DOI: 10.1002/ejoc.200700702

A Cyclobutadiene Intermediate in the Intramolecular Cycloaddition of 4,15-Bis(phenylethynyl)[2.2]paracyclophane[‡]

Jens Kubitschke,[a] Henning Hopf,*[a] Peter G. Jones,[b] Ina Dix,[c] and Ludger Ernst[d]

Dedicated to Professor Roald Hoffmann on the occasion of his 70th birthday

Keywords: Cyclophanes / Cycloadditions / Cylobutadiene / Proximity effects

The pseudo-*geminal*ly substituted paracyclophane 4,5-bis(phenylethynyl)[2.2]paracyclophane (**13**) was prepared and its photochemical behaviour in solution was studied. Irradiation with a medium-pressure mercury lamp converts **13** into two dimers: cyclooctatetraene **14** and bicyclo[4.2.0]octatriene derivative **15**. The structures of both the substrate and the photolysis products were determined by the usual spectroscopic methods and also by X-ray structural analysis; an unusually long C–C bond of 1.659 Å opposite the double bond in the cyclobutene ring of **15** was found. It is suggested that product formation involves cyclobutadiene **16** as an intermediate. Photolysis of **13** in the presence of pentacarbonyliron furnishes cyclopentadienone complex **19** in quantitative yield.

Introduction

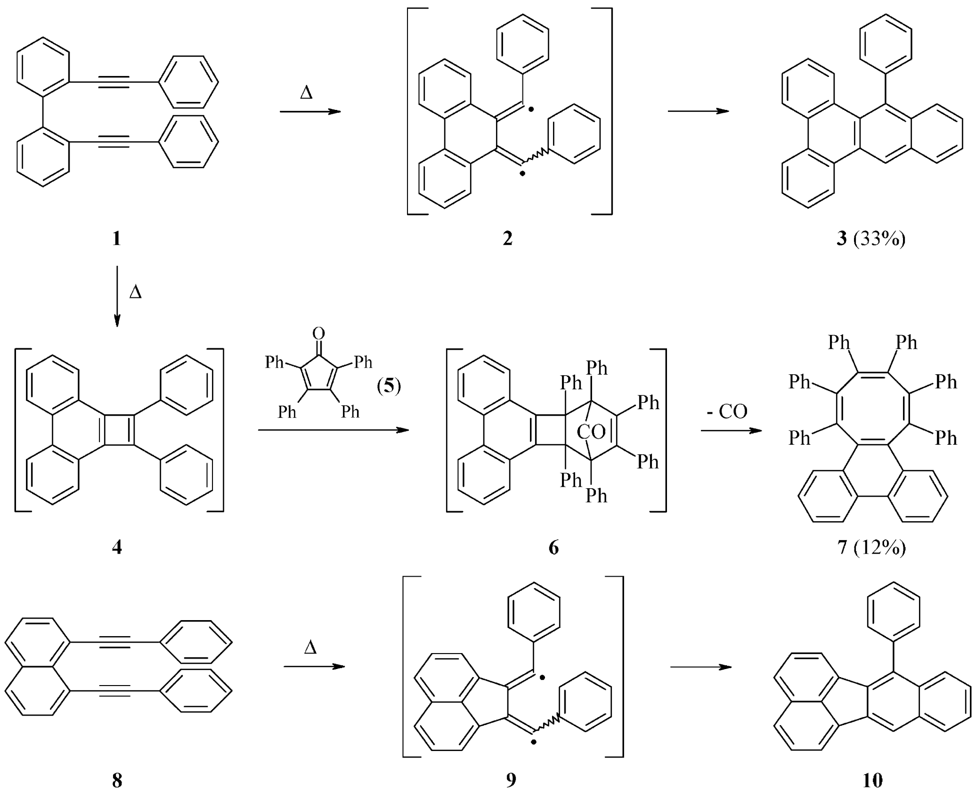
Forty years ago, Dessy[2] and White[3] reported the isomerization of 2,2′-bis(phenylethynyl)biphenyl (**1**). On heating to 150 °C in isooctane for 2 d, this hydrocarbon cycloaromatized to afford 9-phenyldibenz[*a,c*]anthracene (**3**) in more than 80% yield.[3] It was suggested that the first reaction step involved the generation of diradical **2** (a mixture of diastereomers) by forming a σ-bond between the two acetylene moieties assumed to be in close proximity. Clearly, a second ring-closure reaction to form a cyclobutadiene intermediate,[2] which would make the whole process a formal [2+2] cycloaddition, did not take place. The same isomerization can also be induced photochemically[3] (Scheme 1).

In a study published last year, Leung and coworkers revisited this process,[4] and they confirmed the production of **3** as the major thermal cyclization product (33% yield). However, they also repeated the isomerization experiment in the presence of tetraphenylcyclopentadienone (**5**, tetracyclone) as a trapping agent, and under these conditions (260–270 °C, 4 h) they were able to isolate totally substituted cyclooctatetraene **7** in 12% yield. To rationalize this observation, the authors proposed that cycloaddition between the two triple bonds of **1** did indeed occur to provide cyclobutadiene intermediate **4**, which was trapped by **5** to afford [2+4] cycloadduct **6** (not isolated). Under the reaction conditions, decarbonylation took place readily and ultimately led to isolated product **7**.

