Hydroxymethyl-Functionalised 9,10-Bis(1,3-dithiol-2-ylidene)-9,10-Dihydroanthracene π-Electron Donors as Synthetic Intermediates for Supramolecular Structures[‡]

Nicolas Godbert,[a] Martin R. Bryce,*[a] Slimane Dahaoui,[a] Andrei S. Batsanov,[a]
Judith A. K. Howard,[a] and Paul Hazendonk[a]

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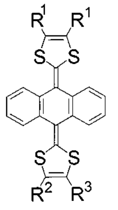
The synthesis of new derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene is reported. ^{1}H NMR studies on compound **4** are consistent with two conformers of the saddle-shaped molecule which interconvert by a boat–boat flipping of the central ring at high temperature. The hydroxymethyl substituent of **4** is readily esterified to yield the benzoyl and 2-naphthaloyl ester derivatives **5a** and **5b**, respectively, and the dimer and the trimer structures **6** and **7**, respectively, by reaction with benzoyl chloride, 2-naphthaloyl chloride, 1,4-benzenedicarbonyl chloride and 1,3,5-benzenetricarbonyl chloride. Deprotonation of 9-(4,5-dimethyl-1,3-dithiol-2-ylidene)-10-(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene **(8)** using lithium bis(trimethylsilyl) amide (LHMDS) followed by in situ quenching of the lithiated intermediate with methylchloroformate gave the diester derivative **10** (96% yield), whereas using LDA gave the monoester **9** as the major product (32% yield). Diester **10** was reduced to the di(hydroxymethyl) derivative **11**. The solution electrochemistry of these new compounds has been studied by cyclic voltammetry: the ester substituents of **9** and **10** are conjugated to the π-framework, causing a positive shift of E^{ox}. The X-ray crystal structures of compounds **4**, **5a**, **5b**·CH_2Cl_2, **10** and **11** are reported. The molecules adopt a saddle-like conformation; the bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system is U-shaped due to the boat conformation of the central quinodimethane ring and folding of both the 1,3-dithiole rings. Each compound displays a dimeric packing motif which is most pronounced for **5a** and **5b**·CH_2Cl_2. Both these structures contain "oligomeric" acceptor···donor stacks: 4-layer ADDA in **5a** and 6-layer DADDAD in **5b** (D = dithiole; A = benzoyl and naphthoyl, respectively) but neither contains infinite stacks.

Introduction

The extensive studies of Hünig et al. on multi-stage redox systems[1] combined with early work on tetrathiafulvalene[2] led to interest in bis(1,3-dithiole) derivatives with extended π-conjugation between the dithiole rings, notably vinylogous[3] and quinonoid[4−22] spacer units, which reduced intramolecular Coulombic repulsion. In this context our attention is focussed on 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene **(1)**[7] and derivatives (e.g. **2** and **3**[19,20]) which undergo a single, quasi-reversible, two-electron oxidation wave to yield a thermodynamically stable dication at $E^{ox} \approx +0.3$ to $+0.4$ V (in MeCN vs. Ag/AgCl) in the cyclic voltammogram. 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 and fully aromatic anthracene system, with the heteroaromatic 6π 1,3-dithiolium cations almost orthogonal to this plane.[5,21] Theoretical calculations have established that steric hindrance introduced by benzoannulation of the central quinodimethane unit determines the saddle-shape of the neutral molecules.[14] The strong electron donor ability of the title ring system has led to its use as a component of intermolecular[5,8,21] and intramolecular[11,17,18,22] charge-transfer systems.



R^1	R^2	R^3	
H	H	H	**1**
Me	Me	H	**2**
Me	Me	CO_2Me	**3**

The emphasis of the present work is the synthesis of new derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene which can serve as versatile reagents, for example **4** and **11** bearing mono- and di-hydroxymethyl functionality, respectively, on one of the dithiole rings. We report esterification reactions of **4**, including the synthesis of the novel dimer and trimer structures **6** and **7**. Solution electrochemical data for these new derivatives, and the X-ray crystal structures of compounds **4**, **5a**, **5b**·CH_2Cl_2, **10** and **11** are presented.

Results and Discussion

Synthesis

We were keen to obtain the hydroxymethyl derivatives **4** and **11** primarily because the hydroxymethyl substituent(s)

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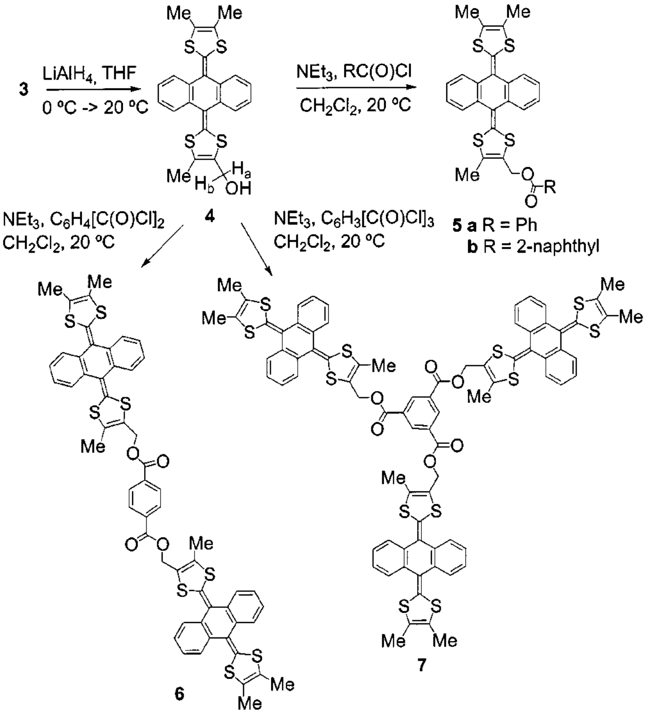
[a] Department of Chemistry, University of Durham,
South Road, Durham DH1 3LE, UK
Fax: (internat.) +44-191/384-4737
E-mail: m.r.bryce@durham.ac.uk

should be suitable for further functionalisation, and they could also engage in intermolecular hydrogen bonding thereby providing increased supramolecular order in solid state structures. Reduction of the methoxycarbonyl group of **3**,[19,20] with lithium aluminium hydride afforded **4** (90% yield) (Scheme 1).



