Synthesis and Crystal Structure of 1,2 : 7,8 : 13,14 : 19,20-tetrabenzocyclotetracosa-1,7,13,19-tetraene-3,5,9,11,15,17,21,23-octayne

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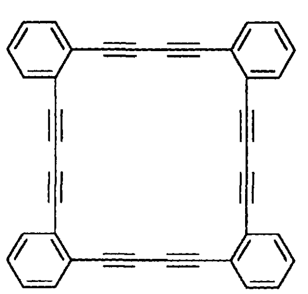
The title compound has been synthesized in a relatively high yield by the Glaser coupling reaction and characterized by X-ray crystallography and spectroscopy.

In connection with our investigations on cyclic polyalkynes tribenzocyclyne (TBC),[1] trithienocyclyne (TTC)[2] and tetrabenzocyclyne (QBC),[3] a cyclicpolydiyne 1,2 : 7,8 : 13,14 : 19,20-tetrabenzocyclotetracosa-1,7,13,19-tetraene-3,5,9,11,15,17,21,23-octayne (QBCO) was synthesized and crystallographically characterized.

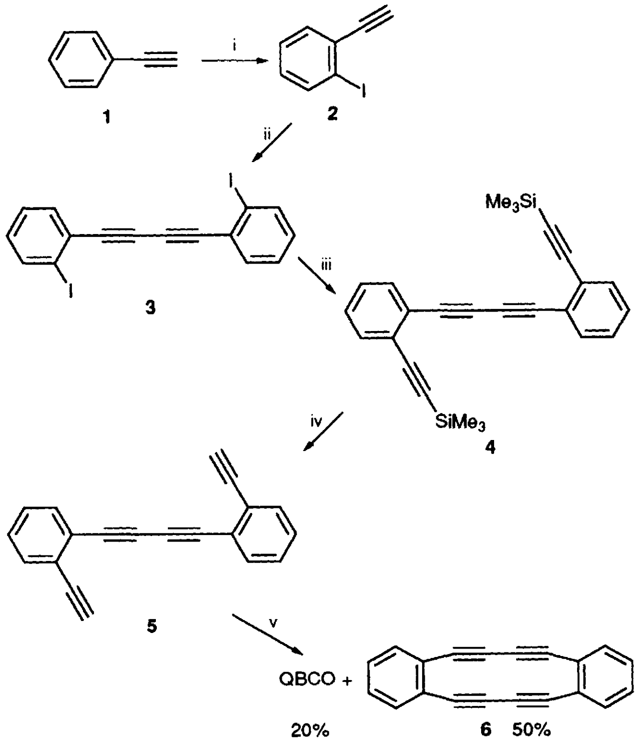
This cyclic diacetylene is intriguing for various reasons: (*i*) It is a multidentate ligand with close distances between adjacent diacetylenes; thus, it could act as a template leading to the formation of transition metal clusters. (*ii*) It is flexible and can provide a larger cavity than QBC does. The larger cavity may be able to accommodate two metal atoms with some interaction between them. Such behaviour is of great significance in the design of supramolecules. (*iii*) It is a candidate for lithium-induced cyclization reactions[4] and is predicted to form a symmetric polycyclic aromatic hydrocarbon. (*iv*) Diacetylenes are known to polymerize in the solid state by exposure to UV light, γ-irradiation or thermal annealing.[5] Using such methods, this unusual cyclic polydiacetylene, QBCO, may polymerize to give a novel, conjugated carbon backbone. Substituted analogues of QBCO have been mentioned as components of mixtures of products from the Glaser coupling cyclization reactions of substituted *o*-diethynyl benzene.[6] Sondheimer *et al.* reported the synthesis of 1,3,7,9,13,15,19,21-octadehydro[24]annulene in 1970.[7] We report herein the stepwise synthesis of QBCO in high yield, its crystal structure and spectroscopic analysis.

