Highly brominated biphenylenes as precursors for the convenient synthesis of 5,6,8,10-tetrabromobenzocyclooctene

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An efficient synthesis is described of hexabromides **5** and **6** by photobromination of biphenylene (**1**). Double dehydrobromination of hexabromides **5** and **6** with t-BuOK affords 5,6,8,10-tetrabromobenzocyclooctene (**7**) in nearly quantitative yield. The tetrabromide **7** is a valuable precursor for the preparation of functionalised substituted benzocyclooctenes (benzo[8]annulenes).

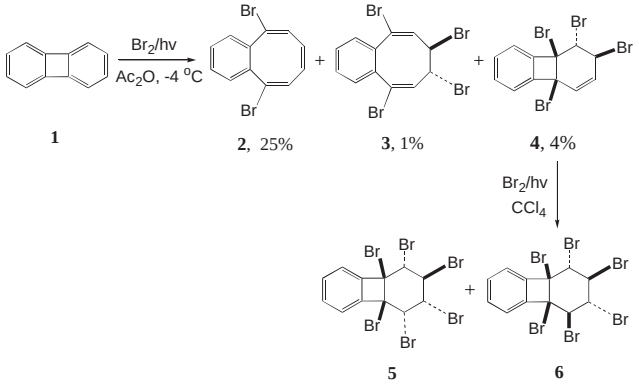
Keywords: bromination, photobromination, biphenylene, [**8**]annulenes, benzocyclooctenes, crystal structures

Because of its unusual physical and chemical properties and partial antiaromaticity, biphenylene has received a great deal of attention from both theorists and experimentalists.[1,2] Biphenylene can be anticipated as a building block of new carbon allotropes,[3] and its derivatives can be used as spacers and building blocks for functionalised organic materials.[4]

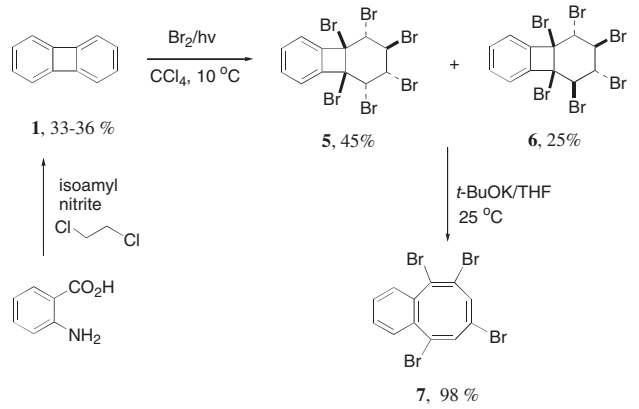
Bromination of biphenylene and its derivatives is a fundamental reaction in biphenylene and benzocyclooctene chemistry. However, bromination of biphenylene has hitherto been tedious and unsatisfactory. It has been observed that biphenylene generally shows low reactivity towards bromine at room temperature, when substantial amounts of unreacted biphenylene were recovered.[1,5,6]

Barton *et al.*[6] have investigated the bromination of biphenylene and the nature of the intermediates. They found that the reaction mechanism, and therefore the formed products, can be changed depending on the reaction conditions such as the presence of excess of bromine, the solvent type, application of light or heat, *etc*. It was reported that photobromination of biphenylene in the presence of ultraviolet light in acetic anhydride gave **5**, 10-dibromobenzocyclooctene (**2**) and 1,2,3a,8b-tetrabromo-1,2,4a,8b-tetrahydrobiphenylene (**4**) as primary products, while on further bromination the dibromide **2** gave tetrabromide **3**, and tetrabromide 4 afforded hexabromides **5** and **6**.[6b] Preliminary X-ray studies have been made (Scheme 1).[6b]

We here describe an efficient bromination of biphenylene, which selectively affords the normal addition products (**5** and **6**), and a rapid and convenient synthetic methodology for 5,6,8,10-tetrabromobenzocyclooctene (**7**).