Scheme 1. Synthesis of **4−7**

Reaction of **4** with benzoyl chloride and 2-naphthaloyl chloride gave the corresponding ester derivatives **5a** and **5b**, (99 and 67% yields), and analogous two- and threefold reactions with 1,4-benzenedicarbonyl chloride and 1,3,5-benzenetricarbonyl chloride gave the dimeric and trimeric compounds **6** and **7**, respectively, in 99 and 78% yields. The only previous multi[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene] derivatives are structurally very different from **6** and **7**: they are dimers linked by an oxygen bridge between C(2) of the anthracene units, synthesized by Martín et al. directly from the corresponding bis(anthraquinone) precursor.[9]

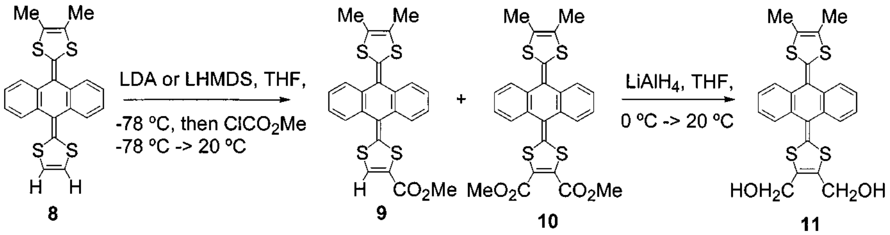
By analogy with the preparation of **3** by monolithiation of compound **2** with lithium diisopropylamide (LDA), followed by in situ trapping with methylchloroformate,[19,20] we have explored the possibility of difunctionalising analogue **8** (which is readily available in ca. 1 g batches)[7] using the same protocol. Treatment of **8** with LDA (1.1 equiv.) at −78 °C in THF, followed by quenching with methylchloroformate, gave a mixture of the mono- and diester derivatives **9** and **10**, respectively (Scheme 2). The former compound always predominated and could be isolated in an optimised yield of 32% after chromatography. LDA (2.2 equiv.) gave a mixture of **9** (25%) and **10** (20%). However, when the base was changed to LHMDS (4.0 equiv.) the diester derivative **10** was the major product (optimised yield 96%). Diester **10** was reduced to the di(hydroxymethyl) derivative **11** (95% yield) by analogy with the preparation of **4**. Analogues of **11** have been obtained recently using different methodologies.[17,18]

Dynamic NMR Studies

^1H NMR studies on **4** showed that the molecule is not planar in solution. The difference in chemical shift for the two diastereotopic protons H_a and H_b observed at 20 °C suggests that the molecule exists as the two conformers **A** and **B** (Figure 1) which interconvert slowly (by a boat−boat flipping of the central ring) on the NMR timescale at this temperature giving a four-line AB system $J_{AB} \approx 13$ Hz). However, at 100 °C these four lines have coalesced, i.e. interconversion is fast, with H_a and H_b no longer differentiated. The two diastereotopic protons were analysed as an AB system undergoing mutual exchange. Rate measurements were carried out by comparing the experimental spectra with simulations. Analysing the data according to the Eyring relationship gave an activation enthalpy, $\Delta H^{\ddagger}$ = 73.5 kJ/mol, and an activation entropy $\Delta S^{\ddagger}$ = 11.5 J/mol·K, with standard deviations of 0.9 kJ/mol and 8.4 J/mol·K, respectively. The error in $\Delta S^{\ddagger}$ is too large for reliable interpretation, requiring a more thorough investigation to reduce the interpolation error in the Eyring plot. More detailed experiments on analogues of compound **4** will be reported in due course. These data provide the first evidence that the solution structure of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system is saddle shaped, as observed in the solid state by X-ray crystallography[5] and predicted by theoretical calculations.[14]

Solution Electrochemical Studies

Solution electrochemical data for the new derivatives of the title system are consistent with their substitution patterns. These data are collated in Table 1. A notable feature is that the electron-withdrawing ester substituent(s) of compounds **9** and **10** results in a positive shift of the quasi-



Scheme 2. Synthesis of **9−11**

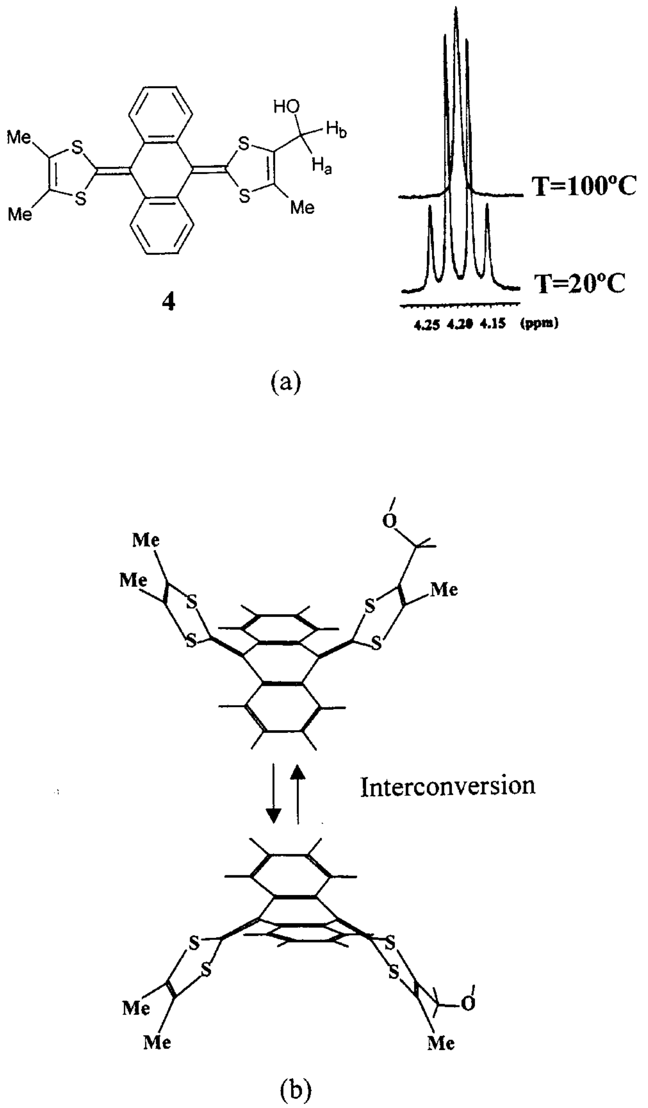


Figure 1. (a) ^1H NMR Spectra of H_a and H_b of **4** in $(CD_3)_2SO$ at 100 °C and 20 °C; (b) Proposed conformations of **4** in solution