Our synthetic approach is outlined in Scheme 1. *o*-Iodophenylacetylene **2** was made by iodinating **1** using literature methods.[8] We found that this is an efficient and economical way to get compound **2** and it can be run on a large scale (16 g of **2** in one reaction). Conversion of **2** to **3** was realized with copper(II) acetate in the mixed-solvent system of pyridine (py) and methanol at room temperature. Compound **4** was formed from **3** by the palladium–copper catalysed coupling reaction with trimethylsilylacetylene (2.2 equiv.) under an inert atmosphere. Compound **5**, which was obtained by the desilylation reaction of **4** with potassium fluoride and water in THF and methanol, was cyclized by using copper(I) chloride in a highly dilute solution of pyridine (1 mmol dm^{-3}) to afford a mixture of tetramer QBCO and dimer **6**.[9] The yields of QBCO and **6** depend on the reaction conditions. Eglinton *et al.*[9] reported that when copper(II) acetate was used, the reaction of **5** produced **6**, but no QBCO was detected. Our attempt at using the same oxidative reagent copper(II) acetate (6 equiv.) and **5** (0.01 mol dm^{-3}) in pyridine and methanol (1 : 1) resulted in formation of a large quantity of insoluble material. Nevertheless, we still isolated QBCO in low yield. When air was bubbled into a 1 mol dm^{-3} solution of **5** in pyridine with a large excess of copper(I) chloride (120 equiv.) at room temperature, almost all of the crude products were soluble in diethyl ether. We found that a slow flow of air through the solution favoured the formation of **6** (over 65% yield). The whole synthetic process is easy to handle and all of the products are readily purified. QBCO is a white solid, quite stable at room temperature contrary to **6**, and very soluble in chloroform. All the compounds have been characterized by spectroscopy.† The structures of QBCO and **4** have also been verified by X-ray crystallography.‡



QBCO

Crystallization of QBCO from methylene chloride gave crystals suitable for X-ray structure determination. The thermal ellipsoid diagram of the structure is shown in Fig. 1. Similar to QBC,[3] QBCO is also saddle shaped. For the two molecules in the asymmetric unit, the diyne units show small deviations from linearity with the C≡C–C angles ranging from 174.0(7) to 179.4(6)°. The angles between the least-squares planes of two opposing benzene rings are 67.9 and 98.2° for molecule A and 90.0 and 72.1° for molecule B. The distances between the middles of opposing diynes are 6.258 and 7.264 Å for molecule A and 6.54 and 7.285 Å for molecule B. The mean bond length of the alkynes (1.194 Å) corresponds exactly with that of free butadiyne. This suggests that π



Scheme 1 *Reagents and conditions*: i, (a) Bu^{t}OK, Bu^{n}Li–THF, (b) MgBr$_2$·, Et$_2$O, (c) I$_2$–THF −78°C, (d) H$_2$O, ii, Cu(OAc)$_2$–py–MeOH, room temp., iii, trimethylsilylacetylene, room temp., (PhCN)$_2$PdCl$_2$–Ph$_3$P–CuI; iv, KF–H$_2$O, room temp., THF–MeOH; v, CuCl (120 equiv.)–air, **5** (1 mmol dm^{-3} in py), room temp.

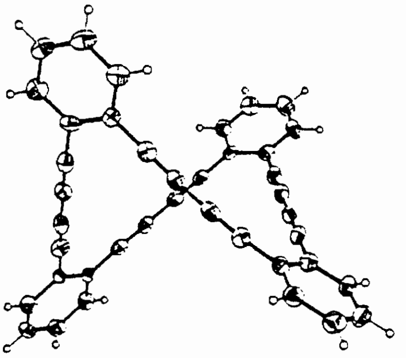


Fig. 1 X-Ray crystal structure of QBCO with thermal ellipsoids drawn at 50% probability

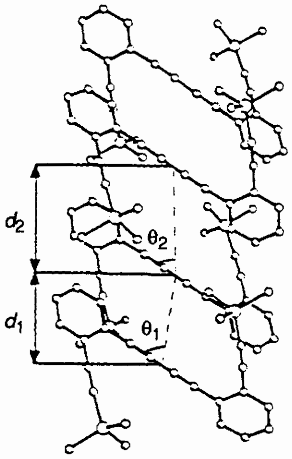


Fig. 2 Packing pattern of compound **4**; d_1 = 5.002 Å, θ_1 = 72.5°; d_2 = 5.756 Å, θ_2 = 54.5°

electrons are localized to a great extent in this cyclic polydiyne.

