Construction of a tube-like molecule *via* sequential cyclopropylidene dimerisation and intramolecular [π2s+π2s] cycloaddition reactions

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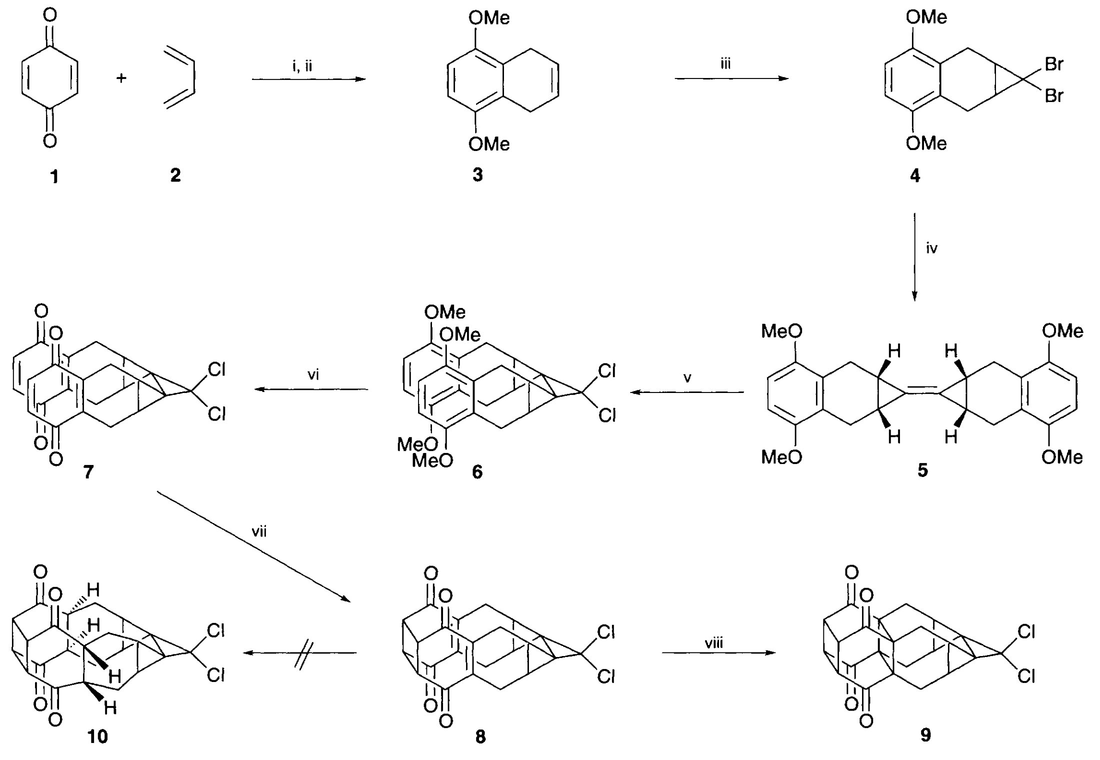
The *syn*-cyclopropylidene dimer 5, obtained by reaction of compound 4 with methyllithium, is readily elaborated to the bis-*p*-benzoquinone 7 which undergoes intramolecular [π2s+π2s] cycloaddition to give the tube-like molecule 8.

A topic of current interest is the assembly of molecular frameworks which deliberately create geometrically well-defined and close spatial relationships between functionalities such that new or enhanced interactions of these groups can be anticipated.[1] We now describe a novel and potentially versatile means for achieving these ends. The key design feature associated with the present work is the formation and cyclofunctionalisation of a *syn*-cyclopropylidene dimer,[2] a reaction sequence which permits formation of symmetrical molecules wherein the constituent halves are brought into sufficiently close contact for useful reaction to occur. These ideas are exemplified by the synthesis of the macrocyclic cavity molecule **8**, the likes of which could serve as building blocks for the construction of molecular tubes[3] and/or provide a platform for the synthesis of the elusive hexaprismane ring-system.[4]

