The first Diels–Alder reaction of a 9,10-bis(1,3-dithiol-2-ylidene)-9,10dihydroanthracene derivative: synthesis and crystal structure of a novel donor– π –anthraquinone diad

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An exocyclic diene derivative of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene undergoes Diels–Alder reaction with naphthoquinone to provide the D– π –A diad 10.

Derivatives of the π -electron donor **1** are emerging as versatile components of organic conductors,¹ nonlinear optical materials,² multi-stage redox assemblies³ and cyclophanes.⁴ System **1**



offers a unique combination of redox and structural properties, *viz.* a quasi-reversible two-electron oxidation process to yield a thermodynamically stable dication [E^{ox} +0.30 to +0.40 V (*vs.* Ag/AgCl)].⁵ The neutral molecule adopts a saddle-shape; on oxidation the anthracene ring becomes aromatic and planar, with the 1,3-dithiolium cations almost orthogonal to this plane.^{1b,5d}

We are developing methodology for the synthesis of new derivatives of $1.^{6}$ Herein we describe the first Diels–Alder reaction involving system 1, *viz*. the reaction of the transient exocyclic diene derivative 9 with naphthoquinone to afford the aromatised adduct 10. This study is timely in the light of interest in the Diels–Alder trapping of diene derivatives of tetra-thiafulvalene⁷ and 1,3-dithiole-2-one systems.⁸

Bis(chloromethyl) compound **8** is the precursor to our target diene **9** (Scheme 1). Hexylsulfanyl substituents enhance the solubility. The bis-DPTBS protected diol 2^9 was methylated with MeOTf to afford the unstable salt **3** which was sufficiently pure for immediate reaction with the anion of anthrone, which gave ketone derivative **4** (70% yield from **2**). Horner– Wadsworth–Emmons olefination with the anion of reagent **5**¹⁰ gave compound **6** (77% yield), which yielded the diol derivative **7** (88% yield). Reaction of a concentrated solution of diol **7** and PPh₃ in a mixture of CCl₄ and MeCN at 90 °C¹¹ gave the stable bis(chloromethyl) derivative **8** in 45% yield (SOCl₂ in CCl₄ at 20 °C gave only 10% of **8**). A mixture of **8**, KI, 18-crown-6 and 1,4-naphthoquinone was heated in toluene for 5 h, whereupon 2,3-dichloro-5,6-dicyanoquinone (DDQ) was added. After further heating the aromatised adduct **10**[†] was isolated (63% yield from **8**).

The good stability of the dichloro compound **8** contrasts with the attempted preparation of the bis(bromomethyl) derivative of **7** using conditions described^{7c,9} for other 4,5-bis(bromomethyl)-1,3-dithiole systems. Reaction of diol **7** with CBr₄ and PPh₃ in THF at 0 °C gave a complex mixture of products (TLC analysis) from which the bis(bromomethyl) derivative (if present) could not be isolated; instead, the formyl derivative **14**[†] was obtained. The yield of **14** was optimised (61%) by using a dilute solution of **7** and CBr₄ and PPh₃ (3.0 equiv.). Formyl derivatives as byproducts during the synthesis of related



Scheme 1 Reagents and conditions: i, MeOTf, CH_2Cl_2 , 20 °C, 1 h; ii, anthrone, pyridine–AcOH, 55 °C, 3 h, then 120 °C, 3 h; iii, 5, LDA, -78 °C, 2 h, then add 4, THF, -78 °C to 20 °C, 12 h; iv, Bu₄NF, THF, 20 °C, 1.5 h; v, PPh₃ (3.0 equiv.), CCl₄, (excess), MeCN, reflux, 1 h; vi, KI (3 equiv.), 18-crown-6 (3 equiv.), 1,4-naphthoquinone (4 equiv.), PhMe, 90 °C, 5 h, then DDQ (4 equiv.), 90 °C, 4 h.

4,5-bis(bromomethyl)-1,3-dithiole systems has been noted previously,¹² but no mechanism for their formation has been published.¹³ A possible route is shown in Scheme 2. Loss of bromide from intermediate **11** would give **12** and hence the intermediate **13**, which could undergo an oxy-Cope type rearrangement to give **14**.

The structures of compounds **10** and **14** (Fig. 1 and 2) were confirmed by X-ray crystal structure analysis.[‡] The asymmetric



Scheme 2 Reagents and conditions: i, PPh₃ (3.0 equiv.), CBr₄ (3.0 equiv.), CH₂Cl₂, 20 $^{\circ}$ C, 16 h.



