

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

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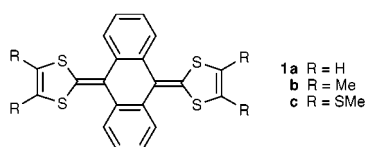
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An exocyclic diene derivative of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene undergoes Diels–Alder reaction with naphthoquinone to provide the D– $\pi$ –A diad **10**.

Derivatives of the  $\pi$ -electron donor **1** are emerging as versatile components of organic conductors,<sup>1</sup> nonlinear optical materials,<sup>2</sup> multi-stage redox assemblies<sup>3</sup> and cyclophanes.<sup>4</sup> System **1**

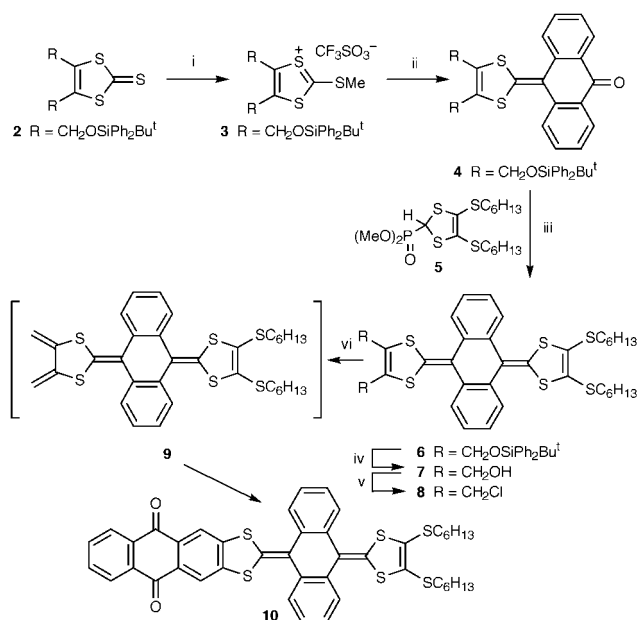


offers a unique combination of redox and structural properties, *viz.* a quasi-reversible two-electron oxidation process to yield a thermodynamically stable dication [ $E^{\text{ox}}$  +0.30 to +0.40 V (*vs.* Ag/AgCl)].<sup>5</sup> The neutral molecule adopts a saddle-shape; on oxidation the anthracene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

We are developing methodology for the synthesis of new derivatives of **1**.<sup>6</sup> 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 tetrafulvalene<sup>7</sup> and 1,3-dithiole-2-one systems.<sup>8</sup>

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**<sup>9</sup> 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**<sup>10</sup> gave compound **6** (77% yield), which yielded the diol derivative **7** (88% yield). Reaction of a concentrated solution of diol **7** and PPh<sub>3</sub> in a mixture of CCl<sub>4</sub> and MeCN at 90 °C<sup>11</sup> gave the stable bis(chloromethyl) derivative **8** in 45% yield (SOCl<sub>2</sub> in CCl<sub>4</sub> 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**<sup>†</sup> was isolated (63% yield from **8**).

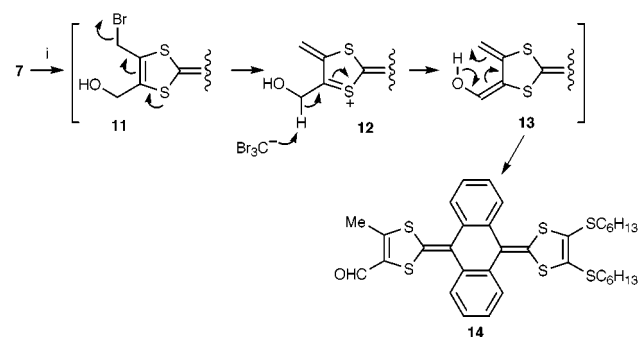
The good stability of the dichloro compound **8** contrasts with the attempted preparation of the bis(bromomethyl) derivative of **7** using conditions described<sup>7c,9</sup> for other 4,5-bis(bromomethyl)-1,3-dithiole systems. Reaction of diol **7** with CBr<sub>4</sub> and PPh<sub>3</sub> in THF 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**<sup>†</sup> was obtained. The yield of **14** was optimised (61%) by using a dilute solution of **7** and CBr<sub>4</sub> and PPh<sub>3</sub> (3.0 equiv.). Formyl derivatives as byproducts during the synthesis of related



**Scheme 1** Reagents and conditions: i, MeOTf, CH<sub>2</sub>Cl<sub>2</sub>, 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, Bu<sub>4</sub>NF, THF, 20 °C, 1.5 h; v, PPh<sub>3</sub> (3.0 equiv.), CCl<sub>4</sub>, (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,<sup>12</sup> but no mechanism for their formation has been published.<sup>13</sup> 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.<sup>‡</sup> The asymmetric



**Scheme 2** Reagents and conditions: i, PPh<sub>3</sub> (3.0 equiv.), CBr<sub>4</sub> (3.0 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, 20 °C, 16 h.