Although it could be argued that the proximity of the two triple bonds in **1** might not be as favourable as intuitively anticipated, because of the rotation around the central single bond, this is not the case for 1,8-bis(phenylethynyl)naphthalene (**8**), a hydrocarbon that was pyrolyzed by Shechter and coworkers in the late 1960s.[5] Again, a polynuclear aromatic hydrocarbon, **10**, is formed and its most reasonable precursor is diradical **9**. An attempt to trap a possible cyclobutadiene intermediate with pentacarbonyliron met with failure and yielded only an (acecyclone)tricarbonyliron complex rather than the expected tricarbonyl(cyclobutadiene)iron derivative.[6] From the reported X-ray structure of **8**, a distance of 310.3 pm can be calculated between the midpoints of the triple bonds.[7]

[‡] Cyclophanes, LX. Part LIX: Ref.[1]

[a] Institut für Organische Chemie, Technische Universität Braunschweig,
Hagenring 30, 38106 Braunschweig, Germany
Fax: +49-531-391-5388
E-mail: H.Hopf@tu-bs.de
[b] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig,
Postfach 3329, 38023 Braunschweig, Germany
Fax: +49-531-391-5387
E-mail: P.Jones@tu-bs.de
[c] Institut für Anorganische Chemie, Universität Göttingen,
Tammannstrasse 4, 37077 Göttingen, Germany
E-mail: inadix@shelx.uni-ac.gwdg.de
[d] NMR-Laboratorium der Chemischen Institute der Technischen Universität Braunschweig,
Hagenring 30, 38106 Braunschweig, Germany
Fax: +49-531-391-8192
E-mail: L.Ernst@tu-bs.de

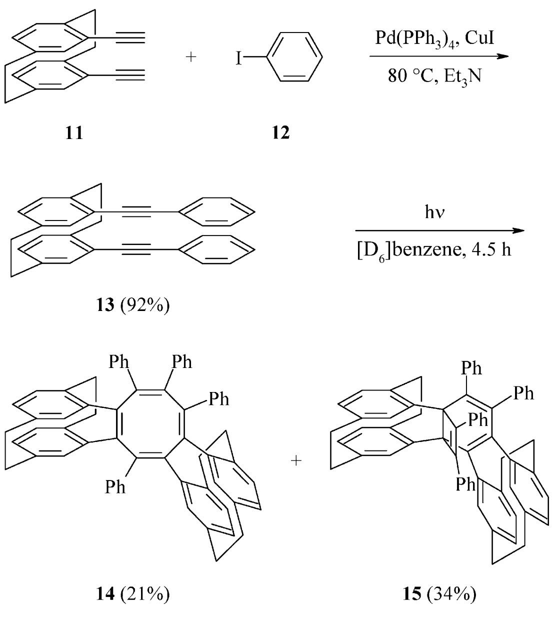


Scheme 1. Formation of cyclobutadiene intermediates from sterically fixed triple bonds.

Results and Discussion

Photoaddition Experiments

Having demonstrated that [2.2]paracyclophane is an excellent spacer to hold numerous functional groups in a parallel orientation at a distance of ca. 300–330 pm, provided that these substituents are positioned in a pseudo-*geminal* orientation (i.e. directly above each other),[8] we decided to prepare the phane analogue of the above systems, viz. 4,15-bis(phenylethynyl)[2.2]paracyclophane (**13**, Scheme 2).



Scheme 2. Preparation and photolysis of 4,15-bis(phenylethynyl)-[2.2]paracyclophane (**13**).

To our satisfaction, this hydrocarbon – a formal dimer of tolane with a fixed geometry – is readily available in excellent yield by coupling the recently prepared[9] 4,15-diethynyl[2.2]paracyclophane (**11**) with iodobenzene (**12**) under Sonogashira conditions.[10] Upon irradiation of **13** in perdeuteriobenzene at room temperature, the starting material was consumed completely after 4.5 h, and two new products were formed in ca. 2:3 ratio. These were separated by silica gel column chromatography and shown by spectroscopic and X-ray data to be cyclooctatetraene **14** (21%) and bicyclo[4.2.0]octatriene derivative **15** (34%); the remainder of the reaction mixture was evidently polymeric material that stayed on the chromatography column.

Structure Determination of 13–15

Of the expected 56 different ^{13}C NMR signals for **14**, 54 were observed separately at the observation frequency of 151 MHz. Full assignment was not possible, however, because only a few HMBC cross peaks between the ^{13}C NMR chemical shifts of the cyclooctatetraene ring and the phenyl or paracyclophanyl ^{1}H NMR chemical shifts could be observed. Hence, signal assignments were only achieved for the sets of nuclei within the individual phenyl (ph1–ph4) and paracyclophanyl groups (pc1, pc2) (see Experimental

Section). In the 600 MHz ^{1}H NMR spectrum of **14**, the *ortho* and *meta* proton signals of one (ph4) of the four phenyl substituents are very broad at room temperature, which indicates hindered rotation of this substituent.

As far as the assignment of the NMR signals is concerned, the situation in **15** is only slightly better than that in **14**. Here also, 54 out of 56 different ^{13}C NMR signals can be observed separately. Scarce correlations between the phenyl groups or between phenyl and paracyclophanyl groups make it difficult to determine their relative arrangement. However, the paracyclophanyl unit denoted as "pc1" in the Experimental Section is the one bound to the bridgehead carbon atoms of the bicyclo[4.2.0]octatriene moiety, as evidenced by the H,C-HMBC correlations of the bridgehead carbon nuclei with the isolated aromatic protons of pc1.

The structures of **13**–**15** were next investigated by single-crystal X-ray crystallography. Compound **13** (Figure 1) shows the typical features of simple [2.2]paracyclophanes, for example, elongated single bonds in the bridges (ca. 1.59 Å), distortion of the rings to flattened boats with the bridgehead atoms 0.15–0.17 Å out of plane, narrow ring angles (ca. 117°) at the bridgehead atoms, distances between bridgehead atoms of ca. 2.7–2.8 Å and distances between other "opposite" atoms of ca. 3.05–3.15 Å.

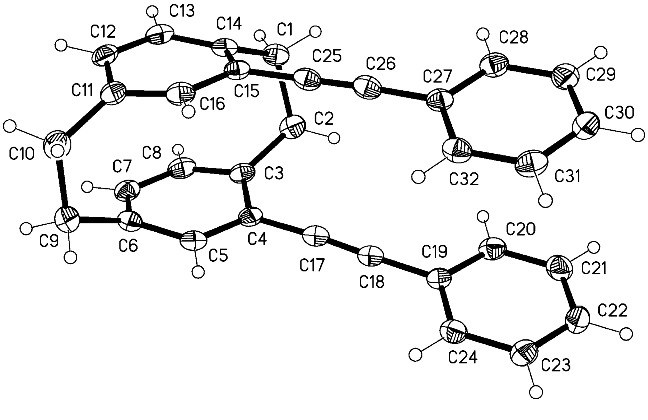


Figure 1. Structure of compound **13** in the crystal. Ellipsoids represent 50% probability levels.