Table 1. Cyclic voltammetric data[a]

Compound	E^{ox}_{pa}/V	E^{ox}_{pc}/V	ΔE/V[b]
4	0.37 (2e)	0.16	0.21
5a	0.45 (2e)	0.21	0.24
5b	0.45 (2e)	0.08	0.37
6	0.47 (4e)	0.12	0.35
7	0.49 (6e)	0.19	0.30
8	0.38 (2e)	0.23	0.15
9	0.51 (2e)	0.25	0.26
10	0.59 (2e)	0.39	0.20
10 (−30 °C)	0.59 (2e)	0.30	0.29
11	0.34 (2e)	−0.02	0.36

[a] Compound 2×10^{-3} M, versus Ag/AgCl, electrolyte $Bu_4N^+ClO_4^-$ (0.1 M), dichloromethane, 20 °C (except where stated for **10**), scan rate 100 mV s^{-1}. – [b] $E^{ox}_{pa} - E^{ox}_{pc}$ (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).

reversible, two-electron redox wave (neutral → dication species), which is consistent with mesomeric conjugation, as observed previously in ester[23] and thioamide[24] derivatives of tetrathiafulvalene. Compared to compound **8**, the value of E^{ox} for **9** and **10** is positively shifted by 130 and 210 mV, with the addition of one and two ester substituents, respectively. Data for **10** obtained at −30 °C establish that the oxidation potential (E^{ox}_{pa}) is unchanged by lowering the temperature, whereas the coupled reduction wave (E^{ox}_{pc}) is negatively shifted by 90 mV, which is qualitatively similar to other derivatives of **1**.[6,14] The smaller positive shift of E^{ox} for **5a** and **5b** (80 mV) compared to **4** has precedent in related derivatives of 4-hydroxymethyl-TTF.[25] The large variation in the values of ΔE for the monomers (*cf* 150 mV for **8** and 370 mV for **5b**) is puzzling, and we note that similar unexplained variations in ΔE have been noted by Martín et al. for dimers of **1**.[9]

The data for the dimer and trimer systems **6** and **7** are consistent with each donor unit acting independently: the molecules display a four-electron wave (i.e. tetracation formation) and a six-electron wave (i.e. hexacation formation) respectively. The peaks for E^{ox}_{pa} and E^{ox}_{pc} could not be resolved by reducing the scan rate. This result is consistent with the single, four-electron wave observed for the previous (structurally very different) dimeric systems.[9] A comparison of **5a**, **6** and **7** reveals that the E^{ox} values are not significantly changed within the series, although a slight trend in seen in the value of E^{ox}_{pa}: the system becomes slightly harder to oxidise in the sequence monomer < dimer < trimer. Figure 2 shows the cyclic voltammograms of compounds **5a** and **7**. (Note the different current scales for the two compounds: this is a consequence of the lower solubility of **7**.)

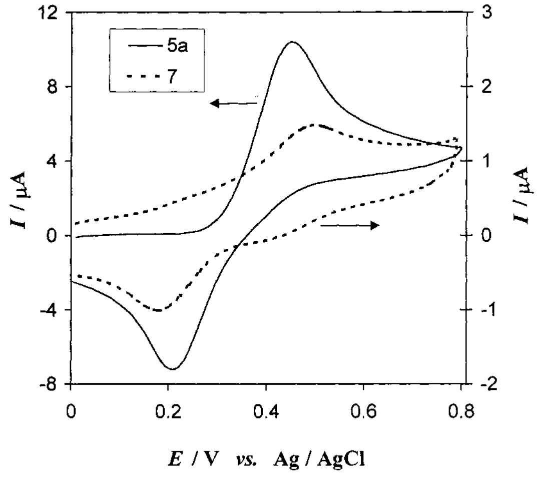


Figure 2. Cyclic voltammograms of **5a** and **7**; note the different current scales; for conditions see Table 1

X-ray Crystal Structures of Compounds 4, 5a, 5b·CH₂Cl₂, 10 and 11

X-ray structural studies of **4**, **5a**, **5b**·CH_2Cl_2, **10** and **11** have shown that each molecule adopts a normal[20,21] saddle-like conformation (Figures 3−7). The anthracenediylidene moiety is folded along the C(9)···C(10) vector by an angle φ; both dithiole rings tilt in the opposite direction and then fold inwards along the S(1)···S(2) and S(3)···S(4) vectors by δ_1 and δ_2 angles, so that the outlying planar S(1)−C(16)−C(17)−S(2) and S(3)−C(21)−C(22)−S(4) moieties of these rings form a (rather narrow) dihedral angle θ. These dihedral angles are listed in Table 2. The "saddles" usually have an approximate C_s symmetry, the mirror plane passing through the C(15), C(9), C(10), and C(20) atoms. Only in **5a** is this symmetry somewhat distorted (see Figure 4) by a twist of (surprisingly) the symmetrically substituted dithiole ring: the S(3)−C(21)−C(22)−S(4) plane forms an angle of 82° (rather than 90°) with the C(15)−C(9)−C(10)−C(20) plane.

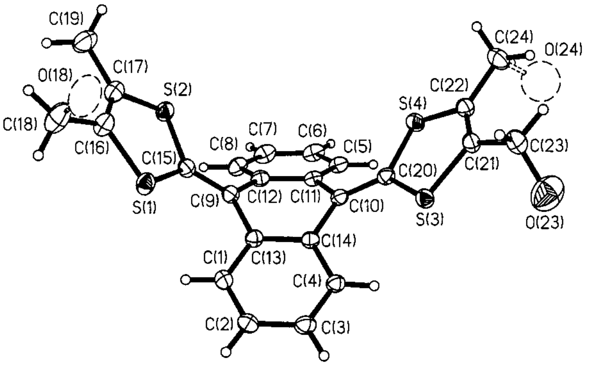


Figure 3. Molecular structure of **4**; the hydroxyl O atom occupies positions O(16), O(23) and O(24) with the probabilities of 0.4, 0.5 and 0.1, respectively; its H atom was not located; thermal ellipsoids are drawn at the 50% probability level.