Fig. 1 Molecular structure of 10.



Fig. 2 Molecular structure of 14; CH_3 and CHO substituents are evenly distributed between C(19) and C(20).

unit in the crystal of **10** contains only one independent molecule, while that of **14** comprises two molecules of similar but non-identical conformations; in one molecule, one of the *n*hexyl chains is disordered. The anthracenediylidene system is folded along the C(9)...(10) vector by *ca*. 39° in **10** and 41° in **14** and both dithiole rings are folded inward along the S…S vectors (by 8–14°). The anthracenediylidenebis(dithiole) system is Ushaped, with an acute angle between the S(1)C(16)C(17)S(2) and S(3)C(19)C(20)S(4) planes: 83° in **10**, 82° in **14**.

The *n*-hexyl chains adopting all-*trans* conformations lie parallel to the nearly planar anthraquinone (10) or formylthiole (14) system. Such parallelism particularly highlights the packing motif characteristic for 'molecular saddles': namely, a pseudo-dimer of mutually engulfing molecules, symmetrically related *via* an inversion centre.^{6b}

Cyclic voltammetry shows a quasi-reversible two-electron oxidation wave at E^{ox} +0.64 V (**10**) and E^{ox} +0.54 V (**14**). Additionally for **10** a quasi-reversible reduction wave of the AQ moiety is observed at E^{red} -0.95 V [CV data were recorded *vs*. Ag/AgCl, electrolyte Bu₄N+ClO₄⁻ (0.1 M), CH₂Cl₂, 20 °C, scan rate 100 mV s⁻¹].

The UV–VIS spectrum of compound **10** displays two bands characteristic of system $1^{5d,6}$ at 348 and 428 nm: no absorption was observed at longer wavelengths where intramolecular charge-transfer (ICT) bands would be expected. Studies aimed at photoinducing ICT in system **10**, and increasing the acceptor strength of the AQ moiety,¹⁴ are in progress.

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Notes and references

† Selected data for **10**: shining black crystals, mp 229–230 °C (from CH₂Cl₂–hexane); $\delta_{\rm H}$ (CDCl₃) 8.30–8.25 (m, 2H), 8.07 (s, 2H), 7.80–7.77 (m, 2H), 7.73–7.68 (m, 2H), 7.65–7.60 (m, 2H), 7.40–7.35 (m, 4H), 2.82–2.72 (m, 4H), 1.64–1.52 (m, 4H), 1.38–1.22 (m, 12H), 0.83 (t, 6H, *J* 6.8); $\lambda_{\rm max}$ (CH₂Cl₂)/m (lg ε) 348 (4.58), 428 (4.53). For **14**: orange prisms, mp 178–179 °C (from CH₂Cl₂–hexane); $\delta_{\rm H}$ (CDCl₃) 9.70 (s, 1H), 7.65–7.56 (m, 4H), 7.33–7.30 (m, 4H), 2.84–2.74 (m, 4H), 2.43 (s, 3H), 1.63–1.53 (m, 4H), 1.40–1.25 (m, 12H), 0.87 (t, 6H, *J* 6.4).

‡ Crystal data for **10**: C₄₄H₄₀O₂S₆, *M* = 793.1, *T* = 120 K, triclinic, space group *P*1̄ (No. 2), *a* = 9.925(2), *b* = 12.940(3), *c* = 15.319(5) Å, *α* = 94.16(1), *β* = 94.13(1), *γ* = 99.06(1)°, *U* = 1930.8(9) Å³, *Z* = 2, *D_c* = 1.36 g cm⁻³, 13240 reflections (6762 unique), *R* = 0.039 [4525 data, *I* > 2σ(*I*)], *wR*(*F*²) = 0.086. For **14**: C₃₄H₃₈OS₆, *M* = 655.0, *T* = 120 K, triclinic, space group *P*1̄ (No. 2), *a* = 15.208(3), *b* = 16.298(3), *c* = 16.510(3) Å, *α* = 111.95(1), *β* = 95.52(1), *γ* = 113.86(1)°, *U* = 3320(1) Å³, *Z* = 4, *D_c* = 1.31 g cm⁻³, 25912 reflections (12113 unique), *R* = 0.042 [8781 data, *I* > 2σ(*I*)], *wR*(*F*²) = 0.096 (Mo-Kα radiation). CCDC 182/1460. See http://www.rsc.org/suppdata/cc/1999/2433/ for crystallographic data in .cif format.

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