The central eight-membered rings of compound **14** (two independent molecules, one shown in Figure 2) display the expected alternation of double and single bond lengths. However, the precision is limited by the presence of five solvent molecules and the consequent weak diffraction. The configuration is also as expected, in that C1, C2, C5 and C6 lie in one plane and C3, C4, C7 and C8 in another plane parallel to the first one. The bond lengths (in contrast to **15**, see below) do not show any major distortions associated with the annelation of the central ring with the cyclophane units (the phane residues are annelated across the C1=C2 bond and the C4–C5 bond in the central ring). The angles from the phane rings at C1 and C2, through the newly formed double bond bridges, are significantly narrowed (by 4–6°) from the ideal 120°.

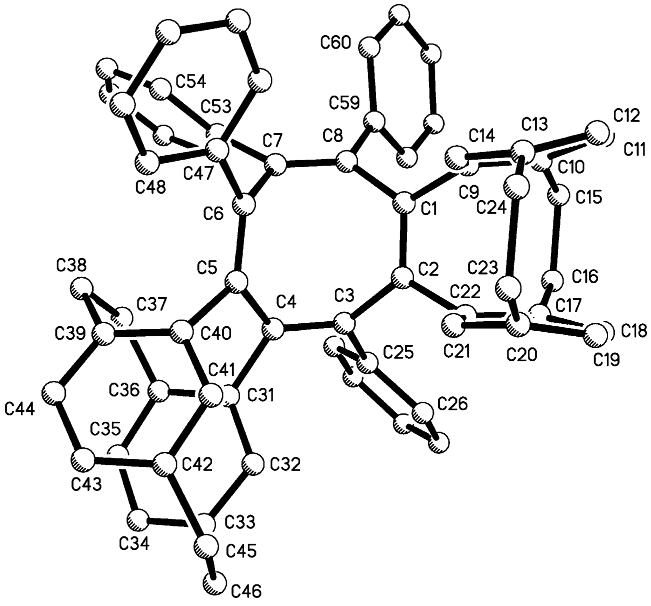


Figure 2. Structure of one of the two independent molecules of **14** in the crystal. Hydrogen atoms are omitted for clarity, and the atoms are drawn as simple circles. Selected bond lengths in the two molecules (Å), esd. 0.004 Å: C1–C2 1.334, 1.358, C2–C3 1.499, 1.498, C3–C4 1.351, 1.345, C4–C5 1.493, 1.499, C5–C6 1.359, 1.354, C6–C7 1.528, 1.519, C7–C8 1.333, 1.348, C1–C8 1.485, 1.481.

The higher degree of annelation in **14** leads to departures from the standard cyclophane geometry. Firstly, the boat form of the rings is less ideal, although still approximately valid, with slightly smaller bridgehead deviations (0.11–0.15 Å). Secondly, the angles between the rings (calculated excluding bridgehead atoms) are significantly increased, to 13–16°, whereby the tilting leads to corresponding differences in distances between opposite ring atoms. By using a temporary ring numbering of C(i) and C(iv) for the old cyclophane bridgeheads and C(ii) for the new bridgeheads, the distances are ca. 2.7–2.8 Å for C(i) and C(iv), 2.6–2.7 Å for C(ii), 2.8 Å for the nonbridged C(iii) and 3.2–3.4 Å for C(v) and C(vi).

The most notable feature of the structure of **15** (Figure 3) is the very long C–C bond of 1.659(2) Å opposite the double bond in the cyclobutene ring. A search of the Cambridge Database[11] provided only two examples of longer bonds in this position, which are also in strained polycyclic systems [1.669 Å[12] and 1.677(3) Å[13]]. The six-membered ring is approximately planar (mean deviation 0.04 Å), but it has significantly non-zero absolute torsion angles about C4–C5 and C1–C6 (both 14°). The positions of the double bonds are unambiguously established by the bond lengths, which may however be regarded as somewhat lengthened with respect to the standard double bond length of 1.330 Å for butadienes.[14] The higher degree of annelation in **15** again (as in **14**, see above) leads to departures from the standard cyclophane geometry. These are qualitatively and quantitatively very similar to those of **14**. All other analytical data (see Experimental Section) also agree with the proposed structure of the two dimers.

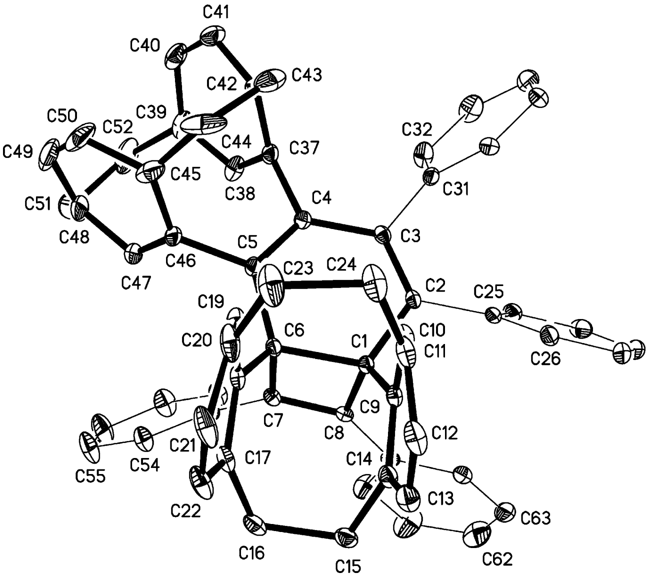
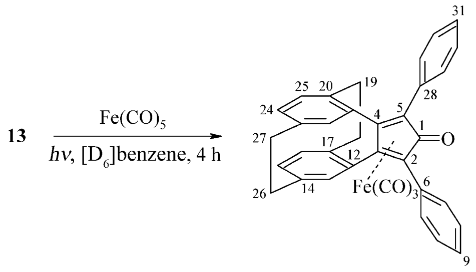


Figure 3. Structure of compound **15** in the crystal. Hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability levels. Selected bond lengths (Å), esd. 0.002 Å: C1–C8 1.536, C1–C2 1.533, C2–C3 1.355, C3–C4 1.470, C4–C5 1.362, C5–C6 1.520, C6–C7 1.524, C7–C8 1.353, C1–C6 1.659(2).

