Intermediates for the Synthesis of Linear Chains of 1,2:4,5-Fused Cyclohexa-1,4-diene Rings and Beltenes by Repeated Diels–Alder Reactions

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A synthetic strategy for the preparation of chains of 1,2:4,5-fused cyclohexa-1,4-diene rings, both linear and cyclic (beltenes), based on the repetitive Diels–Alder cycloaddition of *p*-benzoquinone with a tetramethylene-ethane synthon (3,4-dimethylenetetrahydrothiophene 1,1-dioxide) is described. This route has been developed to yield 5,11-dihydroxy-4,6,7,9,10,12-hexahydro-1*H*,3*H*-anthracene-[2,3-*c*:6,7-*c*']dithiophene 2,2,8,8-tetraoxide **16**, a potential precursor of a tricyclic doubly-exocyclic diene, and 7,10-bis(*tert*-butyldimethylsilyloxy)-1,4,5,6,11,12-hexahydronaphthacene-1,4-dione **22**, a potential precursor for the double dienophile 5,6,11,12-tetrahydronaphthacene-1,4,7,10-diquinone, but the generation of these Diels–Alder components and their combination to form a [9]-beltene derivative has not been accomplished. The synthesis of linear derivatives has proceeded as far as a protected heptacyclic derivative, 7,16-diacetoxy-1,4,10,13-tetrakis(*tert*-butyldimethylsilyloxy)-5,6,8,9,14,15,17,18-octahydroheptacene **25**. The ^{1}H NMR spectrum of this compound is unexpectedly temperature dependent.

Cyclohexa-1,4-diene rings are planar[1] but can be readily deformed about an axis through the methylene carbon atoms. In principle, a number (*n*) of such rings can then be fused in a 1,2:4,5-manner to yield a cyclic array, which has been called an [*n*]-beltene.[2,3] Force field calculations show that beltenes with six or more constituent rings are relatively unstrained and that from [8]-beltene onwards, these molecules contain a substantial cavity.[3] In larger beltene-like molecules, some of the rings could be made aromatic with little extra cost in strain energy, and several related structures with the same 1,2:4,5-fusions have been discussed, including [*n*]-collarenes,[4] which consist of alternating cyclohexa-1,4-diene and benzene rings, and even the fully aromatic [*n*]-cyclacenes.[5] A series of such compounds would be of great interest as molecular hosts, especially if equipped with the appropriate functionality. We were particularly attracted to the incorporation of quinone/hydroquinone rings in the structures. These compounds should be redox-active and little work has been done on host molecules containing these common groups. Although quinones will not fold as easily as the cyclohexa-1,4-dienes, they should still afford some flexibility in this sense. Moreover, quinones are quite good dienophiles,[6] and it was always clear that the major route to the construction of these molecules would be through Diels–Alder cycloadditions. Since we began work in this area, major advances by other groups have been reported.[7,8] Most notably, Stoddart and his co-workers have reported a very elegant synthesis of 'kohnkene' (which can be regarded as a derivative of [12]-beltene), conversion of kohnkene to a [12]-cyclacene derivative, preparation of [12]collarene and attempts to prepare [12]beltene.[4,9,10,11] They have also described the elaboration of more complex belt- and cage-like structures.[12]

In addition to the challenge of preparing cyclic beltene derivatives, there is a growing interest in the preparation of extended linear molecules of defined shape,[13,14,15] and many of the intermediates required to prepare beltenes could alternatively be used to generate long linear arrays of cyclohexa-1,4-diene rings. In this paper, we describe our efforts to develop a simple and flexible synthetic route to a series of these compounds.

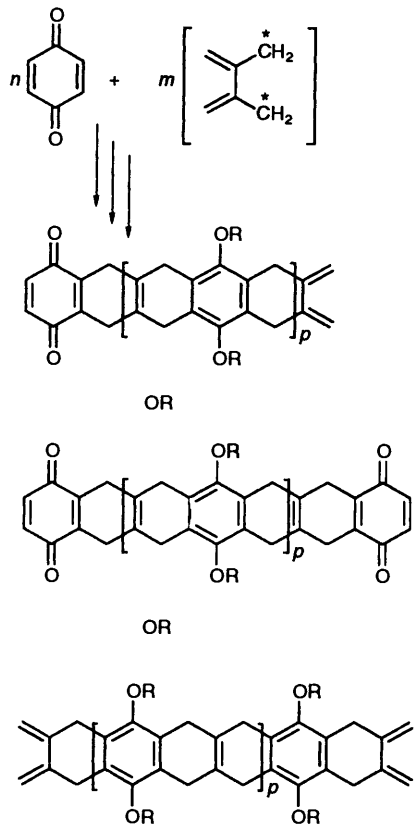
Results and Discussion

As stated above, the Diels–Alder cycloaddition evidently would be the main method for the construction of beltenes. Since we were aiming to incorporate quinones in our products, the obvious strategy would be to use *p*-benzoquinone as the dienophile. It is normally easy to achieve mono-addition to this, if desired.[16] Furthermore, the products of cycloaddition can be converted into hydroquinones or their derivatives, which can act as protected or latent quinones. 2,3-Dialkylquinones normally undergo further reaction at the unsubstituted double bond, thus ensuring that a linear sequence of rings should be constructed.[17] Reaction with a tetramethylene-ethane synthon, which could be successively activated to undergo sequential addition of two dienophiles, could therefore form the basis of an extremely economical route to compounds with chains of 1,2:4,5-fused cyclohexa-1,4-diene rings suitable for use in the preparation of beltenes, Scheme 1. In principle, almost any length of linear array can be assembled from these two components.

