NMR ($CDCl_3$): δ = 2.02 (s, 6 H), 2.14 (s, 3 H), 5.93 (s, 1 H), 7.36 (m, 4 H), 7.75 (m, 4 H). – $^{13}$C NMR ($CDCl_3$): δ = 13.8, 15.9, 111.0, 120.8, 121.2, 122.1, 125.1, 125.3, 125.7, 129.3, 133.0, 135.1, 135.2, 136.0. – UV (MeCN): $\lambda_{max}$ (lg ε) = 360 nm (4.18), 430 (4.43). – CV: $E^{ox}$ = 0.320 V. – MS (EI); *m/z* (%): 422 (37) [M$^+$], 149 (50), 84 (100). – HRMS: $C_{23}H_{18}S_4$ (422.6): calcd. 422.0359; found 422.0359.

**9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-10-(4-formyl-5-methyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (10):** Into a solution of **8** (159 mg, 0.376 mmol) in dry tetrahydrofuran (50 mL) at –78°C, was added lithium diisopropylamide (0.26 mL of 1.5 M solution in cyclohexane, 0.39 mmol). The reaction was stirred for 3 h at –78°C to give a yellow solution containing anion **9**. *N,N*-Dimethylformamide (0.055 mL, 0.71 mmol) was then added and the reaction was stirred overnight at 20°C. The reaction mixture was acidified with HCl (1 M), and then extracted into dichloromethane (3 × 100 mL). The organic layer was separated and dried ($MgSO_4$) and evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as the eluent to afford **10** as an orange solid (22 mg, 13%). M.p. 160°C (dec.). – $^1$H NMR ($CDCl_3$): δ = 1.93 (s, 6 H), 2.40 (s, 3 H), 7.26 (m, 4 H), 7.64 (m, 4 H), 9.67 (s, 1 H). – IR (powder): $\tilde{\nu}$ = 1635 (C=O) $cm^{-1}$. – UV (MeCN): $\lambda_{max}$ (lg ε) = 358 nm (3.90), 422 (4.08). – CV: $E^{ox}$ = 0.450 V. – MS (EI); *m/z* (%): 450 (100) [M$^+$], 306 (63), 252 (31). – HRMS: $C_{24}H_{18}OS_4$ (450.6): calcd. 450.0308; found 450.0308.

**9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-10-(5-methyl-4-methylthiocarbamoyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (11):** Into a solution of **8** (102 mg, 0.241 mmol) in dry tetrahydrofuran (50 mL) at –78°C was added lithium diisopropylamide (0.17 mL of 1.5 M solution in cyclohexane, 2.55 mmol). The reaction was stirred for 3 h, then methyl isothiocyanate (0.10 mL, 1.46 mmol) was added and the reaction was stirred overnight at 20°C. Workup and purification as described for **10**, gave **11** as an orange solid (20 mg, 17%). M.p. 197–200°C. – $^1$H NMR ($CDCl_3$): δ = 1.92 (s, 6 H), 2.03 (s, 3 H), 2.99 (d, 3 H, *J* = 4.8 Hz), 7.30 (m, 4 H), 7.52 (m, 2 H), 7.66 (m, 2 H), (NH not observed). – $^{13}$C NMR ($CDCl_3$): δ = 13.1, 15.0, 32.6, 120.9, 125.3, 125.3, 125.5, 125.6, 125.8, 125.9, 126.2, 127.3, 129.3, 131.1, 134.0, 134.3, 134.4, 135.1. – UV (MeCN): $\lambda_{max}$ (lg ε) = 362 nm (4.11), 430 (4.32). – CV: $E^{ox}$ = 0.365 V. – MS (EI); *m/z* (%): 495 (100) [M$^+$], 447 (36), 350 (40). – HRMS: $C_{25}H_{21}NS_5$ (495.8): calcd. 495.0362; found 495.0362.