The synthesis of the pivotal *syn*-cyclopropylidene dimer **5** was readily achieved by the route shown in Scheme 1. Thus, the compound[5] derived from a Diels-Alder reaction between *p*-benzoquinone **1** and buta-1,3-diene **2**, was converted into the corresponding bis-*O*-methyl ether **3** (98%, mp 45–48 °C; lit.,[6] mp 50 °C) under standard conditions. This last compound was then subjected to reaction with dibromocarbene, generated under phase transfer conditions, and in this manner the *gem*-dibromocyclopropane **4** (28%, mp 101.5–103 °C; lit.,[7] mp 102–103 °C) was obtained. Treatment of compound **4** with methyl lithium in diethyl ether at −80 °C resulted in a number of products including the *syn*-cyclopropylidene dimer **5**[†,‡] (11%, mp 161–173 °C) and its *anti*-isomer (14%, mp 248–255 °C). Dimer **5** (isolated by fractional crystallisation techniques) was subjected to reaction with dichlorocarbene, a process which resulted in the exclusive formation of the tricyclane **6** (91%, mp 231–242 °C). Inspection of molecular models and X-ray crystal structures of related systems[8] suggested that this cyclofunctionalisation step reduces the face-to-face distance between the two aromatic rings from *ca.* 7 Å in **5** to <4 Å in **6**. As a result of such close contacts it was anticipated that the bis-*p*-benzoquinone derived from compound **6** should be appropriately set up for a facile intramolecular [π2s+π2s] cycloaddition reaction leading to forma-



Scheme 1 *Reagents and conditions*; i, C_6H_6, sealed tube, 18 °C, 96 h; ii, $(MeO)_2SO_2$ (20 equiv.), K_2CO_3 (20 equiv.), Me_2CO, 56 °C, 16 h; iii, $CHBr_3$ (5 equiv.) 50% aq. NaOH (4 equiv.), C_6H_6, TEBAC (1 mol%), 0–18 °C, 16 h; iv, MeLi (2.2 equiv.) Et_2O, −80 °C, 4 h; v, Cl_3CCO_2Et (16 equiv.), NaOMe (11 equiv.), C_6H_6, 0–18 °C, 16 h; vi, AgO (8 equiv.), 6 mol dm^{-3} HNO_3 (1 drop), 1,4-dioxane, 18 °C, 0.66 h; vii, 300 W lamp (white light), C_6H_6, 1 h; viii, natural sunlight, $CDCl_3$, 6 weeks. TEBAC = triethylbenzylammonium chloride.