Table 2. Dihedral angles (°)

	4	5a	5b		10	11
φ	37.3	41.4	39.7	38.1	37.4	37.4
δ_1	6.1	16.7	11.3	14.9	16.7	9.0
δ_2	9.9	4.6	6.3	8.4	8.7	6.2
θ	89.4	78.4	72.9	77.5	100.2	91.3

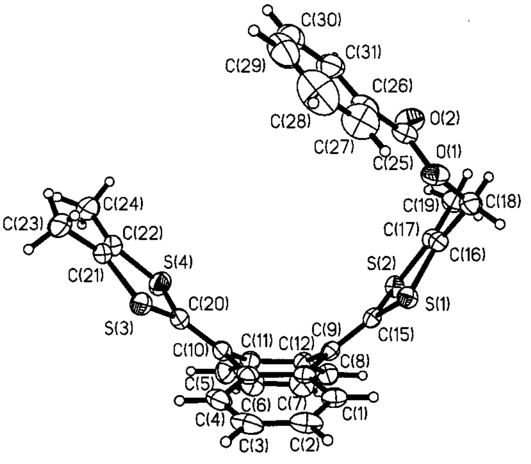


Figure 4. Molecular structure of **5a**; note the slightly different orientations of the dithiole rings

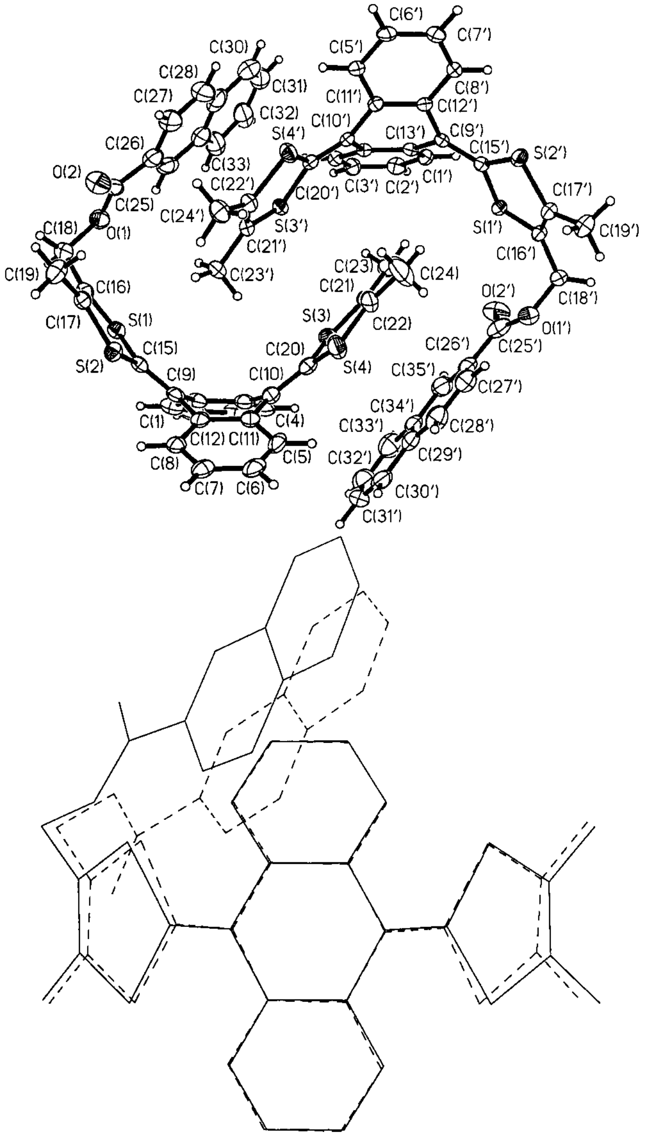


Figure 5. Two independent molecules of **5b** in the crystal (a) and comparison of their conformations (b)

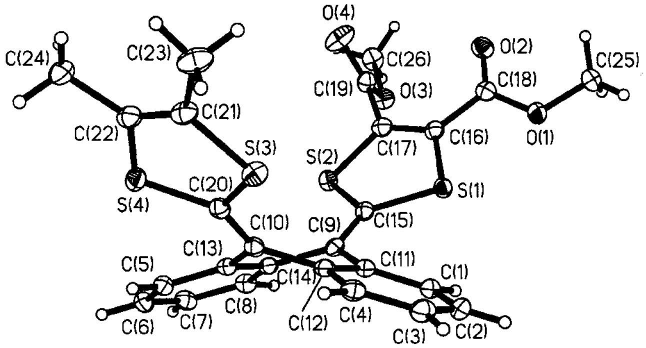


Figure 6. Molecular structure of **10**

The packing motif is also broadly similar to that displayed by all but one[20] of the derivatives of **1** studied so far: pseudo-dimers of molecules, related by an inversion centre and mutually engulfing each other with their U-shaped bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene moieties. Obviously, this motif ensures the most dense packing and to conform to it, molecular folding increases with the size of the substituents (see Table 2). Ultimately, the mo-

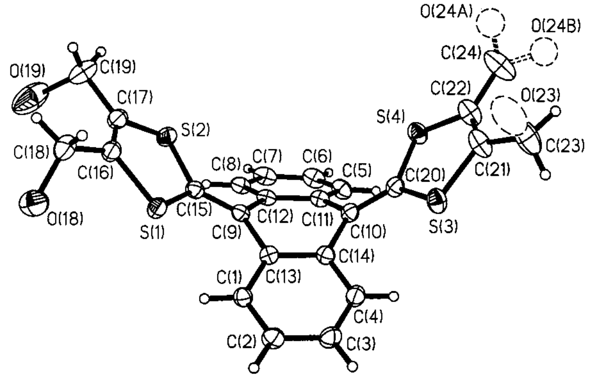


Figure 7. Molecular structure of **11**; two hydroxyl groups are disordered between positions O(18), O(19), O(23) with occupancies 0.5, O(24A) and O(24B) with occupancies 0.3 and 0.2; the hydroxyl H atoms were not located