**9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-10-(4-methoxycarbonyl-5-methyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (12):** Into a solution of **8** (504 mg, 1.19 mmol) in dry tetrahydrofuran (150 mL) at –78°C was added lithium diisopropylamide (0.87 mL of 1.5 M solution in cyclohexane, 1.30 mmol) over a period of 15 min. The reaction was stirred for 3 h, then methyl chloroformate (0.27 mL, 3.54 mmol) was added over 15 min and the reaction was stirred overnight at 20°C. Workup and purification as described for **10**, with hexane/dichloromethane (3:1 v/v) as eluent, afforded **12** as a yellow solid (475 mg, 83%). M.p. 218–220°C. – $^1$H NMR ($CDCl_3$): δ = 1.83 (s, 6 H), 2.28 (s, 3 H), 3.69 (s, 3 H), 7.20 (m, 4 H), 7.51 (m, 2 H), 7.57 (m, 2 H). – $^{13}$C NMR ($CDCl_3$): δ = 13.4, 15.7, 52.4, 117.2, 121.0, 121.2, 123.7, 125.4, 125.5, 125.7, 125.9, 126.1, 126.4, 129.5, 134.2, 134.8, 135.5, 145.8, 160.9. – IR (powder): $\tilde{\nu}$ = 1714 (C=O) $cm^{-1}$. – UV (MeCN): $\lambda_{max}$ (lg ε) = 358 nm (4.18), 426 (4.40). – CV: $E^{ox}$ = 0.425 V. – MS (EI); *m/z* (%): 480 (100) [M$^+$], 306 (37), 175 (35). – $C_{25}H_{20}O_2S_4$ (480.0): calcd. C

62.47, H 4.19; found C 62.40, H 4.12. − Crystals for X-ray analysis were grown from $CDCl_3$.

**9-(4-Benzoylsulfanyl-5-methyl-1,3-dithiol-2-ylidene)-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (13):** Into a solution of compound **8** (199 mg, 0.471 mmol) in dry tetrahydrofuran (50 mL) at −78°C was added lithium diisopropylamide (0.38 mL of 1.5 M solution in cyclohexane, 0.57 mmol) over a period of 15 min. The reaction was stirred for 3 h at −78°C. Finely-powdered elemental sulfur (78 mg, 2.37 mmol) was added and the reaction was stirred for a further 2 h at −78°C before benzoyl chloride (0.275 mL, 2.37 mmol) was added. The colour of the solution turned darker yellow, and the reaction was stirred overnight at 20°C. Workup and purification as described for **12**, gave **13** as a yellow solid (138 mg, 53%). M.p. 160°C (dec.). − $^1$H NMR ($CDCl_3$): δ = 1.84 (s, 6 H), 1.97 (s, 3 H), 7.19 (m, 4 H), 7.39 (t, *J* = 7.5 Hz, 2 H), 7.53 (m, 5 H), 7.86 (d, *J* = 7.9 Hz, 2 H). − $^{13}$C NMR ($CDCl_3$): δ = 13.1, 14.9, 108.1, 120.8, 120.9, 121.0, 123.0, 125.1, 125.2, 125.4, 125.5, 125.7, 125.8, 126.0, 126.1, 126.8, 126.9, 131.3, 133.9, 134.2, 134.7, 134.9, 135.3, 135.4, 135.7, 139.3, 187.7. − IR (powder): $\tilde{\nu}$ = 1737 (C=O) $cm^{-1}$. − UV (MeCN): $\lambda_{max}$ (lg ε) = 364 nm (4.16), 430 (4.38). − CV: $E^{ox}$ = 0.420 V. − MS (EI); *m/z* (%): 558 (5) [$M^+$], 84 (100), 64 (71). − $C_{30}H_{22}OS_5$ (558.0): calcd. C 64.48, H 3.97; found C 64.29, H 4.25.

**9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-10-(4-methylsulfanyl-5-methyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (14):** Into a solution of compound **13** (97 mg, 0.174 mmol) in dry tetrahydrofuran (35 mL) at 20°C was added sodium methoxide (0.39 mL of 0.5 M solution in methanol, 0.195 mmol). The reaction was stirred for 1 h until a dark red solution formed. Then iodomethane was added (0.10 mL, 1.61 mmol) and the reaction was stirred overnight at 20°C. The reaction mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as eluent to afford **14** as a yellow solid (65 mg, 80%). M.p. 220°C (dec.). − $^1$H NMR ($CDCl_3$): δ = 1.86 (s, 6 H), 2.03 (s, 3 H), 2.20 (s, 3 H), 7.20 (m, 4 H), 7.51 (m, 2 H), 7.59 (m, 2 H). − $^{13}$C NMR ($CDCl_3$): δ = 13.1, 14.5, 19.3, 118.3, 120.8, 125.2, 125.3, 125.4, 125.6, 125.8, 125.9, 132.0, 134.8, 135.0, 135.2, 197.9. − UV (MeCN): $\lambda_{max}$ (lg ε) = 360 nm (3.89), 432 (4.38). − CV: $E^{ox}$ = 0.355 V. − MS (EI); *m/z* (%): 468 (100) [$M^+$], 350 (50), 57 (60) − $C_{24}H_{20}S_5$ (468.0): calcd. C 61.50, H 4.30; found C 61.30, H 4.26. − Crystals for X-ray analysis were grown from $CS_2/CH_2Cl_2$.