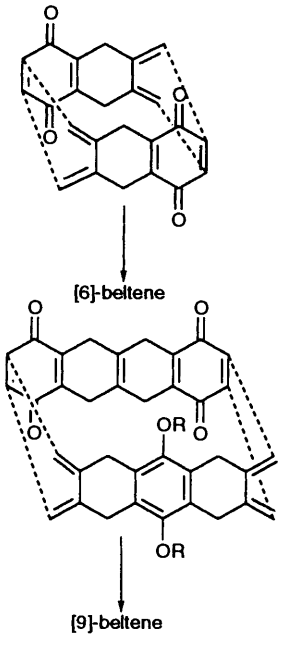
Although a long enough linear array of cyclohexadiene rings with appropriate terminal functionality might curl round and form a dihydro-beltene by a single intramolecular Diels–Alder cycloaddition, it was our intention to prepare the beltene skeleton by a double Diels–Alder reaction to give a tetrahydro-beltene. As we showed by force field calculations,[3] tetrahydro-beltenes are lenticular when viewed from above, and modelling shows that the intramolecular Diels–Alder reaction which closes the macro-ring would be stereoelectronically most favourable when the original two components contribute the same number of atoms to the macrocyclic ring. Based on this reasoning, it should be favourable to construct a beltene containing an even number of cyclohexadiene rings by the dimerisation of a precursor which was a diene at one end and a dienophile at the other, while a beltene containing an odd number of rings should be constructed from a double diene and a double dienophile. This is illustrated in Scheme 2 for the formation of a [6]- and a [9]-beltene.

Shortly after starting our work in this area, we learnt that Angus and Johnson[18] had already attempted the synthesis of a [6]-beltene derivative based on this strategy. Their product was not completely characterised, but the synthesis of a more elaborate (and fully characterised) derivative of [6]-beltene by the same strategy was reported shortly afterwards.[19,20]

The final consideration, in terms of synthetic planning, was control of the stereochemistry of the successive Diels–Alder



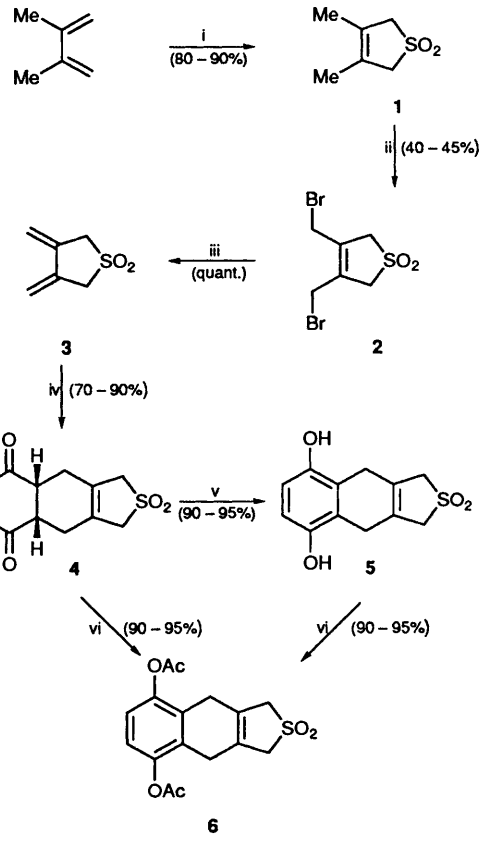
Scheme 1 Beltene synthons potentially available from repetitive Diels–Alder cycloadditions of *p*-benzoquinone and a tetramethylene ethane synthon



Scheme 2 Formation of [6]- and [9]-tetrahydrobeltene derivatives by double Diels–Alder reaction between two components contributing equal numbers of atoms to the macro-rings

cycloadditions. Since our eventual targets were always compounds with sp^2 bridgeheads, we planned to remove the hydrogen atoms from the bridgehead by aromatisation of the enedione (dihydroquinone) to a hydroquinone at each stage, thus avoiding the potential accumulation of mixtures of isomeric products. The extremely elegant triple diastereoselectivity[10] displayed by the reactions used by Stoddart and co-workers to construct kohnkene is a consequence of the very special dienes and dienophiles used. In general, our cautious approach is justified to avoid this potentially serious problem. However, we recognised at an early stage that the cyclohexa-1,4-diene rings in our intermediates might be rather susceptible to aromatisation and this has indeed proved to be a serious drawback of our approach (see below).

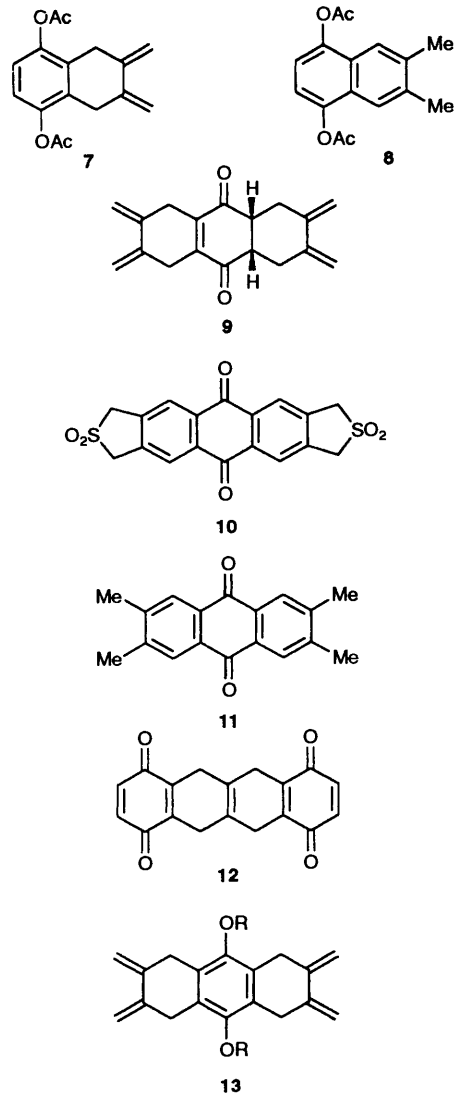
Our initial route to a structure incorporating both a masked diene and a latent quinone is summarised in Scheme 3.



