Redox-active, Functionalised [3]- and [4]-Dendralenes

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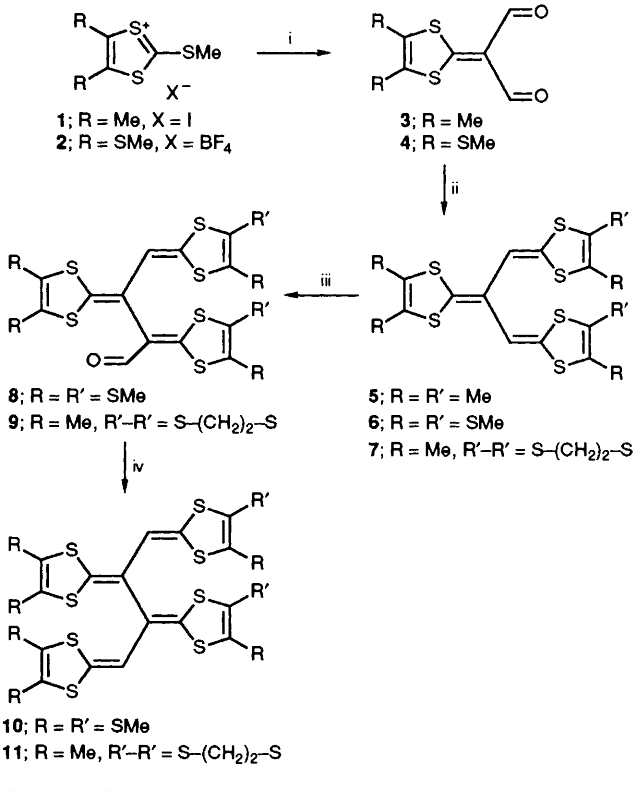
A series of [3]- and [4]-dendralenes, functionalised with 1,3-dithiole groups, are synthesised and shown by cyclic voltammetry to undergo reversible multi-stage redox reactions to yield tri- and tetra-cation species, respectively; the X-ray crystal structure of a [3]-dendralene derivative is reported.

Polyenes of the dendralene family are challenging synthetic targets that in recent years have attracted much attention owing to their unusual cross-conjugated properties and their versatile synthetic potential.[1–5] Dendralenes substituted with redox-active groups are very rare.[3] Such systems are of particular interest if they can be easily oxidised (or reduced) to form stable cross-conjugated radicals, the electronic, structural and spectroscopic properties of which are unexplored. It has been proposed that controlled electron propagation in such radical species could be exploited in the development of soliton switches in molecular electronic devices.[6]

We now describe the expedient synthesis of a series of [3]- and [4]-dendralenes **5–7**, **10** and **11**, that are functionalised with electron-donor 1,3-dithiole substituents. We report the solution electrochemistry of these systems and the X-ray crystal structure of [3]-dendralene derivative **5**. The novel synthetic step in constructing the dendralene framework is the reaction of methylenemalonaldehyde derivatives **3** and **4** with Horner–Wittig reagents **12–14**, that we have developed recently during studies on new π-donors for organic metals.[7]

The synthesis is shown in Scheme 1. The sodium salt of malonaldehyde reacts with the 2-methylthio-1,3-dithiolium cation salts **1**[7a] and **2**[7b] to yield compounds **3** and **4** (34–50% yields).[8]† Twofold reaction of dialdehydes **3** and **4** with the



1; R = Me, X = I
2; R = SMe, X = BF_4
3; R = Me
4; R = SMe
8; R = R′ = SMe
9; R = Me, R′–R′ = S–(CH$_2$)$_2$–S
5; R = R′ = Me
6; R = R′ = SMe
7; R = Me, R′–R′ = S–(CH$_2$)$_2$–S
10; R = R′ = SMe
11; R = Me, R′–R′ = S–(CH$_2$)$_2$–S

Scheme 1 *Reagents and conditions*: i, malonaldehyde sodium salt, acetonitrile, 20 °C, ii, reagent **12–14** (2 equiv.), n-butyllithium (2 equiv.), tetrahydrofuran (THF), −78 °C; iii, oxalyl chloride, dimethylformamide, −5 °C, then aqueous NaOH (5 mol dm^{-3}); iv, reagent **12** or **13**, n-butyllithium, THF, −78 °C

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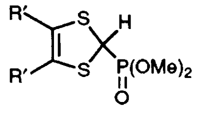
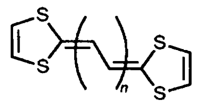
† All new compounds gave satisfactory elemental analyses and mass spectra. Melting points and ^{1}H NMR spectroscopic data [δ, 250 MHz in CDCl$_3$, (except compound **11**) relative to SiMe$_4$] for dendralene derivatives **5–7**, **10** and **11** are as follows. Compound **5**: >230 °C, 5.72 (2H, s), 1.92 (6H, s) and 1.89 (12H, s); compound **6**: oil, 5.65 (2H, s), 2.35, 2.34 and 2.33 (each 6H, s); compound **7**: 232 °C, 5.80 (2H, s), 3.28 (8H, s) and 1.93 (6H, s); compound **10**: 87–92 °C, 5.68 (2H, s), 3.47, 3.45, 3.43 and 3.40 (each 6H, s); compound **11**: 192–195 °C, δ_H (CS$_2$) 5.55 and 5.43 (both 1H, s), 3.24 and 3.21 (both 4H, s), 1.95 and 1.90 (both 3H, s) and 1.85 (6H, s).