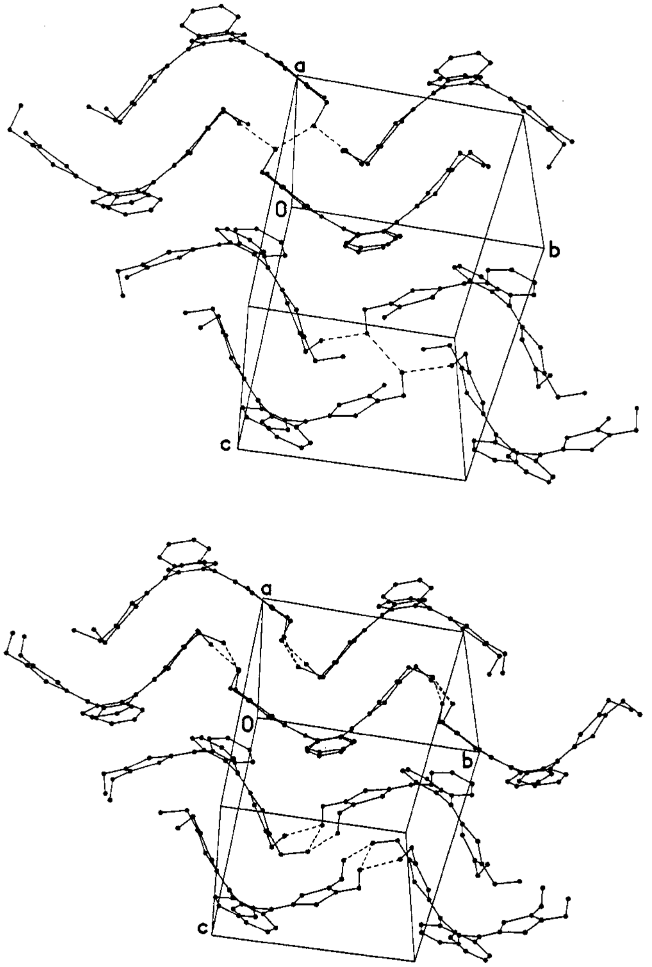


Figure 8. Crystal packing of **4** (top) and **11** (bottom), showing possible contacts between disordered O atoms. H atoms are omitted

lecule adopts a U-shape with the substituents at the dithiole rings nearly parallel. Thus, in **5b** the dihedral angle between the naphthyl group and the S(3)−C(21)−C(22)−C(23)−C(24)−S(4) fragment is 19° in both independent molecules, while the corresponding angle in **5a** (with the benzoyl group) does not exceed 10°. For symmetrically substituted molecules, the dimer has a roughly C_s symmetry, which is distorted in **5a** and **5b** by relative rocking of the molecules.

Molecule **4** (Figure 3) is disordered between three possible positions, so that the methyl and hydroxymethyl substituents at C(16), C(21) and C(22) are statistically mixed. Such a disorder is unusual, although the steric demands of the two groups are similar: normally the ordered structure is stabilised by hydrogen bonds. The present compound contains no strong hydrogen bond acceptor except the hydroxyl group oxygen itself. Even so, it seems *a priori* possible for the molecules to be linked by a chain of hydrogen bonds, RO−H···O(R)−H···O(R)−H, such as exist in the crystals of higher alcohols. However, such a chain is incompatible with the pseudo-dimeric packing motif (see above) and so its nonrealisation is an evidence of the high stability of this motif. This conclusion is further confirmed by the crystal structure of **11** (Figure 7), which is isomorphous with **4** (Figure 8). The molecule of **11** is also disordered (with equal probability) between two orientations, with the hydroxymethyl substituents at C(16), C(17) or at C(21), C(22). The C(24)−O(24)H group is further disordered between two positions, differing by a rotation around the C−C bond. In both structures the CH_3/CH_2OH groups of four molecules (two dimers) converge in the same area. The

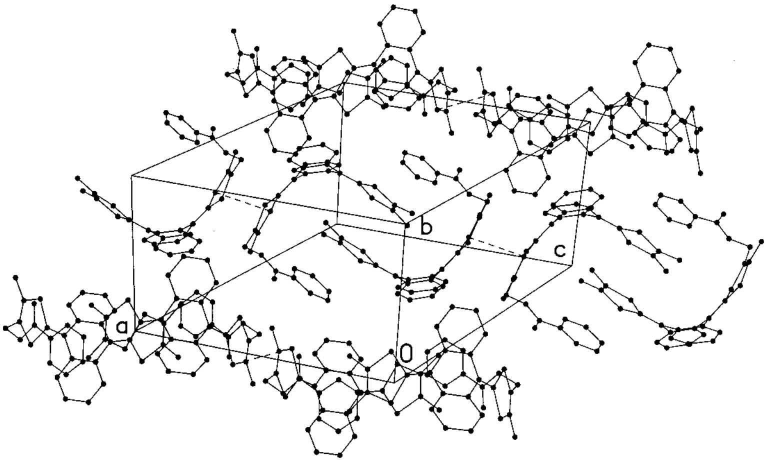


Figure 9. Crystal packing of **5a**

resulting O···O distances, 2.86−2.91 Å in **4** and 2.67−2.86 Å in **11**, are in the range typical for strong hydrogen bonds. Since the oxygen positions are partially occupied, only some (or none) of these distances may be real. It seems likely that in fact methyl and hydroxymethyl groups congregate with their like, forming hydrophobic and hydrophilic clusters, but in any case the formation of continuous molecular chains is impossible.

The dimeric motif is most pronounced for **5a** and **5b**. In the former structure, the dimers form chains which are arranged in a herringbone motif (Figure 9). The asymmetric unit of **5b**·CH_2Cl_2 comprises two **5b** and two dichloromethane molecules. The (**5b**)$_2$ pseudo-dimers form a close-packing layer (Figure 10) and the CH_2Cl_2 occupies continuous channels between the layers and is intensely disordered. In the dimer of **5a**, the electron-rich dithiole moiety (D) lies in proximity to the electron-poor benzoyl group (A) of the other molecule. The dithiole S(4)−C(22) bond is eclipsed with the phenyl C(30)−C(31) bond, the shortest D···A contact being S(4)···C(30) 3.59 Å. However, although the donor and acceptor moieties are nearly parallel (interplanar angle 10°) they have *anti*-orientations with respect to their contacting bonds, thus the π-overlap is very limited. In **5b** the conditions for charge transfer are more favourable. Here each naphthoyl group is sandwiched between two dithiole groups, one belonging to the other molecule of the same dimer and the other belonging to a different dimer. The former dithiole ring is eclipsed with the substituted ring of the naphthalene; the latter overlaps with the same ring *and* with the carboxy group. The contacting π-conjugated systems A and D are practically parallel (interplanar angles 0.4 to 3.6°), the S···C contacts of 3.50−3.64 Å are close to the sum of the van der Waal's radii (3.61 Å).[26] Both structures contain "oligomeric" stacks: 4-layer ADDA in **5a** and 6-layer DADDAD in **5b**, but neither structure contains infinite stacks.