**9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-10-[4-(6-hydroxyhexylsulfanyl)-5-methyl-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene (15):** Into a solution of compound **13** (100 mg, 0.179 mmol) in dry tetrahydrofuran (50 mL) at 20°C was added sodium methoxide (0.39 mL of 0.5 M solution in methanol, 0.195 mmol). The reaction was left for 1 h before 6-bromohexan-1-ol was added (0.07 mL, 0.535 mmol), and the reaction was stirred overnight at 20°C. The reaction mixture was evaporated in vacuo and excess 6-bromohexan-1-ol was removed by Kügelrohr distillation at 140°C at ca. 0.1 Torr, and the distillate was discarded. The residue was purified by column chromatography on silica gel with ethyl acetate/dichloromethane (1:4 v/v) as eluent to afford **15** as a red oil (93 mg, 93%). − $^1$H NMR ($CDCl_3$): δ = 1.37 (m, 4 H), 1.55 (m, 4 H), 1.92 (s, 6 H), 2.09 (s, 3 H), 2.66 (m, 2 H), 3.60 (t, *J* = 6.6 Hz, 2 H), 7.26 (m, 4 H), 7.58 (m, 2 H), 7.64 (m, 2 H), (OH not observed). − $^{13}$C NMR ($CDCl_3$): δ = 13.1, 14.7, 25.2, 28.1, 28.9, 29.6, 32.5, 35.9, 62.8, 117.1, 120.8, 122.3, 125.2, 125.3, 125.6, 125.8, 125.8, 125.9, 131.3, 133.0, 133.1, 134.8, 135.0, 135.2. − UV (MeCN): $\lambda_{max}$ (lg ε) = 366 nm (4.14), 432 (4.39). − CV: $E^{ox}$ = 0.380 V. − MS (EI); *m/z* (%): 554 (100) [$M^+$], 350 (76), 220 (31). − HRMS: $C_{29}H_{30}OS_5$ (554.9): calcd. 554.0985; found 554.0985.

**(2-Cyanoethylsulfanyl)-2-methylsulfanyl-4-5-methylthio-1,3-dithiolium Trifluoromethylsulfonate (17):** Into a solution of thione **16**[15a] (1.029 g, 4.10 mmol) in dry dichloromethane (100 mL) at 20°C, was added methyl trifluoromethylsulfonate (0.90 mL, 7.97 mmol). The reaction was left for 1 h until a dark yellow solution formed. The reaction mixture was concentrated in vacuo to ca. 10 mL and the resulting suspension washed with dry diethyl ether (50 mL) which was then decanted off and discarded. The reaction mixture was then evaporated in vacuo affording **17** as an unstable red oil which was quickly used without further purification. − $^1$H NMR ($CDCl_3$): δ = 2.85 (s, 3 H), 2.92 (t, *J* = 6.6 Hz, 2 H), 3.22 (s, 3 H), 3.33 (t, *J* = 6.4 Hz, 2 H).