Scheme 3 *Reagents:* i, SO_2; ii, NBS, $CHCl_3$; iii, NaI, acetone; iv, *p*-benzoquinone, CH_2Cl_2; v, conc. HCl, MeOH; vi, Ac_2O, pyridine

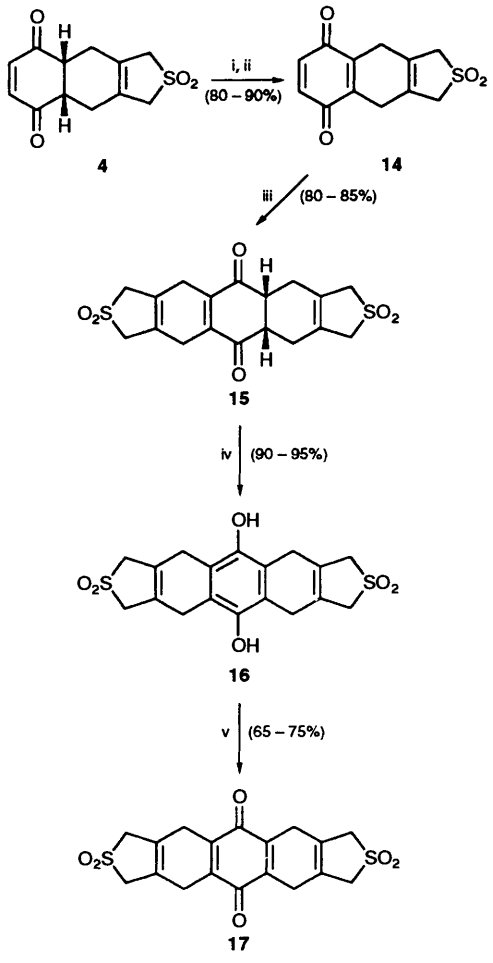
The reaction of liquid sulfur dioxide with 2,3-dimethylbuta-1,3-diene to give the cyclic sulfone **1**[21] in 80–90% yield was conveniently performed under autogenous pressure in a thick-walled Schlenk tube. Polymerisation was occasionally encountered, but was suppressed by the rigorous exclusion of air and the addition of hydroquinone in methanol. The dibromo-derivative **2** was obtained by the allylic bromination of compound **1** with *N*-bromosuccinimide in dry chloroform;[21] although this reaction inevitably produces a mixture of bromination products, the required compound **2** may be readily isolated in 40–45% yield by a simple crystallisation. Reaction with a large excess of sodium iodide in acetone then gave an almost quantitative yield of the known[22] diene-sulfone **3** (collected in dichloromethane). Because of its tendency to polymerise, this product was used immediately, without complete removal of the solvent, and the cycloaddition with *p*-benzoquinone led to the ene-dione-sulfone **4** in good yield (70–90%).

The acid-catalysed tautomerism of the ene-dione-sulfone **4** occurred almost quantitatively in methanol containing hydrochloric acid, to give the hydroquinone-sulfone **5**, which, with acetic anhydride in pyridine, formed the diacetyl-derivative **6**, which could be produced directly from the ene-dione-sulfone **4**



by the same procedure. Thermolysis of the diacetoxy-sulfone **6** required a surprisingly high temperature (> 200 °C, the parent sulfone decomposes rapidly above 150 °C) and at 225–230 °C/0.1 mmHg gave a sublimate which contained not only the diacetoxy-diene **7** but also the isomeric naphthalene **8** (NMR evidence).

Potential precursors to double diene systems were prepared as follows (Scheme 4). The quinone-sulfone **14** could be obtained by ceric ion oxidation of the hydroquinone-sulfone **5**, or more directly (in 80–90% yield) from the ene-dione-sulfone **4** by treatment with trifluoroacetic acid–acetic acid–water, followed by the addition of sodium nitrite.[23] Reaction of the quinone-sulfone **14** with the diene-sulfone **3** afforded the ene-dione-disulfone **15** (80–85%), but the thermal extrusion of sulfur dioxide from this disulfone was again unsatisfactory owing to partial aromatisation of the expected double diene **9**. Isomerisation of the ene-dione-disulfone **15** in aqueous trifluoroacetic acid gave a nearly quantitative yield of the hydroquinone-disulfone **16**. This could be recrystallised from hot dimethyl sulfoxide, but it oxidised slowly in solution to form a product showing IR and NMR spectra consistent with its formulation as the anthraquinone-disulfone **10**. All attempts to prepare alkylated or silylated derivatives of compound **16** under the normal base-promoted conditions failed, even the use of imidazole in DMF led to oxidative aromatisation. Thermolysis of the hydroquinone-disulfone **16** at 250 °C/0.1