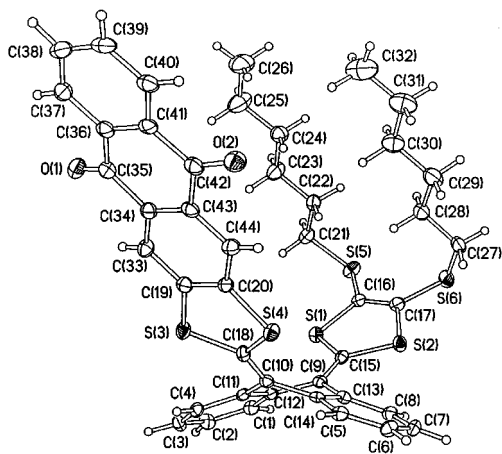


Fig. 1 Molecular structure of **10**.

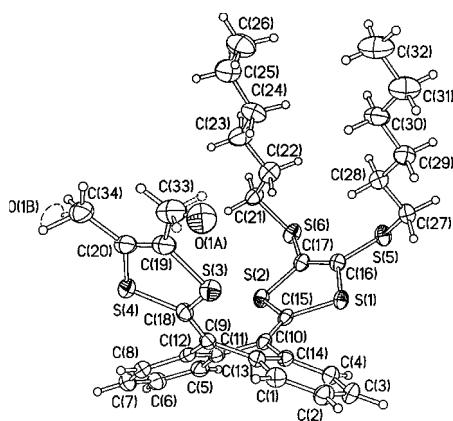


Fig. 2 Molecular structure of **14**; CH<sub>3</sub> and CHO substituents are evenly distributed between C(19) and C(20).

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 U-shaped, 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.<sup>6b</sup>

Cyclic voltammetry shows a quasi-reversible two-electron oxidation wave at  $E^{\text{ox}} +0.64$  V (**10**) and  $E^{\text{ox}} +0.54$  V (**14**). Additionally for **10** a quasi-reversible reduction wave of the AQ moiety is observed at  $E^{\text{red}} -0.95$  V [CV data were recorded *vs.* Ag/AgCl, electrolyte Bu<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (0.1 M), CH<sub>2</sub>Cl<sub>2</sub>, 20 °C, scan rate 100 mV s<sup>-1</sup>].

The UV–VIS spectrum of compound **10** displays two bands characteristic of system **1**<sup>5d,6</sup> 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,<sup>14</sup> are in progress.

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## Notes and references

† Selected data for **10**: shining black crystals, mp 229–230 °C (from CH<sub>2</sub>Cl<sub>2</sub>–hexane);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 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);  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm (lg  $\epsilon$ ) 348 (4.58), 428 (4.53). For **14**: orange prisms, mp 178–179 °C (from CH<sub>2</sub>Cl<sub>2</sub>–hexane);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 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**: C<sub>44</sub>H<sub>40</sub>O<sub>2</sub>S<sub>6</sub>, *M* = 793.1, *T* = 120 K, triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 9.925(2), *b* = 12.940(3), *c* = 15.319(5) Å,  $\alpha$  = 94.16(1),  $\beta$  = 94.13(1),  $\gamma$  = 99.06(1)°, *U* = 1930.8(9) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.36 g cm<sup>-3</sup>, 13240 reflections (6762 unique), *R* = 0.039 [4525 data, *I* > 2σ(*I*)], *wR*(*F*<sup>2</sup>) = 0.086. For **14**: C<sub>34</sub>H<sub>38</sub>O<sub>2</sub>S<sub>6</sub>, *M* = 655.0, *T* = 120 K, triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 15.208(3), *b* = 16.298(3), *c* = 16.510(3) Å,  $\alpha$  = 111.95(1),  $\beta$  = 95.52(1),  $\gamma$  = 113.86(1)°, *U* = 3320(1) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.31 g cm<sup>-3</sup>, 25912 reflections (12113 unique), *R* = 0.042 [8781 data, *I* > 2σ(*I*)], *wR*(*F*<sup>2</sup>) = 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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