**10-[4-(2-Cyanoethylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-anthracene-9-(10*H*)-one (20):** Into a solution of anthrone **18** (773 mg, 3.98 mmol) in dry 2-propanol (50 mL) at 20°C was added lithium diisopropylamide (2.65 mL, of 1.5 M solution in cyclohexane, 3.98 mmol). The reaction was stirred for 15 min until a bright yellow solution formed. Then salt **17** (1.653 g, 3.98 mmol) in dry tetrahydrofuran (50 mL) was added and the reaction mixture was stirred overnight. The mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (1:1 v/v) as the eluent to afford crude compound **19** as a red solid. [$^1$H NMR ($CDCl_3$): δ = 2.00 (s, 3 H), 2.26 (s, 3 H), 2.47 (m, 2 H), 2.73 (m, 2 H), 4.91 (s, 1 H), 7.51 (m, 4 H), 7.69 (m, 2 H), 8.15 (m, 2 H)]. This solid (398 mg, 0.889 mmol) was dissolved in dry toluene (100 mL) at 20°C and *p*-toluene sulfonic acid (100 mg, 0.526 mmol) was added. The reaction mixture was refluxed for 16 h to give a dark red solution. The mixture was evaporated in vacuo and the residue purified by column chromatography on silica gel with dichloromethane as eluent to afford **20** as a red solid (293 mg, 18% based on **16**). M.p. 142−145°C. − $^1$H NMR ($CDCl_3$): δ = 2.04 (s, 3 H), 2.24 (t, *J* = 6.8 Hz, 2 H), 2.58 (t, *J* = 6.8 Hz, 2 H), 7.04 (t, *J* = 7.8 Hz, 2 H), 7.26 (m, 4 H), 7.85 (d, *J* = 7.4 Hz, 2 H). − $^{13}$C NMR ($CDCl_3$): δ = 18.7, 18.1, 31.3, 117.4, 119.6, 120.3, 126.1, 127.2, 127.3, 130.7, 131.9, 134.1, 138.2, 138.4, 183.4. − IR (powder): $\tilde{\nu}$ = 1635 (C=O) $cm^{-1}$. − MS (EI); *m/z* (%): 425 (61) [$M^+$], 236 (100), 91 (66). − $C_{21}H_{15}NOS_4$ (425.6): calcd. C 59.27, H 3.55; found C 59.51, H 3.70.

**10-[4-(6-Hydroxyhexylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]anthracene-9-(10*H*)-one (21):** Into a solution of **20** (200 mg, 0.471 mmol) in dry tetrahydrofuran (50 mL) at 20°C was added cesium hydroxide monohydrate (94 mg, 0.528 mmol). The reaction was stirred for 1 h until a dark red solution formed. 6-Bromohexan-1-ol (0.2 mL, 1.53 mmol) was added and the reaction was stirred overnight at 20 °C then evaporated in vacuo and excess 6-bromohexan-1-ol was removed by Kügelrohr distillation at 140°C at ca. 0.1 Torr, and the distillate was discarded. The residue was purified by column chromatography on silica gel with hexane/dichloromethane (1:1 v/v) as eluent to afford **21** as a red oil (198 mg, 89%). − $^1$H NMR ($CDCl_3$): δ = 1.47 (m, 8 H), 2.41 (s, 3 H), 2.79 (t, *J* = 7.2 Hz, 2 H), 3.60 (t, *J* = 7.2 Hz, 2 H), 7.44 (t, *J* = 7.8 Hz, 2 H), 7.65 (t, *J* = 7.8 Hz, 2 H), 7.77 (d, *J* = 7.8 Hz, 2 H), 8.26 (d, *J* = 7.8 Hz, 2 H). − $^{13}$C NMR ($CDCl_3$): δ = 19.2, 25.1, 28.0, 29.4, 32.4, 36.2, 62.6, 119.0, 125.1, 126.1, 127.1, 127.6, 129.0, 130.5, 131.8, 138.5, 140.3, 183.4. − IR (Powder): $\tilde{\nu}$ = 1649 (C=O) $cm^{-1}$. − MS (EI); *m/z* (%): 472 (100) [$M^+$], 236 (58), 55 (79). − HRMS: $C_{24}H_{24}O_2S_4$ (472.7): calcd. 472.0659; found 472.0644.

**10-[4-(6-*tert*-Butyldiphenylsilyloxyhexylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]anthracene-9-(10*H*)-one (22):** Into a solution of compound **21** (305 mg, 0.646 mmol) in dry dimethylformamide (50 mL) was added *tert*-butylchlorodiphenylsilane (0.18 mL, 0.692 mmol) and imidazole (345 mg, 5.07 mmol). The reaction was