12; R' = Me
13; R' = SMe
14; R'-R' = S-(CH2)2-S



15; n = 1
16; n = 2

phosphorus-stabilised carbanion generated from the appropriate Horner–Wittig reagent **12**,[7a] **13**[7b] or **14**[7c] proceeded very efficiently to afford [3]-dendralene systems **5–7**, respectively (62–82% yields). A formyl group was then attached to the dendralene framework of **6** and **7** by a Vilsmeier reaction of Me_2NCHCl^+, yielding compounds **8** and **9** (53–65% yields), which underwent a further Horner–Wittig reaction, using reagents **12** and **13**, to provide the [4]-dendralene derivatives **10** and **11** (57–63% yields).

Attractive and versatile features of this methodology are as follows: (*i*) both symmetrically substituted systems (*e.g.* **5**, **6** and **10**) and unsymmetrical systems bearing different 1,3-dithiole groups (*e.g.* **7** and **11**) can be prepared; (*ii*) iterative formylation and Horner–Wittig reactions using [4]-dendralenes **10** and **11** should provide access to higher homologues.

The X-ray molecular structure of [3]-dendralene derivative **5** is shown in Fig. 1.‡ The mean planes of the 1,3-dithiole rings A and B form a dihedral angle of 8.8°, while ring C is almost orthogonal, forming dihedral angles with rings A and B of 80.0 and 81.7°, respectively. The double bonds C(1)=C(2) and C(7)=C(8) are strongly conjugated, being on average 0.04 Å longer than the C(13)=C(14) bond, which has a normal C=C double bond length.[9] The central C(1)–C(7) bond length (1.409 Å) is significantly shorter than the central (single) bond in conjugated butadienes (average length 1.455 Å)[10] and corresponds to a bond order of *ca.* 1.4,[10] while the non-conjugated C(7)–C(13) bond remains single (1.499 Å). The closest S···S intermolecular contact is 3.96 Å, which is longer than twice the van der Waals radius of sulfur (1.80 Å).[11]

The solution electrochemical properties of compounds **5–7**, **10** and **11** have been studied by cyclic voltammetry; the data are collated in Table 1, and the voltammograms of compounds **6** and **10** are shown in Fig. 2. Compounds **5–7**, **10** and **11** each exhibit three reversible waves. The first two waves both correspond to one-electron processes for each of the compounds; for the [3]-dendralenes **5–7** the third wave is a one-electron transfer, while for the [4]-dendralenes **10** and **11**, it is a two-electron transfer. The redox potentials of the first two waves ($E_1{}^{1/2}$ and $E_2{}^{1/2}$) are similar to the values reported previously for related bis(1,3-dithiole-2-ylidene) derivatives **15**.[7b,12] As expected,[7b] methyl substituents attached to the periphery of the dendralene system significantly reduce the oxidation potential relative to the alkylthio analogues (*cf.* compounds **5** and **6**). The considerably higher potential of $E_3{}^{1/2}$ for the [3]-dendralene derivatives is typical of the oxidation of an isolated 1,3-dithiole-2-ylidene system. This is consistent with the conformation of the [3]-dendralene dications in solution being similar to that of the neutral system **5** in the solid state, discussed above.

The cyclic voltammetric data for the [4]-dendralenes **10** and **11** provide a fascinating comparison with the [3]-dendralene analogues **6** and **7**, respectively. The values of both E_1 and E_2 are lower (by *ca.* 0.1 V) for the [4]-dendralenes. The most striking results, however, concern the third oxidation wave:

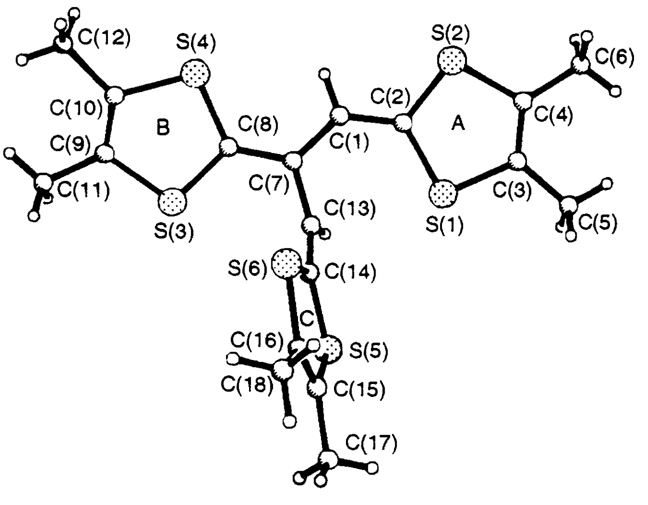


Fig. 1 X-Ray molecular structure of [3]-dendralene derivative **5**, showing the crystallographic numbering scheme. Bond lengths (Å, excluding the methyl groups) are: S(1)–C(2) 1.772(10), S(1)–C(3) 1.744(5), S(2)–C(2) 1.714(6), S(2)–C(4) 1.751(9), S(3)–C(8) 1.731(6), S(3)–C(9) 1.758(10), S(4)–C(8) 1.755(9), S(4)–C(10) 1.759(6), S(5)–C(14) 1.739(8), S(5)–C(15) 1.741(6), S(6)–C(14) 1.750(5), S(6)–C(16) 1.753(9), C(1)–C(2) 1.365(10), C(1)–C(7) 1.409(8), C(3)–C(4) 1.311(12), C(7)–C(8) 1.381(10), C(7)–C(13) 1.499(12), C(9)–C(10) 1.319(12), C(13)–C(14) 1.334(10), C(15)–C(16) 1.328(11).

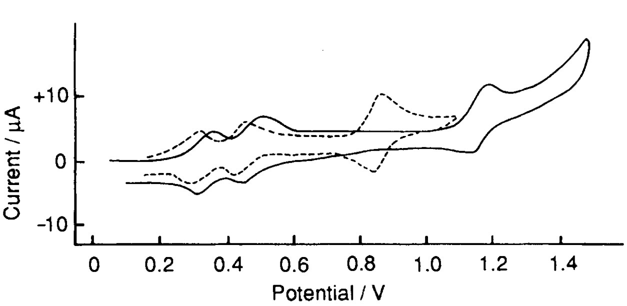


Fig. 2 Cyclic voltammograms of compounds **6** (—) and **10** (- - -)

Table 1 Cyclic voltammetric data for [3]- and [4]-dendralenes[a]

Compound	$E_1{}^{1/2}$/V[b]	$E_2{}^{1/2}$/V	$E_3{}^{1/2}$/V
5	0.084	0.327	1.246
6	0.360	0.490	1.195
7	0.245	0.470	1.244
10	0.258	0.366	0.687(2e)
11	0.227	0.393	0.807(2e)

[a] Compound *ca.* 10^{-3} mol dm^{-3}, in dichloromethane, electrolyte tetrabutylammonium hexafluorophosphate *ca.* 10^{-2} mol dm^{-3}, Pt electrode, *vs.* Ag/AgCl, 20 °C, using a BAS 100 electrochemical anlyser. [b] $E^{1/2}$ is the average of the anodic and cathodic peak potentials.

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‡ *Crystal data* for compound **5**: $C_{18}H_{20}S_6$, M = 428.7, triclinic, a = 9.968(3), b = 10.636(5), c = 12.085(5) Å, α = 65.89(3), β = 67.07(3), γ = 67.52(4)°, U = 1038.3(8) Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.37 g m^{-3}, $F(000)$ = 448, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, μ = 6.57 cm^{-1}.

The intensities of 2710 independent reflections with $2\theta \leqslant 45°$ were measured on a Siemens R3m/V diffractometer at 20 °C by Wyckoff (limited ω) scan technique, of which 1977 reflections with $I > 2\sigma(I)$ were used in calculations, performed with SHELXTLPLUS programs.[13] The structure was solved by direct methods. All non-hydrogen atoms were refined by full-matrix least-squares analysis in anisotropic approximation, with all hydrogen atoms included in riding model. Weighting scheme $w^{-1} = \sigma^2(F) + 0.0005\,F^2$ was used. The refinement of 217 parameters converged at $R = 0.061$, $R_w = 0.070$ and goodness-of-fit of 2.02. The residual difference Fourier map exhibited no features outside the range of 0.33 to −0.38 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

this is a two-electron process for the [4]-dendralenes, representing the oxidation of the dication to the tetracation species, and the potential at which this process occurs ($E_3^{1/2}$) is dramatically reduced, by *ca.* 0.5 V, compared with the [3]-dendralenes! This low potential for the [4]-dendralenes clearly implies that this process involves an extensively conjugated π-system. The coalescence of the third and fourth oxidation waves is reminiscent of the behaviour of compound **16**, in which the two 1,3-dithiole rings are separated by four sp^2 carbon atoms.[12]

Detailed spectroscopic studies of these novel oxidised polyene systems will be reported separately.

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