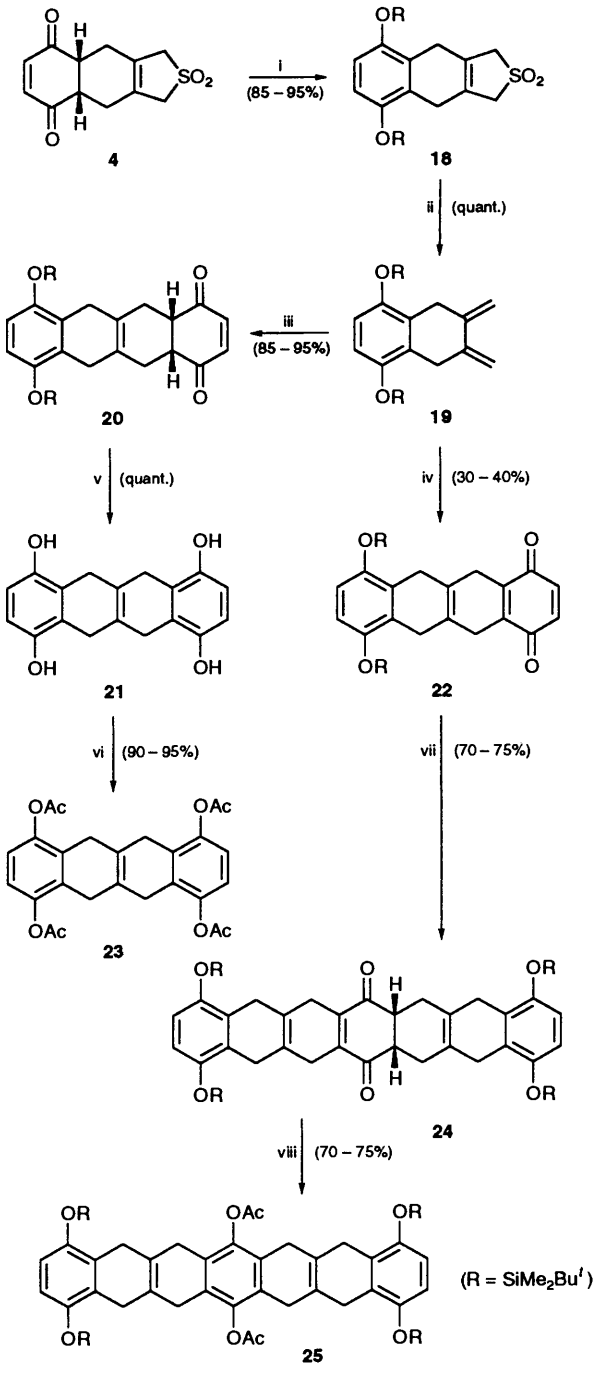


Scheme 4 *Reagents:* i, CF_3CO_2H, $MeCO_2H$, H_2O; ii, $NaNO_2$; iii, Compound **3**, DMF; iv, CF_3CO_2H, H_2O; v, CF_3CO_2H, $NaNO_2$

mmHg led cleanly to the known[24] tetramethylanthraquinone **11**.

Oxidation of the hydroquinone-disulfone **16** to the corresponding quinone **17** was readily achieved in *ca.* 70% yield by the addition of sodium nitrite to a suspension of compound **16** in trifluoroacetic acid, but thermolysis of this product also failed to yield a double diene.

A much better procedure for the generation of a diene system by the extrusion of sulfur dioxide from a sulfone resulted from the use of lithium aluminium hydride.[25] Although this method failed with the highly insoluble hydroquinone-disulfone **16**, it ultimately led to the formation of a seven-ring chain as outlined in Scheme 5. Conversion of the ene-dione-sulfone **4** into the bis(silyl ether)-sulfone **18** (85–95%) by means of *tert*-butylchlorodimethylsilane in the presence of imidazole,[26] and treatment of the product with lithium aluminium hydride, gave the diene **19**, which was used immediately without purification for the next stage. Reaction with 1 equivalent of *p*-benzoquinone led to the ene-dione **20** in moderate yield, but it was found more convenient to use 2 equivalents of the dienophile in methanol, which resulted in oxidation of the initial adduct to give the more easily purified quinone **22** (in 30–40% yield from compound **18**). Treatment of the ene-dione **16** with aqueous trifluoroacetic acid produced the tetrahydroxy compound **21**, but this appeared to be of limited stability and was not obtained analytically pure; it was characterised as the tetraacetyl derivative **23**. Attempts to obtain the doubly dienophilic bisquinone **12**, either from the tetrahydroxy compounds **21** using sodium nitrite in aqueous acid or silver oxide, or from



Scheme 5 *Reagents:* i, Bu^tMe_2SiCl, imidazole, DMF; ii, $LiAlH_4$, Et_2O; iii, *p*-benzoquinone (1 equiv.), acetone; iv, *p*-benzoquinone (2 equiv.), MeOH; v, CF_3CO_2H, H_2O; vi, Ac_2O, pyridine; vii, compound **19**, EtOAc, reflux; viii, Ac_2O, pyridine, 4-dimethylaminopyridine

the quinone **22** using aqueous trifluoroacetic acid followed by sodium nitrite, or ceric ammonium nitrate,[27] or pyridinium chlorochromate,[28] were all unsuccessful. It was sometimes possible to isolate the product as a bright yellow solid, but its colour invariably faded and attempted purification resulted in intractable material.

Reaction of the quinone **22** with the diene **19** proceeded in good yield in refluxing ethyl acetate with the formation of an adduct, which appeared to have the expected heptacyclic structure **24** from its ^1H and ^{13}C NMR spectra. In particular, the methylene protons adjacent to the CH–CH bridgeheads were non-equivalent, as expected. One other set of methylene protons showed non-equivalence, as did one set of $SiMe_2$ groups; the remaining two sets of methylene protons and the other set of $SiMe_2$ groups were apparently equivalent, presumably due to unresolvably small chemical shift differences. None of these signals was broadened (see below).

The adduct **24** could be aromatised and acetylated with acetic anhydride in pyridine, catalysed by 4-dimethylaminopyridine,[29] to give a diacetoxy compound, formulated as **25** (70–75%). While the analytical data, IR and the ^{13}C NMR spectra for this compound are completely in accord with the predicted structure, the ^1H NMR spectrum showed one surprising feature. The signals for the methylene protons consisted of one sharp peak at δ 3.21 and one very broad signal at δ 3.17. When the spectrum was recorded at −50 °C, this latter signal appeared as an AB quartet (J_{AB} *ca.* 15 Hz). This implies a high barrier for inversion of at least some of the cyclohexa-1,4-diene rings in this compound, which is not in accord with literature precedents. As stated in the introduction, cyclohexa-1,4-diene rings are normally flat and, even if they are folded, the barriers to ring inversion are generally believed to be very low.[30,31] Of course, in compound **25**, as many as four folded rings might have to be inverted, but this would only raise the overall barrier if the intermediates were significantly less stable than the lowest energy conformation, and this does not seem very likely.[3] We have also considered whether the sheer bulk of this molecule (RMM 1024), and especially the large TBDMS groups, could have a significant effect, but we know of no example of such a ponderal effect. We have carefully considered the possibility that the structure of this compound is incorrectly assigned, but have been unable to arrive at a plausible alternative. Finally, the presence of two different protective groups in compound **25** opens up the possibility of selective deprotection of the end rings; oxidation to a bisquinone would then afford a double dienophile suitable for further extension of the chain of rings.