stirred overnight at 20°C and then evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (1:1 v/v) as eluent to afford **22** as a red oil (413 mg, 90%). – $^1$H NMR ($CDCl_3$): δ = 1.06 (s, 9 H), 1.37 (m, 4 H), 1.55 (m, 4 H), 2.40 (s, 3 H), 2.79 (t, *J* = 7.6 Hz, 2 H) 3.65 (t, *J* = 6.4 Hz, 2 H), 7.42 (m, 8 H), 7.67 (m, 6 H), 7.79 (m, 2 H), 8.29 (d, *J* = 7.6 Hz, 2 H). – $^{13}$C NMR ($CDCl_3$): δ = 19.5, 25.6, 27.2, 28.4, 29.8, 32.6, 36.7, 64.0, 119.3, 125.6, 126.5, 127.5, 127.9, 129.3, 129.8, 130.9, 130.9, 132.1, 134.3, 135.8, 138.9, 140.7, 183.7. IR (Powder): $\tilde{\nu}$ = 1653 (C=O) cm$^{-1}$. – MS (EI); *m/z* (%): 710, (100) [M$^+$], 653 (99), 135 (79). – HRMS: $C_{40}H_{42}O_2S_4Si$ (711.1): calcd. 710.1904; found 710.1902.

**9-[4-(6-*tert*-Butyldiphenylsilyloxyhexylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (24):** Into a solution of **23**[2b] (117 mg, 0.488 mmol) in dry tetrahydrofuran (150 mL) at −78°C was added lithium diisopropylamide (0.34 mL of 1.5 M solution in cyclohexane, 0.506 mmol) over a period of 15 min. The reaction was stirred for 3 h until a pale cloudy solution formed. Then compound **22** (171 mg, 0.241 mmol) was added over 15 min and the reaction was stirred overnight at 20°C and then evaporated in vacuo and the residue purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as eluent to afford **24** as a yellow oil (138 mg, 70%). – $^1$H NMR ($CDCl_3$): δ = 1.05 (s, 9 H), 1.36 (m, 4 H), 1.56 (m, 4 H), 1.93 (s, 6 H), 2.36 (s, 3 H), 2.76 (m, 2 H), 3.65 (t, *J* = 6.6 Hz, 2 H), 7.30 (m, 4 H), 7.41 (m, 6 H), 7.54 (m, 2 H), 7.66 (m, 6 H). – $^{13}$C NMR ($CDCl_3$): δ = 13.1, 19.2, 25.3, 26.9, 28.1, 29.6, 31.6, 32.3, 34.6, 36.2, 63.7, 120.8, 120.9, 123.7, 124.2, 125.8, 126.1, 127.6, 129.5, 130.4, 133.5, 134.0, 134.6, 135.2, 135.5. – MS (EI); *m/z* (%): 824 (100) [M$^+$], 350 (89), 220 (66). – HRMS: $C_{45}H_{48}OS_6Si$ (825.3): calcd. 824.1900; found 824.1900.

**9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-10-[4-(6-hydroxyhexylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene (25):** Into a solution of compound **24** (137 mg, 0.167 mmol) in dry tetrahydrofuran (50 mL) was added tetrabutylammonium fluoride (0.5 mL of 1.0 M solution in water, 0.5 mmol). After stirring for 1 h at 20°C a dark red solution had formed. The reaction mixture was stirred at 20°C overnight and then evaporated in vacuo and the residue was purified by column chromatography on silica gel with dichloromethane as eluent to afford **25** as a yellow oil (77 mg, 79%). – $^1$H NMR ($CDCl_3$): δ = 1.39 ( m, 4 H), 1.56 (m, 4 H), 1.93 (s, 6 H), 2.37 (s, 3 H), 2.77 (m, 2 H), 3.61 (t, *J* = 6.5 Hz, 2 H), 4.35 (t, *J* = 7.0 Hz, 1 H), 7.28 (m, 4 H), 7.52 (m, 2 H), 7.66 (m, 2 H). – $^{13}$C NMR ($CDCl_3$): δ = 13.1, 19.1, 25.2, 28.1, 29.6, 32.5, 36.0, 60.4, 62.8, 120.9, 123.8, 124.0, 125.3, 125.7, 126.1, 127.7, 130.2, 133.5, 134.5, 135.2. – MS (EI); *m/z* (%): 586 (21) [M$^+$], 350 (100), 220 (100). – HRMS: $C_{29}H_{30}OS_6$ (586.9): calcd. 586.0621; found 586.0634.