Discussion

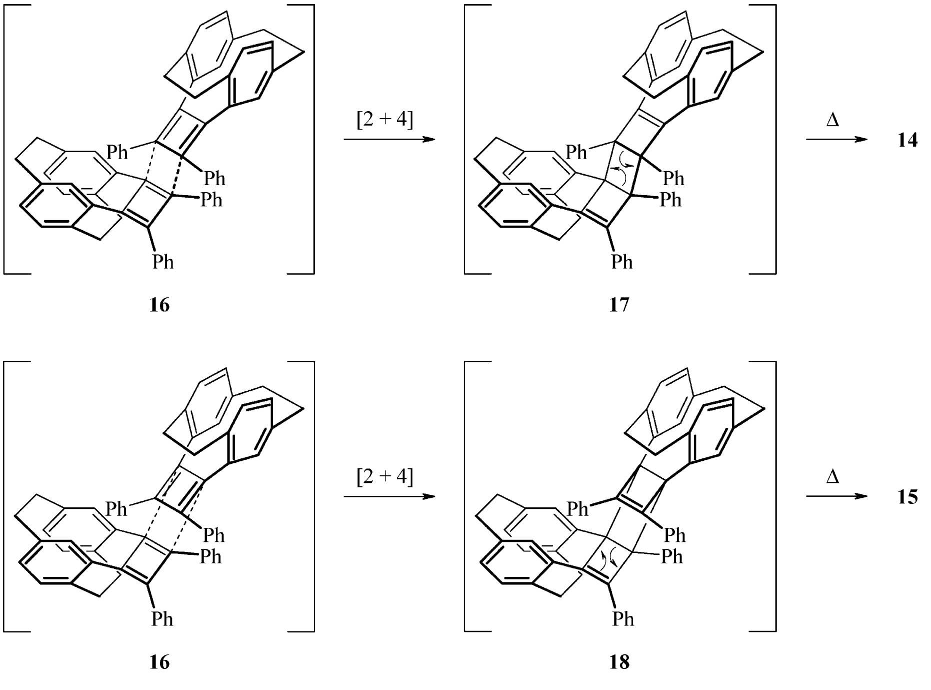
The simplest mechanistic rationale to explain the structures of **14** and **15** involves the postulation of cyclobutadiene intermediate **16** during the photoreaction. The distance of 3.385 Å between the midpoints of the two triple bonds of substrate **13** is in the proper range for a chemical process to occur. Although for conformationally mobile systems such as **1** a tetrahedrane intermediate might also be discussed,[4,6] this is clearly impossible for **13** (or **8**). As shown in Scheme 3, intermediate **16** can engage in a dimerization process by two modes depending on how the [2+4] cycloaddition takes place. If one molecule of **16** as the dienophile adds to the phenyl-substituted end of a second molecule functioning as the diene, dimeric hydrocarbon **17** results; this subsequently reduces its strain (three consecutive four-membered rings!) by opening to cyclooctatetraene **14**.

The second alternative – the reaction takes place at the cyclophane substituted end of **16** (Scheme 3) – at first sight does not appear significantly different. However, if the central cyclobutane ring of corresponding intermediate **18** reverted to two double bonds, this would involve the breaking of a σ-bond that simultaneously is also a bridge bond in a cyclophane; this is a process requiring more energy than the cycloreversion of the terminal cyclobutene ring (see arrows in **18**). In other words, the rigid cyclophane clamp prevents the ring opening of the central four-membered ring, whereas the terminal ring can readily undergo an electrocyclic reaction to yield isomeric dimer **15**. Rigid hydro-



19 (97%)

Scheme 4. Preparation of tricarbonyliron complex **19** from diacetylene **13**.



Scheme 3. Dimerization of cyclobutadiene intermediate **16** generated by photolysis of **13**.

carbon **13** thus behaves differently in this respect with regard to similarly rigid diacetylene **8**. In contrast, photolysis of **13** in the presence of pentacarbonyliron furnishes cyclopentadienone complex **19** (as did **8** in a comparable trapping experiment: see above) and not the tricarbonyliron complex of cyclobutadiene intermediate **16** (Scheme 4). Obviously, a subtle balance of strain, proximity and electronic effects controls the outcome of reactions between two parallel triple bonds.

Experimental Section

General Remarks: DSC was performed with commercial DC plates (Polygram Sil G/UV$_{254}$) purchased from Macherey, Nagel & Co. (Düren). Column chromatography was performed with Kieselgel 60 (70–230 mesh) purchased from Merck (Darmstadt). Melting points were determined with a Büchi 530 melting point apparatus or by differential scanning calorimetry (DSA), Rheometric Scientific (Piscataway, USA) and are uncorrected. Photolysis was performed with a mercury medium-pressure lamp, TQ 150, Heraeus Noblelight. NMR spectra were recorded with the following instruments: Bruker Avance II 300 [^{1}H NMR (300.1 MHz), ^{13}C NMR (75.5 MHz)], Bruker Avance II 600 with TCI cryoprobehead [^{1}H NMR (600.1 MHz), ^{13}C NMR (150.9 MHz)]. Tetramethylsilane (δ_H = 0.00 ppm) and $CDCl_3$ (δ_C = 77.01 ppm) were used as internal references. IR spectra were recorded with a Bruker Tensor 27 by employing the diamond ATR technique. UV/Vis spectra were recorded with a Varian Cary 100 Bio. MS (EI) was determined with a Finnigan Mat 90 (70 eV) instrument.