Conclusions

The failure to generate a doubly-exocyclic diene **13** from precursors such as **16** may be attributed to their insolubility and susceptibility to aromatisation. The former difficulty might be overcome by the use of long-chain R groups, but it proved impossible to introduce these by the usual base-catalysed processes that led to the formation of the anthraquinone-disulfone **10**. Although these problems, together with the instability of the doubly dienophilic bisquinone **12**, have stalled our approach to the synthesis of a [9]-beltene, the preparation of long linear arrays of six-membered rings is readily accomplished by using some of the intermediates described above in suitable diene-dienophile combinations.

Experimental

IR spectra were determined for Nujol mulls using a Perkin-Elmer 881 spectrophotometer. NMR spectra were measured with a JEOL GX270 instrument, observing ^1H at 270 MHz and ^{13}C at 68 MHz, for solutions in $CDCl_3$ unless stated otherwise (Me_4Si as internal standard); coupling constants *J* are given in Hz. Electron-impact mass spectra were recorded with an AE1 MS902 spectrometer; new compounds for which no mass spectral data are quoted showed no significant spectra up to 300 °C.

3,4-*Dimethyl*-2,5-*dihydrothiophene* 1,1-*Dioxide* **1**.—The reaction vessel was a nitrogen-filled thick-walled Schlenk tube (containing a small magnetic follower) fitted with a Young's tap. A solution of hydroquinone (340 mg) in methanol (5 cm^3) was added, followed by 2,3-dimethylbuta-1,3-diene (7.0 cm^3, 5.08 g, 61.8 mmol) and the tube was cooled to *ca.* −40 °C. Sulfur dioxide (*ca.* 15 cm^3) from a canister was then condensed in the

cooled mixture, the vessel was sealed and the mixture was stirred magnetically at room temp. for 4 days. The pressure was then released, allowing the excess of sulfur dioxide to escape and the crystalline residue was collected, washed with methanol and recrystallised from the same solvent to give the adduct **1** (7.75 g, 80%), m.p. 136–137 °C (lit.,[21] 136–137 °C); δ_H 3.73 (4 H, m) and 1.79 (6 H, m); δ_C 125.7, 60.8 and 14.6.

3,4-*Bis*(*bromomethyl*)-2,5-*dihydrothiophene* 1,1-*Dioxide* **2**.—A mixture of the thiophene dioxide **1** (31.0 g, 212 mmol), *N*-bromosuccinimide (74.9 g, 425 mmol) and dry chloroform (250 cm^3) was heated under reflux for 24 h. While the resulting solution was still warm, it was washed with water (3 × 200 cm^3), dried ($MgSO_4$) and then evaporated under reduced pressure. Treatment of the oily residue with methanol at 0 °C yielded a crystalline solid, which was filtered off, washed with methanol and then diethyl ether and finally dried ($MgSO_4$) to give the dibromo compound **2** (27.1 g, 42%), m.p. 124–125 °C (methanol) (lit.,[21] 124–125 °C); δ_H 4.08 (4 H, s) and 4.02 (4 H, s); δ_C 131.2, 58.4 and 23.9.

5,8-*Dioxo*-1,3,4,4a,5,8,8a,9-*octahydronaphtho*[2,3-c]*thiophene* 2,2-*Dioxide* **4**.—To a stirred solution of the dibromide **2** (16.0 g, 52.6 mmol) in dry acetone (75 cm^3) under an atmosphere of nitrogen, was added a solution of sodium iodide (32.0 g, 213 mmol) in the same solvent (150 cm^3). After being stirred at room temp. for 18 h, the mixture was filtered and the solid was washed thoroughly with acetone. The filtrate and washings were combined and most of the solvent was removed under reduced pressure. Aq. sodium thiosulfate was added until a pale yellow solution was obtained, the product was then extracted with dichloromethane (3 × 40 cm^3) and this solution was washed with water (250 cm^3) and then dried ($MgSO_4$). Evaporation of the solvent at this stage gave 3,4-dimethylene-tetrahydrothiophene 1,1-dioxide **3**;[22] δ_H 5.75 (2 H), 5.20 (2 H) and 3.91 (4 H) (all apparent triplets, *J ca.* 1.5) (*cf.* ref. 22); δ_C 136.2, 112.5 and 57.0. However, since the complete removal of the solvent frequently resulted in the partial polymerisation of the diene-sulfone **3**, the compound was generally used as the dichloromethane solution without isolation.

Freshly recrystallised *p*-benzoquinone (6.65 g, 61.5 mmol) was added to the solution of the dione-sulfone **3**, and the volume of the solution was reduced to *ca.* 50 cm^3; there was a mildly exothermic reaction and some solid product separated. The mixture was stirred under nitrogen at room temp. for 20 h. Diethyl ether (50 cm^3) was added and the solid was filtered off, washed well with diethyl ether and then dried, furnishing the *adduct* **4** as a microcrystalline powder (9.65 g, 73%), which decomposed without melting below 300 °C. A pure sample was obtained by recrystallisation from ethyl acetate (Found: C, 57.15; H, 4.9; S, 12.9. $C_{12}H_{12}O_4S$ requires C, 57.13; H, 4.80; S, 12.71%); ν_{max}/cm^{-1} *ca.* 1702, 1672 and 1592; $\delta_H([^2H_6]DMSO)$ 6.78 (2 H, s), 3.81 (4 H, s), 3.5–3.35 (2 H, m) and 2.45–2.1 (4 H, ABq (br signals), *J ca.* 18); $\delta_C([^2H_6]DMSO)$ 199.3, 139.3, 125.5, 58.65, 45.2 and 24.3; *m/z* 252 (M^+) and 188 ($M^+ - SO_2$; base peak).