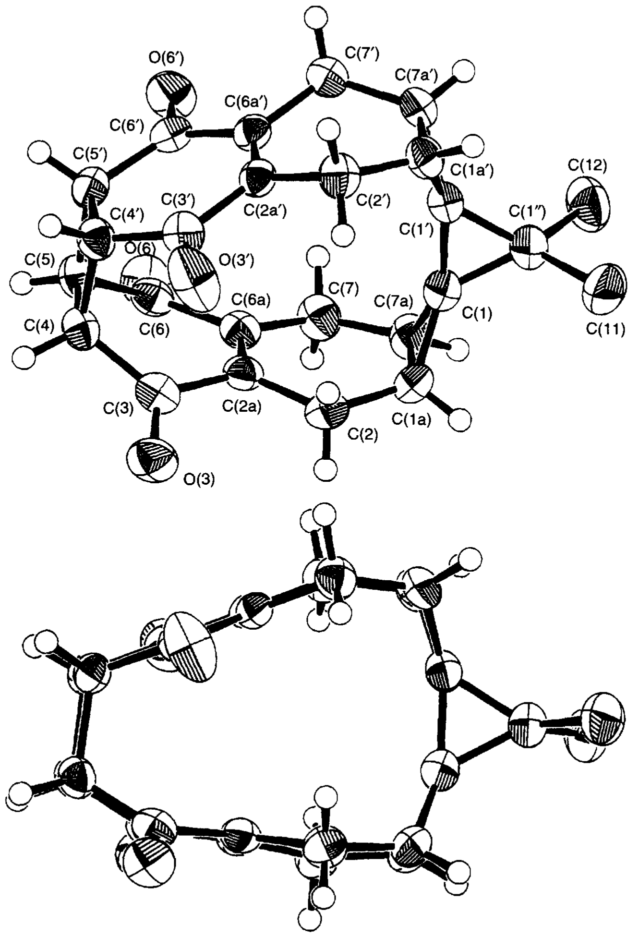


Fig. 1 ORTEP drawings of compound **8** derived from X-ray crystallographic data

tion of the cavity molecule **8**. In the event, oxidative demethylation of compound **6** [using freshly prepared silver(II) oxide in the presence of aqueous nitric acid] provided the bis-*p*-benzoquinone **7** [100%, mp 180 °C (decomp.)] which proved to be photolabile and upon irradiation (sun lamp) was converted into adduct **8**§ [68%, mp 260 °C (decomp.)]. The structure of compound **8** was confirmed by single crystal X-ray analysis (Fig. 1)¶ which highlights the tube-like quality of this material and revealed that the dimensions of the cavity are *ca.* 5.3 Å [distance between midpoints defined by C-(4), C-(4′), C-(5), C-(5′) and C-(1), C-(1′)] × 4.2 Å [distance from mid-point between C-(2) and C-(7) to mid-point between C-(2′) and C-(7′)] × 3.0 Å [distance from C-(2′) to C-(7′)]. Accompanying cavity molecule **8** were quantities of a material believed to be the bis-photoadduct **9**|| [23%, mp 285 °C (decomp.)]. This latter compound, which might well serve as a useful precursor to 'strapped' hexaprismanes, could be prepared in quantitative yield by sustained exposure of the former compound to sunlight. Attempts to hydrogenate the mono-photoadduct **8**, in the hope of generating the more cylindrical molecule **10**, have been unsuccessful so far.

Footnotes

† All new compounds had spectroscopic data [IR, UV (where appropriate), NMR, mass spectrum] consistent with the assigned structure. Satisfactory combustion and/or high resolution mass spectral analytical data were obtained for new compounds and/or suitable derivatives. The yields of new compounds are unoptimised.

‡ Compound **5** is readily prepared in *ca.* 100 mg batches. While the yield of this particular *syn*-dimer is rather low we have observed better outcomes in a number of other cases (> 50% of *syn*-dimer). Furthermore, it appears that the yield of cyclopropylidene dimers can be improved significantly by using CuCl$_2$ in conjunction with butyllithium (see T. Loosli, M. Borer, I. Kulakowska, A. Minger, M. Neuenschwander and P. Engel, *Helv. Chim. Acta*, 1995, **78**, 1144).

§ *Spectral data* for **8**: ^{13}C NMR (100 MHz, CDCl$_3$) δ 192.5 (C), 146.8 (C), 66.8 (C), 44.6 (CH), 36.8 (C), 22.1 (CH$_2$) and 18.6 (CH); ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.12 (s, 4 H), 2.80 (dm, *J* 15 Hz, 4 H), 2.63 (dm, *J* 15 Hz, 4 H) and 2.10 (broadened s, 4 H); *m/z* (EI, 70eV) 430 (7%) 428 (20) 426 (M$^+$, 27), 393 (32) 391 (M$^+$ − Cl, 87) and 355 (M$^+$ − HCl − Cl, 100); ν_{max}(KBr)/cm^{-1} 2921, 1680, 1427, 1389, 1273, 811 and 773; λ_{max}/nm (ethanol) 234 (log ε 3.82) (HRMS: M$^+$ 426.0415. C$_{23}$H$_{16}$^{35}Cl$_2$O$_4$ requires 426.0426).

¶ *Crystal data* for compound **8**: C$_{23}$H$_{16}$Cl$_2$O$_4$, M = 427.28, T = 213(1) K, monoclinic, space group $P2_1/a$, a = 9.057(2), b = 12.200(2), c = 16.968(2) Å, β = 99.54(1) °, U = 1848.9(5) Å^3, D_c (Z = 4) = 1.535 g cm^{-3}, F(000) = 880, μ(Cu-Kα) = 34.14 cm^{-1}, semi-empirical absorption correction; 2898 unique data (2θ$_{max}$ = 120.1 °), 2186 with $I > 3\sigma(I)$; R = 0.037, wR = 0.039, GOF = 2.26. Data were measured on a Rigaku AFC6R rotating anode diffractometer (graphite crystal monochromator, λ = 1.54180 Å). Refinement was by full-matrix least-squares analysis on F using the TEXSAN Structure analysis Software of Molecular Structure Corporation.[9] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1. Any request for this material should quote the full literature citation and the reference number 182/87.

|| Face-to-face bis-photodimers of various methylated *p*-benzoquinones have been obtained in low yield by Cookson[10] and Musso.[11]

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Received, 2nd April 1996; Com. 6/02328B