4,15-Bis(phenylethynyl)[2.2]paracyclophane (13): Argon as a protective gas was passed through a solution of iodobenzene (**12**, 300 mg, 1.47 mmol) in triethylamine (15 mL). Tetrakis(triphenylphosphane)palladium(0) (22 mg, 0.02 mmol), copper(I) iodide (4 mg, 0.02 mmol) and 4,15-diethynyl[2.2]paracyclophane (100 mg, 0.39 mmol)[9] were added, and the reaction mixture was stirred for 30 h at 80 °C. The amine was removed by rotary evaporation; a saturated aqueous solution of ammonium chloride was added to the residue, and the suspension was carefully extracted with dichloromethane. The combined organic phase was dried (magnesium sulfate) and filtered, and the solvent was removed in vacuo. The remaining solid was purified by column chromatography (flash-SiO_2, CH_2Cl_2/pentane, 1:2). Yield: 148 mg (92%), colourless crystals, m.p. 185 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.07 (“s”, 4 H, 9-H, 10-H), 3.10 (*AA′*XX′, 2 H, 1-H$_a$, 2-H$_a$), 3.96 (AA′*XX′*, 2 H, 1-H$_s$, 2-H$_s$), 6.52 (dd, *J* = 7.8, 1.8 Hz, 2 H, 7-H, 12-H), 6.58 (d, *J* = 7.8 Hz, 2 H, 8-H, 13-H), 6.78 (d, *J* = 1.8 Hz, 2 H, 5-H, 16-H), 7.03 (m$_c$, 4 H, 21-H, 23-H, 29-H, 31-H), 7.11 (m$_c$, 2 H, 22-H, 30-H), 7.24 (m$_c$, 4 H, 20-H, 24-H, 28-H, 32-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 141.86 (C-3, C-14), 139.19 (s, C-6, C-11), 135.61 (d, C-5, C-16), 133.97 (d, C-8, C-13), 132.96 (d, C-7, C-12), 131.41 (d, C-20, C-24, C-28, C-32), 127.85 (d, C-21, C-23, C-29, C-31), 127.40 (d, C-22, C-30), 123.85 (s, C-4, C-15, C-19, C-27), 92.81, 89.47 (s, C-17, C-18, C-25, C-26), 34.95 (t, C-9, C-10), 33.78 (t, C-1, C-2) ppm. IR: ṽ = 3034 (w), 2924 (m), 2203 (w), 1597 (m), 1491 (s) cm^{-1}. UV (CH_3CN): λ (log ε) = 193 (4.75), 202 (4.76), 288 (4.70) nm. MS (EI, 70 eV): *m*/*z* (%) = 408 (45) [M]$^+$, 331 (23), 317 (22), 304 (32), 204 (100). $C_{32}H_{24}$ (408.53): calcd. C 94.08, H 5.92; found C 93.98, H 5.87.

Irradiation of 4,15-Bis(phenylethynyl)[2.2]paracyclophane (13): A solution of **13** (70 mg, 0.17 mmol) in perdeuteriobenzene (1.5 mL) was irradiated in a quartz NMR tube, and the progress of the reaction was monitored by ^{1}H NMR spectroscopic analysis. After 4.5 h, the substrate was fully converted; the solvent was removed in vacuo, and the residue was separated by column chromatography (flash-SiO_2, CH_2Cl_2/pentane, 1:2) to provide two fractions: 15 mg (21%) of **14** and 24 mg (34%) of **15**.