5,8-*Dihydroxy*-1,3,4,9-*tetrahydronaphtho*[2,3-c]*thiophene* 2,2-*Dioxide* **5**.—A mixture of the ene-dione **4** (500 mg, 1.98 mmol), methanol (100 cm^3) and conc. hydrochloric acid (0.5 cm^3) was heated under reflux for 18 h. The solution was then concentrated to *ca.* 25 cm^3 under reduced pressure and the resulting crystals were collected by filtration, washed with methanol and then diethyl ether and finally dried to afford the *hydroquinone* **5** (458 mg, 92%), m.p. *ca.* 235 °C (decomp.) (methanol) (Found: C, 57.0; H, 4.9; S, 13.5. $C_{12}H_{12}O_4S$ requires C, 57.13; H, 4.80; S, 12.71%); ν_{max}/cm^{-1} 3374 br and 1621; $\delta_H([^2H_6]DMSO)$ 8.73 (2 H, s), 6.49 (2 H, s), 3.94 (4 H, s) and 3.18 (4 H, s); $\delta_C([^2H_6]DMSO)$ 146.8, 125.0, 119.9, 112.0, 58.6 and 25.4; *m/z* 252 (M^+) and 202 (base peak).

The *diacetyl*-derivative **6** was prepared with acetic anhydride in pyridine in the usual manner; m.p. *ca.* 215 °C (decomp.) (chloroform–ethyl acetate) (Found: C, 57.05; H, 4.9; S, 9.2. $C_{16}H_{16}O_6S$ requires C, 57.13; H, 4.80; S, 9.53%); ν_{max}/cm^{-1} 1764; δ_H 7.02 (2 H, s), 3.84 (4 H, s), 3.27 (4 H, d) and 2.34 (6 H, s); δ_C 169.0, 146.1, 126.1, 124.8, 121.0, 59.0, 25.8 and 20.9; *m/z* 336 (M^+) and 188 (base peak). The diacetyl derivative **6** was also obtained directly from the ene-dione **4** using the same procedure.

5,8-*Dioxo*-1,3,4,5,8,9-*hexahydronaphtho*[2,3-c]*thiophene* 2,2-*Dioxide* **14**.—A stirred suspension of the finely powdered ene-dione **4** (2.00 g, 7.99 mmol) in a mixture of glacial acetic acid (80 cm^3), trifluoroacetic acid (8 cm^3) and water (4 cm^3) was heated under reflux for 1 h. Sodium nitrite (820 mg, 11.9 mmol) was then added in portions over 5 min, and stirring was continued for a further 5 min. The resulting clear yellow solution was cooled and poured into ice–water (200 cm^3), and the mixture was allowed to stand for 30 min. The crystalline solid was filtered off, washed with water and then acetone and then dried to give the yellow *quinone* **14** (1.62 g, 82%). Recrystallisation from acetone afforded a pure sample (decomp. without melting above *ca.* 200 °C) (Found: C, 57.7; H, 4.0; S, 12.95. $C_{12}H_{10}O_4S$ requires C, 57.59; H, 4.03; S, 12.81%); ν_{max}/cm^{-1} 1674, 1651 and 1596; $\delta_H([^2H_6]DMSO)$ 6.88 (2 H, s), 3.95 (4 H, s) and 3.10 (4 H, s); $\delta_C([^2H_6]DMSO)$ 186.2, 137.5, 136.3, 124.1, 58.1 and 24.7. The quinone **14** gradually became brown on exposure to light.

5,11-*Dioxo*-4,4a,5,6,7,9,10,11,11a,12-*decahydro*-1H,3H-*anthra*[2,3-c:6,7-c′]*bisthiophene* 2,2,8,8-*Tetraoxide* **15**.—The quinone **14** (1.47 g, 5.88 mol) was stirred in cold *N*,*N*-dimethylformamide (100 cm^3) until a clear solution was obtained. This was then added to a sample of the diene **3** prepared from the dibromide **2** (2.00 g, 6.58 mmol), and the mixture was stirred at room temp. for 24 h. The addition of water (200 cm^3) then precipitated a solid that was filtered off, washed with water and then acetone, and finally dried to give the adduct **15** (1.88 g, 81%). A pure sample was obtained by repeated recrystallisation from dimethyl sulfoxide–acetone, followed by thorough washing with methanol and then acetone; m.p. decomposed above *ca.* 225 °C (Found: C, 54.8; H, 4.7; S, 16.1. $C_{18}H_{18}O_6S_2$ requires C, 54.81; H, 4.60; S, 16.26%); ν_{max}/cm^{-1} 1679 and 1631; $\delta_H([^2H_6]DMSO)$ 3.92 (4 H, s), 3.79 (4 H, s), 3.55–3.35 (2 H, m), 3.07 (4 H, s) and 2.5–2.1 [4 H, ABq (br signals), *J ca.* 17]; $\delta_C([^2H_6]DMSO)$ 197.8, 140.45, 125.6, 124.2, 58.7, 58.2, 44.9, 25.4 and 24.4.

5,11-*Dihydroxy*-4,6,7,9,10,12-*hexahydro*-1H,3H-*anthra*[2,3-c:6,7-c′]*bisthiophene* 2,2,8,8-*Tetraoxide* **16**.—The ene-dione **15** (1.00 g, 2.54 mmol) was dissolved in warm trifluoroacetic acid (10 cm^3). Water (3 cm^3) was then added and the solution was heated under reflux for 4 h, during which time a crystalline solid gradually separated. The solid was filtered off and washed with water followed by acetone and then dried to afford the crude *hydroquinone* **16** (917 mg, 92%). A pure sample was obtained by repeated recrystallisation from dimethyl sulfoxide, followed by thorough washing with methanol and then acetone; it decomposed at *ca.* 270 °C (rapid heating) with partial melting (Found: C, 55.1; H, 4.7; S, 16.2. $C_{18}H_{18}O_6S_2$ requires C, 54.81; H, 4.60; S, 16.26%); ν_{max}/cm^{-1} 3470; $\delta_H([^2H_6]DMSO)$ 7.85 (2 H, br s), 3.96 (8 H, s) and 3.27 (8 H, s); $\delta_C([^2H_6]DMSO)$ 144.4, 125.1, 119.0, 58.8 and 25.8. After storing for several days, the solution of compound **16** in $(CD_3)_2SO$ showed δ_H 8.23 (4 H, 3) and 4.76 (8 H, s); δ_C(C=O not observed) 139.5, 132.7, 124, 5 and 56.1; the recovered material also showed ν_{max}/cm^{-1} 1677 and 1602.