**9-[4-(6-Benzoyloxyhexylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (26):** Into a solution of compound **25** (74 mg, 0.127 mmol) in dry dichloromethane (50 mL) was added triethylamine (1 mL, excess) and benzoyl chloride (0.20 mL, 1.72 mmol). The reaction was stirred overnight at 20 °C and then evaporated in vacuo and the residue purified initially by column chromatography on silica gel with hexane/dichloromethane (1:1 v/v) as eluent, and then further purified by column chromatography on silica gel with acetone/hexane (1:3 v/v) as eluent to afford **26** as a yellow oil (44 mg, 50%). – $^1$H NMR ($CDCl_3$): δ = 1.38 (m, 4 H), 1.56 (m, 2 H), 1.67 (m, 2 H), 1.84 (s, 6 H), 2.28 (s, 3 H), 2.70 (m, 2 H), 4.21 (t, *J* = 6.5 Hz, 2 H), 7.20 (m, 4 H), 7.35 (t, *J* = 8.0 Hz, 2 H), 7.45 (m, 3 H), 7.59 (m, 2 H), 7.95 (d, *J* = 8.5 Hz, 2 H). $^{13}$C NMR ($CDCl_3$): δ = 13.1, 19.1, 25.6, 28.0, 28.5, 29.5, 36.0, 64.9, 120.8, 120.9, 123.8, 123.9, 125.3, 125.3, 125.8, 126.1, 127.9, 128.3, 129.5, 130.2, 130.4, 132.8, 133.5, 134.6, 135.2, 166.6. – UV (MeCN): $\lambda_{max}$ (lg ε) = 366 nm (4.09), 434 (4.33). – CV: $E^{ox}$ = 0.375 V. – MS (DCI); *m/z* (%): 691 (49) [M$^+$+1], 322 (100), 105 (63). – HRMS: $C_{36}H_{34}O_2S_6$ (691.0): calcd. 690.0985; found 690.0988.

Table 1. Crystal data

| Compound | **12** | **14** | **28** | **29** |
|---|---|---|---|---|
| Formula | $C_{25}H_{20}O_2S_4 \cdot CDCl_3$ | $C_{24}H_{20}S_5$ | $C_{23}H_{14}S_7 \cdot 0.5\ CDCl_3$ | $C_{26}H_{24}S_6$ |
| Molecular mass | 601.02 | 468.7 | 575.44 | 528.81 |
| *T* [K] | 293 | 120 | 150 | 150 |
| Crystal system | triclinic | triclinic | triclinic | triclinic |
| Space group | *P*$\bar{1}$ (No. 2) | *P*$\bar{1}$ (No. 2) | *P*$\bar{1}$ (No. 2) | *P*$\bar{1}$ (No. 2) |
| *a* [Å] | 9.656(1) | 9.077(1) | 11.682(1) | 9.673(1) |
| *b* [Å] | 11.290(1) | 10.287(1) | 13.483(1) | 9.793(1) |
| *c* [Å] | 13.238(1) | 12.014(1) | 17.716(1) | 13.159(1) |
| α [°] | 94.27(1) | 84.79(1) | 79.481(4) | 98.34(1) |
| β [°] | 106.21(1) | 87.92(1) | 71.432(4) | 90.36(1) |
| γ [°] | 96.56(1) | 76.02(1) | 69.885(4) | 93.09(1) |
| *U* [Å$^3$] | 1368.1(2) | 1084.0(2) | 2475.3(2) | 1231.4(2) |
| *Z* | 2 | 2 | 4 | 2 |
| μ(Mo-$K_\alpha$) [mm$^{-1}$] | 0.66 | 0.54 | 0.81 | 0.57 |
| $D_x$ [g cm$^{-3}$] | 1.46 | 1.44 | 1.54 | 1.43 |
| $2\theta_{max}$ [°] | 50 | 55 | 61 | 55 |
| Crystal size [mm] | 0.48×0.26×0.02 | 0.30×0.10×0.08 | 0.25×0.20×0.06 | 0.48×0.24×0.04 |
| Reflections measured | 8191 | 7879 | 19705 | 8965 |
| Unique reflections | 4809 | 4910 | 12778 | 5532 |
| Absorption correction | N/A | Integration | Semi-empirical | Integration |
| Transmission min, max | 0.757, 0.983 | 0.885, 0.966 | 0.786, 0.908 | 0.825, 0.979 |
| $R_{int}$ | 0.166 | 0.028 | 0.031 | 0.022 |
| Reflections with $I \geq 2\sigma(I)$ | 1835 | 3887 | 8252 | 4751 |
| Refined variables | 339 | 306 | 653 | 377 |
| $R[F^2 \geq 2\sigma(F^2)]$ | 0.102 | 0.042 | 0.067 | 0.042 |
| Goodness-of-fit | 1.00 | 1.03 | 1.13 | 1.17 |
| $wR(F^2)$, all data | 0.347 | 0.101 | 0.175 | 0.113 |
| $\Delta\rho_{max,min}$ [eÅ$^{-3}$] | 0.85, −0.59 | 0.42, −0.31 | 1.14, −0.95 | 0.40, −0.35 |