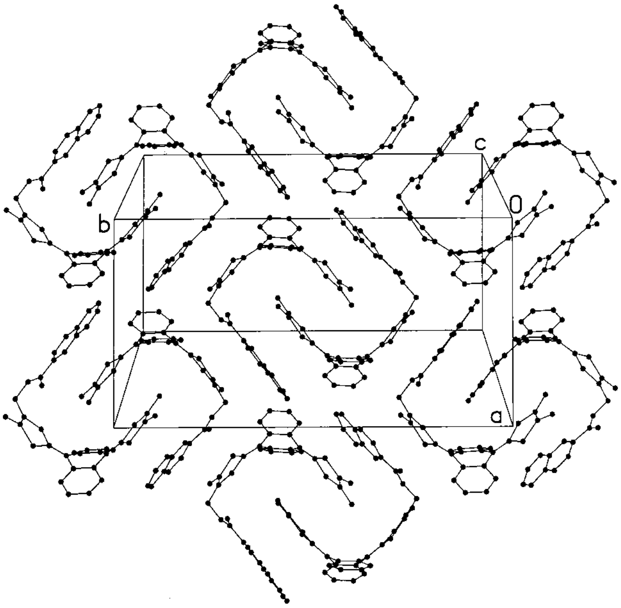


Figure 10. Crystal packing of **5b**, showing a layer of pseudo-dimers (disordered CH_2Cl_2 molecules which occupy channels between the layers are not shown)

In molecule **10** (Figure 6), the introduction of two electron-withdrawing methoxycarbonyl substituents into one dithiole ring shortens the "outer" C−S bonds therein [S(1)−C(16) 1.755(2) Å and S(2)−C(17) 1.748(2) Å, cf. 1.766(2) Å in the dimethyl-substituted ring] and weakens the C(16)=C(17) bond [1.345(2) Å] compared to C(21)=C(22) [1.333(2) Å]. The two methoxycarbonyl groups bonded to C(16) and C(17), have different orientations, forming dihedral angles of 14.5° and 94.6° with the S(1)−C(16)−C(17)−S(2) plane. Thus, only the former CO_2Me group is π-conjugated with the dithiole ring, as indicated by small but significant differences in bond lengths: C(16)−C(18) 1.486(2) vs. C(17)−C(19) 1.510(2) Å, C(18)−O(1) 1.338(2) vs C(19)−O(3) 1.327(2), C(18)−O(2) 1.211(2) vs. C(19)−O(4) 1.198(2) Å. Consequently, the C(15)−S(1) and C(15)−S(2) bonds are nonequivalent [1.769(2) and 1.782(2) Å, respectively] in the same way as we[23,24a] and others[24b] observed previously in mono- or asymmetrically substituted dithiole (or TTF) derivatives.

Conclusion

The synthetic chemistry of the title ring system has been extended to yield new specifically functionalised derivatives, notably those bearing hydroxymethyl and ester substituents. The availability of these derivatives in synthetically-useful quantities should enable these extended π-electron systems to be exploited further in the fields of supramolecular and materials chemistry. The facile esterification reactions of **4**, exemplified by the synthesis of trimer **7**, pave the way for the incorporation of this π-system into organic dendrimer structures which possess well-defined redox behaviour.[25,27]

Experimental Section

The details of equipment and procedures used are the same as those reported previously.[20] All reactions were performed under an atmosphere of dry nitrogen. − ^1H NMR Studies on compound **4** for lineshape analysis were recorded at 500 MHz using a Varian INOVA 500 spectrometer with a standard 5 mm probe over the temperature range 24°C to 80°C, controlled to within 1°C. The temperatures were determined from the peak separation between the signals of the hydroxyl and methylene protons of a neat ethylene glycol sample.

10-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydro-9-(4-hydroxymethyl-5-methyl-1,3-dithiol-2-ylidene)anthracene (4): To a stirred solution of **3**[19] (3.00 g, 6.25 mmol) in dry THF (50 mL) at 0°C was added dropwise lithium aluminium hydride (1.00 g, 26.38 mmol) and the resultant mixture was stirred for 1 h at 0°C and then for 2 h at 20°C. After adding dropwise wet sodium sulfate (in excess), the reaction mixture was stirred for 1 h, during which time the solution changed from green to orange. The reaction mixture was filtered through Celite. After evaporation, the residue was chromatographed on a silica column eluting with dichloromethane to afford **4** (2.55 g, 90%). Recrystallisation was achieved by dissolution in dichloromethane and addition of hexane. M.p. >250 °C. −

^{1}H NMR ([D$_6$]DMSO): δ = 7.56−7.54 (m, 4 H), 7.34−7.30 (m, 4 H), 4.22 (d, J_{AB} = 12.8 Hz, 1 H), 4.18 (d, J_{AB} = 12.8 Hz, 1 H), 1.95 (s, 3 H), 1.92 (s, 6 H). − IR (KBr): $\tilde{\nu}$ = 3400 (br.), 1514, 1512, 1452, 1446, 755, 644 cm^{-1}. − MS (EI): *m/z* (%) = 452 (100) $[M^+]$. − UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 368 (4.03), 436 (4.30) nm. − $C_{24}H_{20}OS_4$ (452.7): calcd. C 63.68, H 4.45; found C 63.39, H, 4.50.