Hydrocarbon 14: Colourless crystals, m.p. 224 °C. ^{1}H NMR (600 MHz, $CDCl_3$; subscripts a and s designate methylene protons oriented *anti* and *syn*, respectively, relative to the cyclooctatetraene ring): δ = 2.09–2.18 (m, 3 H, pc2–2-H$_a$, pc1–1-H$_a$, pc1–2-H$_a$), 2.33–2.39 (m, 1 H, pc2–1-H$_a$), 2.44–2.50 (m, 1 H, pc1–9-H$_a$), 2.53–2.59 (m, 2 H, pc2–9-H$_s$, pc1–2-H$_s$), 2.64–2.81 (m, 4 H, pc2–1-H$_s$, pc2–9-H$_a$, pc2–2-H$_s$, pc1–10-H$_s$), 2.83–2.89 (m, 1 H, pc2–10-H$_a$), 2.92–3.00 (m, 2 H, pc1–9-H$_s$, pc2–10-H$_s$), 3.04–3.11 (m, 2 H, pc1–10-H$_a$, pc1–1-H$_s$), 5.93 (d, *J* = 1.8 Hz, 1 H, pc2–5-H), 6.03 (d, *J* = 1.6 Hz, 1 H, pc1–5-H), 6.08 (d, *J* = 8.0 Hz, 1 H, pc1–8-H), 6.10 (dd, *J* = 8.0, 1.7 Hz, 1 H, pc1–7-H), 6.15 (d, *J* = 8.0 Hz, 1 H, pc2–8-H), 6.25 (dd, *J* = 8.0, 1.9 Hz, 1 H, pc2–7-H), 6.33 (d, *J* = 8.0 Hz, 1 H, pc1–13-H), 6.37–6.41 (m, 3 H, pc1–12-H, pc2–12-, –13-H), 6.47 (d, *J* = 1.8 Hz, 1 H, pc1–16-H), 6.63 (d, *J* = 1.8 Hz, 1 H, pc2–16-H), 7.10–7.19 (m, 7 H, ph2–4-H, ph3–3-H, ph3–4-H, ph3–5-H, ph4–3-H, ph4–4-H, ph4–5-H), 7.20–7.24 (m, 3 H, ph1–4-H, ph2–3-H, ph2–5-H), 7.26–7.29 (m, 2 H, ph1–3-H, ph1–5-H), 7.30–7.40 (very br. m, 2 H, ph4–2-H, ph4–6-H), 7.42–7.45 (m, 2 H, ph3–2-H, ph3–6-H), 7.57–7.60 (m, 2 H, ph2–2-H, ph2–6-H), 8.06–8.08 (m, 2 H, ph1–2-H, ph1–6-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 30.81 (CH_2, pc1–C-2), 33.27 (CH_2, pc2–C-1), 33.60 (CH_2, pc2–C-2), 34.64 (CH_2, pc2–C-9), 34.98 (CH_2, pc2–C-10), 35.92 (CH_2, pc1–C-9), 36.04 (CH_2, pc1–C-10), 36.37 (CH_2, pc1–C-1), 126.80 (CH, ph2–C-4), 126.98 (CH, ph4–C-4), 127.00 (CH, ph3–C-4), 127.19 (ph1–C-4), 127.39 (CH, 2 C, ph3–C-3, ph3–C-5), 127.85 (CH, 4 C, ph2–C-3, ph2–C-5, ph4–C-3, ph4–C-5), 128.20 (CH, 2 C, ph1–C-3, ph1–C-5), 129.67 (CH, pc1–C-12), 129.90 (CH, 2 C, ph2–C-2, ph2–C-6), 130.19 (CH, pc2–C-7), 130.38 (CH, 2 C, ph1–C-2, ph1–C-6), 130.50 (CH, 2 C, ph4–C-2, ph4–C-6), 131.22 (CH, pc1–C-7), 131.24 (CH, pc2–C-12), 131.38 (CH, 2 C, ph3–C-2, ph3–C-6), 132.12 (CH, pc1–C-8), 133.41 (CH, pc2–C-8), 133.66 (CH, pc2–C-13), 134.62 (CH, pc1–C-13), 137.53 (C$_q$, ph1–C-1α), 138.40 (CH, 2 C, pc1–C-16, pc2–C-16), 138.61 (C$_q$, pc2–C-6), 139.43 (C$_q$, pc1–C-6), 140.35 (C$_q$, pc1–C-11), 140.66 (C$_q$, pc2–C-3), 140.79 (C$_q$, ph1–C-1), 141.14 (CH, pc2–C-5), 141.32 (C$_q$, pc1–C-3), 141.66 (C$_q$, pc2–C-14), 142.31 (C$_q$, ph2–C-1), 143.45 (C$_q$, pc1–C-4), 144.83 (C$_q$, pc2–C-15), 145.56 (CH, pc1–C-5), 146.54 (C$_q$, pc2–C-15α), 148.67 (C$_q$, pc2–C-4α), 152.45 (C$_q$, pc1–C-4α) ppm; unassigned: 138.56, 139.65, 140.16, 140.39, 142.23, 142.52, 142.54, 142.70, 143.23, 143.27 (all C$_q$, pc1–C-14, pc1–C-15, pc1–C-15α, pc2–C-4, pc2–C-6, pc2–C-11, ph2–C-1α, ph3–C-1, ph3–C-1α, ph4–C-1,-1α) ppm. IR: ṽ = 3040 (w), 2923 (s), 2852 (m), 1593 (w), 1486 (m), 1439 (m) cm^{-1}. UV (CH_3CN): λ (log ε) = 196 (5.06), 294 (4.18) nm. MS (EI, 70 eV): *m*/*z* (%) = 816 (100) [M]$^+$, 739 (4), 408 (6).

Hydrocarbon 15: Colourless crystals, m.p. 196 °C. ^{1}H NMR (600 MHz, $CDCl_3$; subscripts a and s designate methylene protons oriented *anti* and *syn*, respectively, relative to the bridges connecting the paracyclophane and bicyclo[4.2.0]octatriene systems): δ = 2.41–2.46 (m, 1 H, pc2–9-H$_s$), 2.49–2.57 (m, 2 H, pc1–2-H$_a$, pc1–1-H$_a$), 2.57–2.62 (m, 2 H, pc2–2-H$_a$, pc2–9-H$_a$), 2.66–2.72 (m, 2 H, pc2–10-H$_a$, pc2–1-H$_a$), 2.81–2.85 (m, 1 H, pc2–10-H$_s$), 2.99–3.03 (m, 1 H, pc1–10-H$_a$), 3.14–3.18 (m, 1 H, pc1–9-H$_a$), 3.20–3.31 (m, 2 H, pc1–9-H$_s$, pc1–10-H$_s$), 3.31–3.36 (m, 1 H, pc2–1-H$_s$), 3.59–3.63 (m, 1 H, pc2–2-H$_s$), 3.69–3.78 (m, 2 H, pc1–2-H$_s$, pc1–1-H$_s$), 5.26 (d, *J* = 1.8 Hz, 1 H, pc2–5-H), 6.06 (dd, *J* = 7.9, 1.8 Hz, 1 H, pc2–7-H), 6.09 (d, *J* = 7.9 Hz, 1 H, pc2–8-H), 6.11 (dd, *J* = 7.9, 1.8 Hz, 1 H, pc2–12-H), 6.16 (d, *J* = 1.7 Hz, 1 H, pc2–16-H), 6.18