From the perspective of topochemical polymerization of diacetylenes, we are interested in the crystal packing pattern of compound **4** (Fig. 2). It crystallized in the triclinic $P\bar{1}$ space group. All the molecules are parallel and the closest ones stack in a zigzag manner. There are two different kinds of neighbours for any molecule, one of which is related by an inversion centre and the other is slipped away possibly because of the steric repulsion of C≡C–C–SiMe$_3$ group. The packing parameters shown in Fig. 2 revealed that this packing may allow **4** to undergo a 1,4-addition reaction in the solid state.[10] The topochemical polymerization of **4** as well as QBCO is under investigation.

Research is now in progress towards the synthesis of transition metal complexes and the lithium-induced cyclization reaction of QBCO.

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Footnotes

† *Selected Data* (all ^{1}H and ^{13}C NMR at 300 MHz; solvent CDCl$_3$). For QBCO ^{1}H NMR δ 7.52 (8 H, q), 7.30 (8 H, q); ^{13}C NMR δ 133.5, 129.1, 125.5, 80.9 and 78.2.

For **2** ^{1}H NMR δ 7.83 (1 H, d), 7.48 (1 H, d), 7.27 (1 H, t), 6.99 (1 H, t) and 3.30 (1 H, s); ^{13}C NMR δ 138.7, 133.4, 129.9, 128.6, 127.7, 100.4, 85.1 and 81.0.

For **3** ^{1}H NMR δ 7.84 (2 H, d), 7.54 (2 H, d), 7.31 (2 H, t), 7.04 (2 H, t); ^{13}C NMR δ 138.8, 133.9, 130.3, 128.5, 127.8, 100.9, 84.3 and 77.1.

For **4** ^{1}H NMR δ 7.46 (4 H, m), 7.26 (4 H, m) and 0.279 (18 H, s); ^{13}C NMR δ 132.8, 132.1, 128.9, 128.4, 127.1, 125.3, 103.2, 100.0, 81.2, 78.1 and 0.2.

For **5** ^{1}H NMR δ 7.52 (4 H, m), 7.31 (4 H, m) and 3.37 (2 H, s).

For **6** ^{1}H NMR δ 7.06 (4 H, q) and 6.69 (4 H, m); ^{13}C NMR δ 130.9, 129.7, 128.9, 92.0 and 84.4. Compound **6** was unstable; the solid turned black in air within 2 to 3 h and even did so under vacuum within 10 h. **6** has a larger R$_f$ value (in the solvent system of 1 : 4 methylene chloride : hexanes) than QBCO does, **6** exploded when scratched in air. Solid-state ^{13}C NMR has shown that the explosion product was carbon black. All these properties strongly support that **6** is the cyclic dimer.

‡ Crystal data of QBCO: crystal size 0.20 × 0.20 × 0.65 mm^3, monoclinic space group $P2_1/c$ (No. 14), a = 13.680(3), b = 18.304(4), c = 21.416(4) Å, β = 97.16(3)°, V = 5321(2) Å^3, Z = 8, T = 133 K, D_c = 1.24 g cm^{-3}, Mo-Kα (λ = 0.71073 Å) radiation; 2θ range $3.5° \leqslant 2\theta \leqslant 45°$; 8544 reflections collected, 6953 independent and 3522 observed with $F > 4.0\sigma(F)$, R = 0.0619, R_w = 0.0481 for 722 parameters.

For **4**: crystal size 0.6 × 0.6 × 0.6 mm^3, triclinic space group $P\bar{1}$ (No. 2), a = 9.526(2), b = 10.889(2), c = 12.177(2) Å, α = 95.54 (3), β = 90.36 (3), γ = 92.24 (3)°, V = 1256.2(4) Å^3, Z = 2, T = 294 K, D$_c$ = 1.043 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å); 2θ range $3.5° \leqslant 2\theta \leqslant 45°$; 3931 reflections collected, 3242 independent and 2495 observed $F > 4.0\sigma(F)$, R = 0.0515, R_w = 0.0763 for 254 parameters.

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.

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