10-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydro-9-(5-methyl-4-phenylcarbonyloxymethyl-1,3-dithiol-2-ylidene)anthracene (5a): To a stirred solution of alcohol **4** (100 mg, 0.22 mmol) in dry dichloromethane (10 mL) at 20°C was added benzoyl chloride (26 μL, 0.22 mmol) and triethylamine (61 μL, 0.44 mmol). The resultant mixture was stirred for 2 h. After evaporation, the residue was chromatographed on silica eluting with dichloromethane to give **5a** as an orange powder (122 mg, 99%). An orange prism suitable for X-ray analysis was obtained by recrystallisation from dichloromethane. M.p. 228−231°C. − ^{1}H NMR (CDCl$_3$): δ = 8.0 (dd, J = 7.2 Hz, J = 1.2 Hz, 2 H), 7.6 (m, 4 H), 7.55 (tt, J = 7.6 Hz, J = 1.2 Hz, 1 H), 7.4 (dd, J = 7.2 Hz, J = 7.6 Hz, 2 H), 7.2 (m, 4 H), 5.04 (d, J_{AB} = 13 Hz, 1 H), 5.01 (d, J_{AB} = 13 Hz, 1 H), 2.11 (s, 3 H), 1.92 (s, 6 H). − IR (KBr): $\tilde{\nu}$ = 1724, 1512, 1456, 1444, 1262, 754, 709 cm^{-1}. − UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 368 (4.15), 436 (4.41) nm. − MS (EI): *m/z* (%) = 556 (48) $[M^+]$, 436 (100). − $C_{31}H_{24}O_2S_4$ (556.8): calcd. C 66.65, H 4.21; found C 66.87, H 4.34.

10-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydro-9-[5-methyl-4-(2-naphthyl)-carbonyloxymethyl-1,3-dithiol-2-ylidene]anthracene (5b): Following the same procedure as for compound **5a**, alcohol **4** (52 mg, 0.11 mmol), 2-naphthaloyl chloride (22 mg, 0.11 mmol) and triethylamine (32 μL, 0.22 mmol) in dichloromethane (10 mL) were stirred for 2 h at 20°C. After evaporation and chromatography on silica (dichloromethane as eluent), recrystallisation from dichloromethane/hexane gave **5b** (47 mg, 67%) as orange prisms suitable for X-ray analysis. Mp: 177°C. − ^{1}H NMR (CDCl$_3$): δ= 8.60 (s, 1 H), 8.0−7.7 (m, 4 H), 7.6−7.3 (m, 6 H), 7.2 (m, 4 H), 5.07 (d, J_{AB} = 13 Hz, 1 H), 5.03 (d, J_{AB} = 13 Hz, 1 H), 2.12 (s, 3 H), 1.87 (s, 6 H). − IR (KBr): $\tilde{\nu}$ = 1716, 1523, 1456, 1444, 1279, 1192, 777, 755, cm^{-1}. − UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 368 (4.09), 436 (4.35) nm. − MS (EI): *m/z* (%) = 606 (87) $[M^+]$, 127 (100). − $C_{35}H_{26}O_2S_4$ (606.8) calcd. (+ 1 mol of CH$_2$Cl$_2$) C 62.50, H, 4.08; found C, 62.33, H, 3.98.

6: To a stirred solution of alcohol **4** (55 mg, 0.12 mmol) in dry dichloromethane (10 mL) at 20°C was added terephthaloyl chloride (12.4 mg, 0.06 mmol) and triethylamine (34 μL, 0.24 mmol). The resultant mixture was stirred overnight. After evaporation, the residue was chromatographed on silica eluting with dichloromethane to afford product **6** (122 mg, 99%) as an orange solid. M.p. 250°C (darkening at 220°C). − ^{1}H NMR (CDCl$_3$): δ= 8.02 (s, 4 H), 7.5 (m, 8 H), 7.2 (m, 8 H), 4.96 (d, J_{AB} = 13 Hz, 2 H), 4.92 (d, J_{AB} = 13 Hz, 2 H), 2.03 (s, 6 H), 1.82 (s, 12 H). − IR (KBr): $\tilde{\nu}$ = 1721, 1520, 1455, 1444, 1261, 1242, 1096, 755, 644 cm^{-1}. − UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 368 (4.12), 436 (4.31) nm. − MS (MALDI-TOF): M^+ = 1035. − $C_{56}H_{42}O_4S_8$ (1035.5): calcd. C 64.96, H 4.09; found C 65.13, H 4.35.

7: By analogy with the preparation of **6**, alcohol **4** (80 mg, 0.18 mmol), 1,3,5-benzenetricarbonyl trichloride (15.6 mg, 0.06 mmol) and triethylamine (49 μL, 0.36 mmol) in dry dichloromethane (20 mL) were stirred at 20°C overnight. Chromatography on silica eluting with dichloromethane afforded **7** (70 mg, 78%) as an orange solid. M.p. >250 °C. − ^{1}H NMR (CDCl$_3$): δ = 8.77 (s, 3 H), 7.5 (m, 12 H), 7.2 (m, 12 H), 4.96 (m, 6 H), 2.02 (s, 9 H), 1.79 (s, 18 H). − UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 368 (4.05), 436 (4.32) nm. − MS (MALDI-TOF): M^+ = 1514. − IR (KBr): $\tilde{\nu}$ = 1734, 1444, 1223, 755, 644 cm^{-1}. −$C_{81}H_{60}O_6S_{12}$ (1514.1): calcd. (+ 1 mol of CH$_2$Cl$_2$) C 61.59, H 3.91; found C 61.77, H 3.92.

9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydro-10-(4-methoxycarbonyl-1,3-dithiol-2-ylidene)anthracene (9): To a stirred solution of **8** (0.5 g, 1.22 mmol) in dry THF (30 mL) at −78°C was added lithium diisopropylamide monotetrahydrofuran (ca. 1.5 M in cyclohexane, 0.9 mL, 1.35 mmol). The reaction mixture was stirred at −78°C for 2 h. Methyl chloroformate (0.18 mL, 2.44 mmol) was then added and the mixture was stirred and left to warm to 20 °C overnight. The solvents were removed in vacuo and the residue was purified by chromatography on silica gel with dichloromethane/hexane (1:1 v/v) as eluent to afford **9** (0.19 g, 32%) as an orange solid separated from unchanged **8** and traces of **10**. M.p. 181°C. − ^{1}H NMR (CDCl$_3$): δ = 7.7−7.5 (m, 4 H), 7.4−7.2 (m, 4 H + 1 H), 3.79 (s, 3 H), 1.93 (s, 6 H). − IR (KBr): $\tilde{\nu}$ = 1712, 1564, 1517, 1457, 1445, 1251, 1056, 754, 674, 643 cm^{-1}. − UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 360 (4.08), 428 (4.31) nm. − MS (EI): *m/z* (%) = 466 (100) $[M^+]$. − $C_{24}H_{18}O_2S_4$ (466.7): calcd. C 61.77, H 3.89; found C 62.07, H 4.09.