Thermolysis of the Hydroquinone-disulfone **16**.—The disulfone **16** (100 mg, 0.25 mmol) was placed in a sublimation tube, the pressure was reduced to 0.1 mmHg and the tube was plunged into a Kugelrohr oven preheated to 250 °C. After 1 h the orange-yellow sublimate was collected in chloroform and removal of the solvent then gave 2,3,6,7-tetramethylanthraquinone **11** (51 mg, 76%), m.p. 326–328 °C (glacial acetic acid) (lit.,[24] 330 °C); ν_{max}/cm^{-1} 1670, 1656, 1609 and 1592; δ_H 8.01 (4 H, s) and 2.41 (12 H, s); δ_C *ca.* 184, 134.75, 131.7, 128.1 and 20.2; *m/z* 264 (M^+; base peak).

5,8-*Dioxo*-4,5,6,7,9,11,12-*octahydro*-1H,3H-*anthra*[2,3-c:7,8-c']*bisthiophene* 2,2,8,8-*Tetraoxide* **17**.—To a suspension of the hydroquinone **16** (100 mg, 0.25 mmol) in warm trifluoroacetic acid (2 cm^3) was added sodium nitrite (20 mg, 0.29 mmol). The resulting clear yellow solution was diluted with water (5 cm^3) and the precipitated solid was filtered off, washed with water followed by acetone and then dried, to give the *quinone* **17** as a yellow powder (67 mg, 67%); the product decomposed without melting at *ca.* 245 °C (rapid heating) (Found: C, 55.1; H, 4.0; S, 16.5. $C_{18}H_{16}O_6S_2$ requires C, 55.09; H, 4.11; S, 16.34%); ν_{max}/cm^{-1} 1638; δ_H([$^2H_6$]DMSO) 3.95 (8 H, s) and 3.12 (8 H, s); δ_C([$^2H_6$]DMSO) 185.0, 137.4, 124.4, 58.3 and 24.9.

5,8-*Bis*(tert-*butyldimethylsilyloxy*)-1,3,4,9-*tetrahydronaphtho*-[2,3-c]*thiophene* 2,2-*Dioxide* **18**.—The ene-dione **4** (3.40 g, 13.5 mmol) was dissolved in warm dry *N*,*N*-dimethylformamide (90 cm^3) and then imidazole (5.00 g, 73.5 mmol) and *tert*-butylchlorodimethylsilane (4.90 g, 32.5 mmol) were both added with constant stirring. The mixture was stirred at room temp. for a further 72 h and then poured into ice–water. The resulting precipitate was filtered off, washed well with water and then dried to afford the *bis*(*silyl ether*) **18** (6.08 g, 94%), m.p. 164–165 °C, raised to 165–166 °C after recrystallisation from ethyl acetate–hexane (Found: C, 59.8; H, 8.5; S, 6.8. $C_{24}H_{40}O_4SSi_2$ requires C, 59.96; H, 8.39; S, 6.67%); δ_H 6.57 (2 H, s), 3.85 (4 H, s), 3.27 (4 H, s), 1.00 (18 H, s) and 0.21 (12 H, s); δ_C 146.9, 125.5, 124.3, 115.7, 59.3, 26.7, 25.8, 18.3 and −4.1; *m/z* 480 (M^+) and 416 ($M^+ - SO_2$; base peak).

7,10-*Bis*(tert-*butyldimethylsilyloxy*)-1,4,4a,5,6,11,12,12a-*octahydronaphthacene*-1,4-*dione* **20**.—To a vigorously stirred refluxing suspension of lithium aluminium hydride (315 mg, 8.29 mmol) in dry diethyl ether (20 cm^3) was added, in several portions, compound **18** (400 mg, 0.83 mmol). Stirring under reflux was continued for 1 h, after which the mixture was allowed to cool to room temp., and then further cooled in an ice–water bath and treated with the dropwise addition of ethyl acetate (2 cm^3). The subsequent portionwise addition of a sat. aq. solution of sodium sulfate (5 cm^3) resulted in a clear solution and a sticky white solid. The diethyl ether solution was decanted and the solid was washed with diethyl ether (3 × 20 cm^3). The combined solution and washings were dried ($MgSO_4$) and evaporated under reduced pressure. The oily residue was characterised as the crude *diene* **19**; δ_H 6.52 (2 H, d), 5.31 (2 H, d, *J* 1.5), 4.91 (2 H, d, *J* 1.5), 3.50 (4 H, s), 1.02 (18 H, s) and 0.18 (12 H, s); δ_C 146.1, 143.7, 128.5, 116.2, 108.3, 32.4, 25.85, 18.3 and −4.2. It was used immediately for the next stage without purification.

The diene **19** was dissolved in acetone (5 cm^3) and freshly recrystallised *p*-benzoquinone (100 mg, 0.93 mmol) was added. After standing at room temp. for 22 h, the solution was evaporated under reduced pressure and the residue was crystallised from methanol containing a little diethyl ether at −15 °C. The solid was filtered off, washed with methanol and dried to give the crude (pale brown) *ene-dione* **20** (244 mg, 56%). Repeated recrystallisation from methanol gave an analytically pure sample; the m.p. (*ca.* 145–150 °C) was diffuse and variable (Found: C, 68.4; H, 8.5. $C_{30}H_{44}O_4Si_2$ requires C, 68.65; H, 8.45%); ν_{max}/cm^{-1} 1692 and 1590; δ_H 6.69 (2 H, s), 6.50 (2 H, s), 3.35–3.25 (2 H, m), 3.12 (4 H, s), 2.6–2.4 (2 H, m), 2.25–2.1 (2 H, m), 1.00 (18 H, s), 0.187 (6 H, s) and 0.184 (6 H, s); δ_C 200.1, 146.6, 139.4, 126.3, 123.0, 115.0, 46.8, 30.6, 28.7, 25.8, 18.2 and −4.2; *m/z* 524 (M^+; base peak).