(d, *J* = 7.9 Hz, 1 H, pc2–13-H), 6.25 (d, *J* = 7.9 Hz, 2 H, pc1–8-H, pc1–13-H), 6.46 (dd, *J* = 7.9, 1.9 Hz, 1 H, pc1–7-H), 6.48 (dd, *J* = 7.8, 1.9 Hz, 1 H, pc1–12-H), 6.57–6.60 (m, 2 H, ph4–3-H, ph4–5-H), 6.66–6.68 (m, 2 H, ph4–2-H, ph4–6-H), 6.69–6.72 (m, 1 H, ph4–4-H), 6.75–6.78 (m, 1 H, ph3–4-H), 6.82–6.85 (m, 2 H, ph3–3-H, ph3–5-H), 6.90 (d, *J* = 1.9 Hz, 1 H, pc1–5-H), 7.00–7.02 (m, 2 H, ph3–2-H, ph3–6-H), 7.10 (d, *J* = 1.9 Hz, 1 H, pc1–16-H), 7.12–7.15 (m, 2 H, ph2–3-H, ph2–5-H), 7.20–7.23 (m, 1 H, ph2–4-H), 7.23–7.26 (br. m, 2 H, ph1–3-H, ph1–5-H), 7.31–7.34 (m, 1 H, ph1–4-H), 7.56–7.58 (m, 2 H, ph2–2-H, ph2–6-H), 7.81–7.83 (br. m, 2 H, ph1–2-H, ph1–6-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$; signals with like superscripts may be assigned in reverse order): δ = 33.92 (CH_2, pc2–C-1), 34.74 (CH_2, pc2–C-9), 34.82 (CH_2, pc2–C-10), 35.93 (CH_2, pc1–C-10), 36.10[a] (CH_2, 2 C, pc1–C-2, pc1–C-9), 36.32 (CH_2, pc2–C-2), 36.36[a] (CH_2, pc1–C-1), 70.00 (C_q, pc1–C-15α), 70.61 (C_q, pc1–C-4α), 125.34 (CH, ph4–C-4), 125.50 (CH, ph3–C-4), 126.30 (CH, 2 C, ph4–C-3, ph4–C-5), 126.74 (CH, 2 C, ph3–C-3, ph3–C-5), 127.82 (CH, 2 C, ph2–C-3, ph2–C-5), 127.86 (CH, ph2–C-4), 128.03 (br., CH, 2 C, ph1–C-3, ph1–C-5), 128.36 (CH, ph1–C-4), 128.92 (CH, pc1–C-7), 129.03 (CH, 2 C, ph2–C-2, ph2–C-6), 129.43 (br., CH, 2 C, ph1–C-2, ph1–C-6), 129.71 (CH, pc1–C-12), 129.81 (CH, pc2–C-7), 130.11 (CH, pc2–C-12), 130.98 (CH, 2 C, ph3–C-2, ph3–C-6), 132.01 (CH, pc2–C-13), 133.02 (CH, 2 C, ph4–C-2, ph4–C-6), 134.45 (CH, pc2–C-8), 135.39[b] (CH, pc1–C-8), 135.94 (C_q, ph2–C-1), 136.21[b] (CH, pc1–C-13), 136.44 (C_q, ph3–C-1α), 136.73 (C_q, ph1–C-1), 137.53 (C_q, pc2–C-6), 138.52 (C_q, pc2–C-11), 138.58 (C_q, pc1–C-11), 139.05 (C_q, pc2–C-14), 139.14 (C_q, ph4–C-1α), 139.22 (CH, pc2–C-16), 139.34 (C_q, pc1–C-6), 139.73 (C_q, pc1–C-3), 140.39 (C_q, pc1–C-14), 140.48 (C_q, 2 C, ph1–C-1α, ph2–C-1α), 140.98 (C_q, pc2–C-3), 141.34 (C_q, ph4–C-1), 141.54 (CH, pc1–C-5), 141.73[c] (C_q, pc1–C-4), 141.78[c] (C_q, pc1–C-15), 141.88 (C_q, ph3–C-1), 142.50 (CH, pc1–C-16), 142.68 (C_q, pc2–C-15α), 142.86 (CH, pc2–C-5), 143.47 (C_q, pc2–C-4α), 144.71 (C_q, pc2–C-4), 146.01 (C_q, pc2–C-15) ppm. IR: ṽ = 3048, 2925 (m), 2851 (w), 1595 (w), 1486 (m), 1440 (m) cm^{-1}. UV (CH_3CN): λ (log ε) = 193 (5.13), 282 (4.32) nm. MS (EI, 70 eV): *m*/*z* (%) = 816 (100) $[M]^+$, 739 (4), 638 (15).

X-ray Structural Analysis: Numerical details are summarized in Table 1. Data were registered with a Bruker SMART 6000 (**13**) or 1000 (**14**, **15**) CCD diffractometers by using Cu-K_α or Mo-K_α radiation, respectively. An absorption correction for **13** was performed on the basis of multiple scans by using the program SADABS. Structures were refined against F^2 by using the program SHELXL-97 (Prof. G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included by using a riding model. Special features of the refinement for compound **14** are as follows: Because of the weak data, a large number of restraints were employed to improve the refinement stability (DELU, SIMU, ISOR, SAME). The asymmetric unit contains two independent molecules of **14** and five molecules of deuteriochloroform (the crystals decompose rapidly in air by loss of solvent). The latter could be refined reasonably well, but additional peaks and some high *U* values suggested disorder. For this reason the program SQUEEZE (A. L. Spek, University of Utrecht, Netherlands) was used to remove mathematically the effects of the solvent, which was then omitted from the final refinement. Because of the approximations involved, molecular dimensions and their esd values should be interpreted with caution.

CCDC-626624 (for **13**), -626625 (for **14**) and -626626 (for **15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for compounds **13**–**15**.

Compound	**13**	**14**·2.5$CDCl_3$	**15**
Formula	$C_{32}H_{24}$	$C_{66.5}H_{48}D_{2.5}Cl_{7.5}$	$C_{64}H_{48}$
M_r	408.51	1117.96	817.02
Habit	colourless tablet	colourless tablet	colourless tablet
Crystal size [mm]	0.19 × 0.13 × 0.04	0.35 × 0.3 × 0.08	0.4 × 0.25 × 0.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
Cell constants:			
a [Å]	22.5733(10)	28.214(2)	11.4786(10)
b [Å]	7.8078(4)	12.7439(10)	19.5036(17)
c [Å]	12.2588(5)	29.938(2)	19.5985(17)
α [°]	90	90	90
β [°]	98.093(2)	100.927(2)	101.051(4)
γ [°]	90	90	90
V [Å^3]	2139.1	10569.0	4306.2
Z	4	8	4
D_x [Mg m^{-3}]	1.268	1.405	1.260
μ [mm^{-1}]	0.54	0.45	0.07
$F(000)$	864	4616	1728
T (°C)	–173	–140	–140
λ [Å]	1.5418	0.71073	0.71073
$2\theta_{max}$	138	51	61
Reflections measured	13626	87515	58147
Reflections independent	3660	19760	13125
R_{int}	0.042	0.158	0.086
Parameters	289	1153	577
Restraints	0	2244	0
$wR(F^2$, all reflections)	0.112	0.173	0.168
$R[F, >4\sigma(F)]$	0.053	0.083	0.064
S	1.05	0.89	1.03
max. $\Delta\rho$ [e Å^{-3}]	0.28	0.28	0.38