10-[4,5-Di(methoxycarbonyl)-1,3-dithiol-2-ylidene]-9-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (10): To a stirred solution of **8** (210 mg, 0.51 mmol) in dry THF (15 mL) at −78°C was added lithium bis(trimethylsilyl)amide (ca. 1.06 M in THF, 2 mL, 2.04 mmol). The reaction mixture was stirred at −78°C for 2 h. Methyl chloroformate (0.16 mL, 2.04 mmol) was then added. Workup and purification as described above for **9**, gave **10** (0.26 g, 96%) as an orange-red solid. M.p. >250°C. − ^{1}H NMR (CDCl$_3$): δ = 7.7−7.6 (m, 2 H), 7.5−7.4 (m, 2 H), 7.3−7.2 (m, 4 H), 3.81 (s, 6 H), 1.93 (s, 6 H). − IR (KBr): $\tilde{\nu}$ = 1739, 1718, 1583, 1512, 1454, 1444, 1259, 755, 675, 644 cm^{-1}. − UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 356 (4.19), 428 (4.40) nm. − MS (EI): *m/z* (%) = 524 (100) $[M^+]$. − $C_{26}H_{20}O_4S_4$ (524.7): calcd. C 59.52, H 3.84; found C 59.26, H 3.79.

10-[4,5-Di(hydroxymethyl)-1,3-dithiol-2-ylidene]-9-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (11): Following the same procedure as for compound **4**, compound **10** (200 mg, 0.38 mmol) and lithium aluminium hydride (0.11 g, 3 mmol) afforded **11** (180 mg, 95%) as a orange solid. Recrystallisation from dichloromethane/methanol gave purple prisms suitable for X-ray analysis. M.p. >250°C. − ^{1}H NMR ([D$_6$]DMSO): δ = 7.6−7.5 (m, 4 H) 7.4−7.3 (m, 4 H), 5.42 (t, $J_{OH,H}$ = 5.5 Hz, 2 H), 4.27 (dd, J_{AB} = 13.5 Hz, $J_{H,OH}$ = 5.5 Hz, 2 H), 4.19 (dd, J_{AB} = 13.5 Hz, $J_{H,OH}$ = 5.5 Hz, 2 H), 1.93 (s, 6 H). − IR (KBr): $\tilde{\nu}$ = 3400 (br.), 1519, 1443, 1279, 755, 675, 644 cm^{-1}. − UV/Vis (CH$_2$Cl$_2$): λ_{max} (lgε) = 364 (4.14), 432 (4.40) nm. − MS (EI): *m/z* (%) = 468 (49) $[M^+]$, 450 (100). − $C_{24}H_{20}O_2S_4$ (468.7): calcd. (+ 0.5 mol of H$_2$O) C 60.34, H, 4.43; found C 60.22, H 4.26.

X-ray Crystallography: X-ray diffraction experiments were carried out on a SMART 3-circle diffractometer with a 1 K CCD area detector, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and a Cryostream (Oxford Cryosystems) open-flow N$_2$ gas cryostat. A hemisphere (**5b**, **10**) or full sphere (**4**, **5a** and **11**) of reciprocal space was covered by a combination of 4 or 5 sets of ω scans; each set at different and/or 2θ angles. Reflection intensities were integrated using the SAINT program (Version 5.04, Bruker Analytical X-ray Systems, Madison, WI, 1996). Absorption corrections by numerical methods based on crystal face indexing (**5b**, **10**) or by semi-empirical methods based on the intensities of Laue equivalents (**4**, **5a**) using SADABS software (G. M. Sheldrick, University of Göttingen, 1998), were insignificant. The structures were solved by direct methods and refined by full-matrix least-squares

Table 3. Crystal data and experimental details

Compound	**4**	**5a**	**5b**	**10**	**11**
Formula	$C_{24}H_{20}OS_4$	$C_{31}H_{24}O_2S_4$	$C_{35}H_{26}O_2S_4 \cdot CH_2Cl_2$	$C_{26}H_{20}O_4S_4$	$C_{24}H_{20}O_2S_4$
Formula weight	452.64	556.74	691.72	524.66	468.64
T, K	120	150	100	120	120
Symmetry	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (# 14)	$P2_1/n$ (# 14)	$P2_1/n$ (# 14)	$P\bar{1}$(# 2)	$P2_1/n$ (# 14)
a, Å	11.036(3)	15.803(6)	13.842(5)	9.828(1)	11.193(3)
b, Å	12.871(4)	10.258(4)	26.390(10)	10.459(1)	12.803(4)
c, Å	15.266(5)	18.149(7)	19.064(7)	12.635(1)	15.343(5)
α, °	90	90	90	104.70(1)	90
β, °	101.48(1)	113.94(2)	110.04(1)	91.88(1)	102.48(1)
γ, °	90	90	90	108.47(1)	90
V, Å^3	2125(1)	2689(2)	6542(4)	1182.4(2)	2147(1)
Z	4	4	8	2	4
μ, mm^{-1}	0.46	0.38	0.49	0.44	0.46
Refls collected	25707	26639	46854	8536	26077
Unique refls	5612	7069	15004	5326	5686
$R_{int.}$	0.023	0.030	0.045	0.025	0.044
Refls $I > 2\sigma(I)$	4694	5320	10911	4317	4203
R $[I > 2\sigma(I)]$	0.034	0.040	0.088	0.033	0.040
wR (F^2), all data	0.099	0.105	0.241	0.084	0.115
Refined variables	291	357	809	387	288

against F^2 for all data, using SHELXTL software (Version 5.1, Bruker AXS, Madison, WI, 1998). Crystal data and experimental details are summarized in Table 3.

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-144852 to 144856 for **4**, **5a**, **5b**, **10** and **11**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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