5,6,11,12-*Tetrahydronaphthacene*-1,4,7,10-*tetraol* **21**.—The ene-dione **20** (228 mg, 0.43 mmol) was dissolved in 67% aq. trifluoroacetic acid (3.5 cm^3) and the solution was heated under reflux for 10 min, during which time a crystalline solid separated. The mixture was cooled and the crystals were filtered off, washed with water and then methanol and finally dried. The resulting crude *tetrahydroxy compound* **21** (127 mg, 99%) could not be purified satisfactorily (it appeared to be unstable) and correct analytical figures were not obtained; m.p. > 300 °C; ν_{max}/cm^{-1} 3300, 3240sh, 1626 and 1602; δ_H([$^2H_6$]-DMSO) 8.54 (4 H, s), 6.46 (4 H, s) and 3.13 (8 H, s); δ_C([$^2H_6$]DMSO) 146.8, 122.0, 121.9, 111.6 and 29.5.

The *tetraacetyl derivative* **23**, prepared with acetic anhydride in pyridine in the usual way, had m.p. 295–297 °C (some decomp.) (acetone) (Found: C, 67.2; H, 5.5. $C_{26}H_{24}O_8$ requires C, 67.23; H, 5.21%); ν_{max}/cm^{-1} 1752; δ_H 6.96 (4 H, s), 3.19 (8 H, s) and 2.36 (12 H, s); δ_C 169.2, 145.9, 128.2, 121.0, 120.1, 29.2 and 21.0; *m/z* 464 (M^+) and 43 (base peak).

7,10-*Bis*(tert-*butyldimethylsilyloxy*)-1,4,5,6,11,12-*hexahydronaphthacene*-1,4-*dione* **22**.—The crude diene **19**, prepared from compound **18** (2.40 g, 5.00 mmol) as described above, was dissolved in warm methanol (15 cm^3) and added to a warm solution of freshly recrystallised *p*-benzoquinone (1.08 g, 10.00 mmol) in the same solvent (5 cm^3). After the mixture had been kept at room temp. for 22 h, the tan-coloured solid which separated was filtered off, washed with methanol and dried. Recrystallisation from acetone then yielded the orange-yellow *quinone* **22** (814 mg, 31%), m.p. 168.5–169.5 °C after further recrystallisation (Found: C, 69.1; H, 8.15. $C_{30}H_{42}O_4Si_2$ requires C, 68.92; H, 8.10%); ν_{max}/cm^{-1} 1659sh, 1652 and 1606; δ_H 6.76 (2 H, s), 6.53 (2 H, s), 3.22 (4 H, s), 3.11 (4 H, s), 1.02 (18 H, s) and 0.21 (12 H, s); δ_C 187.1, 146.7, 139.7, 136.3, 126.1, 121.5, 115.2, 30.0, 28.8, 25.9, 18.3 and −4.1; *m/z* 522 (M^+) and 73 (base peak).

1,4,10,13-*Tetrakis*(tert-*butyldimethylsilyloxy*)-5,6,6a,7,8,9,-14,15,16,16a,17,18-*dodecahydroheptacene*-7,16-*dione* **24**.—A mixture of the diene **19**, prepared from compound **18** (880 mg, 1.83 mmol) as described above, and the quinone **22** (724 mg, 1.38 mmol) in ethyl acetate (20 cm^3) was heated under reflux for 22 h. Methanol (20 cm^3) was then added and the mixture allowed to cool. The resulting crystals were filtered off, washed with methanol and then dried, giving the *adduct* **24** (978 mg, 75%), which was recrystallised from ethyl acetate–methanol; it melted if heated suddenly to 185 °C, but on slow heating it partially melted at *ca.* 180 °C and melting was still incomplete at 300 °C (Found: C, 68.8; H, 8.9. $C_{54}H_{82}O_6Si_4$ requires C, 69.03; H, 8.80%); ν_{max}/cm^{-1} 1678, 1633 and 1590; δ_H 6.53 (2 H, d), 6.50 (2 H, s), 3.4–3.3 (2 H, m), 3.20 (4 H, s), 3.13 (4 H, s), 3.07 (4 H, br s), 2.6–2.1 [4 H, ABq (br signals), *J ca.* 16], 1.01 (18 H, s), 1.00 (18 H, s), 0.203 (6 H, s), 0.199 (6 H, s) and 0.185 (12 H, s); δ_C 199.8, 146.8, 146.7, 142.6, 126.45, 126.2, 123.0, 121.7, 115.2, 115.1, 46.8, 30.7, 30.0, 29.6, 29.1, 25.9, 18.3 and −4.1.

7,16-*Diacetoxy*-1,4,10,13-*tetrakis*(tert-*butyldimethylsilyloxy*)-5,6,8,9,14,15,17,18-*octahydroheptacene* **25**.—To a stirred solution of the ene-dione **24** (860 mg, 0.915 mmol) in warm dry triethylamine (8 cm^3) was added acetic anhydride (2 cm^3, 21.2

mmol), followed by 4-dimethylaminopyridine (10 mg, 0.08 mmol). Stirring was continued at room temp. for 16 h, during which time a crystalline solid separated. Acetone (10 cm^3) was added and the solid was filtered off, washed with acetone and dried. Recrystallisation from dichloromethane–ethyl acetate then yielded the *diacetoxy compound* **25** (702 mg, 75%), m.p. 315–316 °C after further recrystallisation (Found: C, 68.0; H, 8.6. $C_{58}H_{86}O_8Si_4$ requires C, 68.05; H, 8.47%); ν_{max}/cm^{-1} 1755 and 1593; δ_H 6.54 (4 H), 3.21 (8 H, s), *ca.* 3.17 (8 H, v br), 2.44 (6 H, s), 1.04 (36 H, s) and 0.22 (24 H, d); δ_C(C=O not observed) 146.7, 143.9, 126.55, 125.8, 121.5, 115.1, 30.3, 29.1, 25.9, 20.7, 18.3 and −4.1.

Acknowledgements

Thanks are due to the SERC for financial support and to Dr. M. J. O'Connell for preliminary investigations.

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Paper 4/04205K
Received 11*th July* 1994
Accepted 2*nd August* 1994