**9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-10-[(5-thio-1,3-dithiolo[4,5-*d*][1,3]dithiol-2-ylidene]-9,10-dihydroanthracene (28):** Into a solution of **27**[16] (216 mg, 0.63 mmol) in dry tetrahydrofuran (50 mL) at −78 °C, was added lithium diisopropylamide (0.46 mL of 1.5 M solution in cyclohexane, 0.69 mmol) over a period of 15 min. The mixture was stirred at −78 °C for 3 h until a dark red solution formed. Then compound **7** (198 mg, 0.61 mmol) was added over 15 min and the mixture was stirred overnight at 20 °C. The reaction mixture was evaporated in vacuo and the residue purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as eluent to afford **28** as a red solid (189 mg, 60%). M.p. 246−249 °C. − $^1$H NMR ($CDCl_3$): δ = 1.93 (s, 6 H), 7.27 (t, *J* = 7.6 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.42 (d, *J* = 7.6 Hz, 2 H), 7.71 (d, *J* = 7.6 Hz, 2 H). − $^{13}$C NMR ($CDCl_3$): δ = 13.1, 29.7, 119.8, 121.0, 122.3, 125.2, 125.5, 125.8, 127.1, 128.8, 130.8, 133.7, 135.2, 135.9, 211.7. − CV: $E^{ox}$ = 0.430 V. − MS (EI); *m*/*z* (%): 514 (82) [$M^+$], 350 (100), 220 (82). − $C_{23}H_{14}S_7$ (514.8): calcd. C 53.66, H 2.74; found C 53.80, H 3.19. − Crystals for X-ray analysis were grown from $CDCl_3$.

**9-(4,5-Diethylsulfanyl-1,3-dithiol-2-ylidene)-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (29):** A solution of **28** (102 mg, 0.20 mmol) in triethylphosphite (10 mL) was heated at reflux for 3 h to give a pale orange solution. The reaction mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as eluent to afford **29** as a yellow solid (46 mg, 50%). M.p. 255−258 °C. − $^1$H NMR ($CDCl_3$): δ = 1.22 (t, *J* = 7.4 Hz, 6 H), 1.87 (s, 6 H), 2.75 (m, 4 H), 7.21 (m, 4 H), 7.47 (m, 2 H), 7.60 (m, 2 H). − CV: $E^{ox}$ = 0.345 V. − MS (EI); *m*/*z* (%): 528 (14) [$M^+$], 350 (45), 468 (38). − HRMS $C_{26}H_{24}S_6$ (528.8): calcd. 528.0304; found 528.0304. Crystals for X-ray analysis were grown from $CDCl_3$.

**X-ray Crystallography:** Single-crystal X-ray diffraction experiments were carried out with a SMART 1 K CCD area detector mounted on a 3-circle diffractometer, using graphite monochromated Mo-$K_\alpha$ radiation (λ = 0.71073 Å). The data collection nominally covered over a hemisphere of reciprocal space,[24] by a combination of 4 sets of ω scans (each scan 0.3°), each set at different ϕ and/or 2θ angles. Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow $N_2$ gas cryostat.[25] Reflection intensities were integrated using SAINT software[24] and corrected for absorption by semi-empirical method (SADABS program[26]) based on multiple measurements of identical reflections and Laue equivalents (for **28**) or by numerical integration (SHELXTL programs[27]) based on real shape of the crystal (for **14** and **29**). No absorption correction was applied for **12**. The structures were solved by direct methods and refined by full-matrix least squares against $F^2$ of all data, using SHELXTL software.[27] Non-H atoms were refined in anisotropic approximation and H atoms in isotropic one, except for disordered groups, where constrained refinement was used. In **12** and **28**, the complex disorder of $CDCl_3$ molecules of crystallisation was only imperfectly approximated, hence the high residual electron density. Crystal data and experimental details are listed in Table 1. Atomic coordinates and thermal parameters, bond lengths and angles for compounds **12**, **14**, **28**, and **29** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-116300 to −116303, respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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