Photolysis of 13 in the Presence of Pentacarbonyliron: In a quartz NMR tube a solution of **13** (50 mg, 0.12 mmol) and pentacarbonyliron (0.05 mL, 0.38 mmol) in perdeuteriobenzene (1.5 mL) was irradiated for 4 h under an atmosphere of argon. The solvent was removed in vacuo, and the remaining solid was purified by column chromatography (flash-SiO_2, CH_2Cl_2). Yield: 67 mg (97 %), yellow crystals, m.p. 207 °C. ^1H NMR (300.1 MHz, $CDCl_3$): δ = 2.65, 3.04 (br. m_c, $N \approx 9.5$ Hz, 2 H each, 18-H, 19-H), 3.11, 3.26 (br. m_c, $N \approx 8.5$ Hz, 2 H each, 26-H, 27-H), 6.43 (br. d, J = 7.9 Hz, 2 H, 16-H, 25-H), 6.62 (br. "s", 2 H, 13-H, 22-H), 6.68 (br. "d", J = 7.9 Hz, 2 H, 15-H, 24-H), 7.27 (br. m_c, 6 H, 8-H, 9-H, 10-H, 30-H, 31-H, 32-H), 8.23 (br. m_c, 4 H, 7-H, 11-H, 29-H, 33-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 32.84 (t, C-18, C-19), 35.50 (t, C-26, C-27), 78.00, 111.37 (both s, C-2, C-5 and C-3, C-4), 128.20, 128.51 (both d, C-8, C-10, C-30, C-32 and C-7, C-11, C-29, C-33), 128.29 (d, C-9, C-31), 132.13, 133.18, 140.67, 141.39 (s, C-6, C-12, C-14, C-17, C-20, C-21, C-23, C-28), 132.26, 134.02, 139.41 (d, C-13, C-15, C-16, C-22, C-24, C-25), 168.89 (s, C-1), 208.42 [s, Fe(CO)] ppm. IR: $\tilde{\nu}$ = 3063 (w), 2940 (w), 2860 (w), 2065 (vs), 2014 (s), 1991 (vs), 1629 (s), 1497 (m), 1452 (m) cm^{-1}. UV (CH_3CN): λ (log ε) = 196 (5.08), 225 (4.61) nm. MS (EI, 70 eV): m/z (%) = 576 (2) $[M]^+$, 548 (16), 520 (13), 492 (100), 436 (59).

---

[1] H. Hopf, J. Hucker, L. Ernst, *Eur. J. Org. Chem.* **2007**, 1891–1904.
[2] S. A. Kandil, R. E. Dessy, *J. Am. Chem. Soc.* **1966**, *88*, 3027–3034.
[3] E. H. White, A. A. F. Sieber, *Tetrahedron Lett.* **1967**, *28*, 2713–2717.
[4] C.-C. Lee, M. Leung, G.-H. Lee, Y.-H. Liu, S.-M. Peng, *J. Org. Chem.* **2006**, *71*, 8417–8423.
[5] a) B. Bossenbroek, H. Shechter, *J. Am. Chem. Soc.* **1967**, *89*, 7111–7112; b) B. Bossenbroek, D. C. Sanders, H. M. Curry, H. Shechter, *J. Am. Chem. Soc.* **1969**, *91*, 371–379.
[6] For further studies on parallel acetylenes, see: a) J. Ipaktschi, H. A. Staab, *Tetrahedron Lett.* **1967**, *8*, 4403–4408 and references cited therein; b) E. Müller, J. Heiss, M. Sauerbier, D. Streichfuss, R. Thomas, *Tetrahedron Lett.* **1968**, *9*, 1195–1200; c) H. A. Staab, H. Mack, E. Wehinger, *Tetrahedron Lett.* **1968**, *9*, 1465–1469; d) H. A. Staab, A. Nissen, J. Ipaktschi, *Angew. Chem.* **1968**, *80*, 241–241; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 226–226; e) R. H. Mitchell, F. Sondheimer, *Tetrahedron* **1968**, *24*, 1397–1405.
[7] A. E. Jungk, G. M. J. Schmidt, *Chem. Ber.* **1971**, *104*, 3272–3288. For the related compound 1,8-bis[2-(6-methoxy-2-naphthyl)ethynyl]naphthalene a distance of 307.8 pm between the triple bonds was reported: G. T. Crisp, Y.-L. Jiang, E. R. T. Tiekink, *Z. Kristallogr. - New Cryst. Struct.* **1998**, *213*, 395–396.
[8] H. Hopf, L. Bondarenko, L. Ernst, P. G. Jones, J. Grunenberg, S. Hentschel, I. Dix, *Chem. Eur. J.* **2007**, *13*, 3950–3963.
[9] a) H. Hopf, H. Hinrichs, I. Dix, L. Bondarenko, *Synthesis* **2004**, 2751–2759; b) H. Hopf, I. Dix, *Synlett* **2006**, 1416–1418.
[10] Review: R. R. Tykwinski, *Angew. Chem.* **2003**, *115*, 1604–1606; *Angew. Chem. Int. Ed.* **2003**, *42*, 1566–1568.
[11] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380–388.
[12] W. Langer, H.-D. Becker, *Z. Kristallogr.* **1993**, *207*, 334–337.
[13] S. Kammermeier, P. G. Jones, R. Herges, *Angew. Chem.* **1997**, *109*, 1825–1828; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1757–1760.
[14] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1–S19.

Received: July 27, 2007