Scheme 1



Scheme 2

Results and discussion

Recently, we have shown that bromination of benzenoid aryl compounds with a projector lamp in an immersion photochemical apparatus efficiently provides radical addition products.[7] Accordingly, we subjected biphenylene (**1**) in CCl_4 to photobromination at 10 °C. After removal of the solvent, the residue was filtered through a short silica gel column. Crystallisation of the reaction material gave hexabromides **5** and **6** as a mixture in 7 : 3 ratio in 80% yield. After recrystallisation combined with repeated silica gel column chromatography, the two stereisomers, **5** and **6**, were separated in pure forms in 45% and 25% yields, respectively (Scheme 2).

It is evident that the use of internal irradiation provides a very high light density, promoting very effective addition in a short time. We assume that the bromination takes place exclusively by radical addition to give nearly complete addition products.

The melting points of compounds **5** and **6** are consistent with those of Barton *et al.*[6b] (Scheme 1). Their 12-line ^{13}C NMR spectrum and their aromatic and four aliphatic ^1H NMR signals are in agreement with biphenylene hexabromide structures. However, from the NMR results, it is not possible to establish the exact configuration of the bromides and the conformation of the cyclohexane rings. Several hexabromotetrahydrobiphenylene stereoisomers (theoretically twelve) can be formed in the reaction. The structures of the stereoisomers **5** and **6** were therefore determined by X-ray crystallographic analysis (Fig. 1).[8]

The X-ray analysis of compounds **5** and **6** shows that the skeleton of the molecule is not changed after successive addition of three molecules of bromine. The conformations of the brominated six-membered rings can be described as boat forms, despite some significant deviations. The deviations are probably due to repulsive interaction between *cis* bromine atoms linked to C4a and C8b which causes strong dipole–dipole and van der Waals interactions. Only the C4a–C8b bond lengths [1.599(8) Å for **5** and 1.637(9) Å for **6**] are longer than the average value. The observed C4a–C8b bond lengths are in good agreement with the theoretical results (1.636 Å for **5** and 1.627 Å for **6,** by MM3). The large strain energy values for

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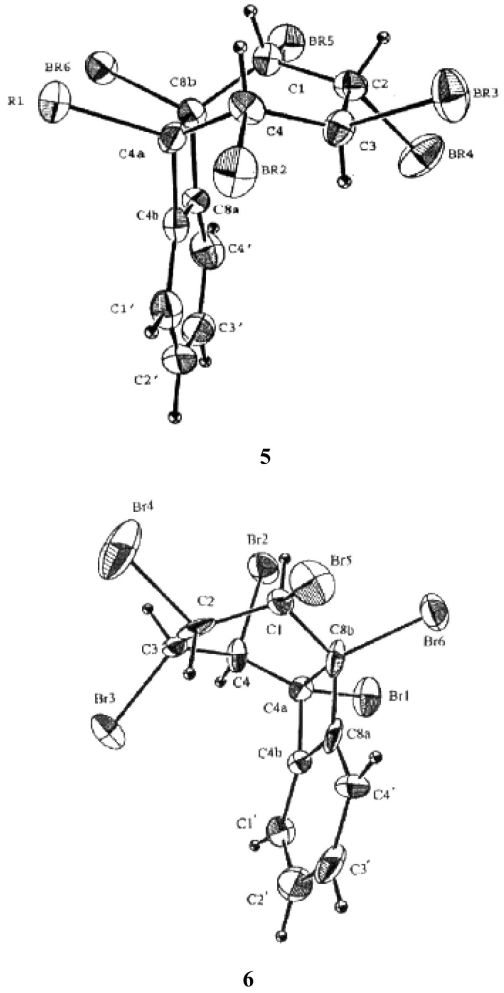
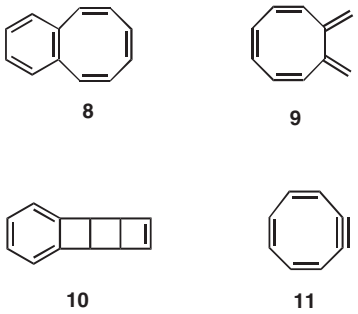


Fig. 1 X ray crystal structures of hexabromides **5** and **6**.

hexabromides **5** and **6** (total energies 79.19 and 93.0 kcal/mol, respectively; by MM3) clearly indicate strong steric interactions of the bulky bromine atoms. The benzene and cyclobutene rings of the compounds are nearly coplanar. In fact, the valence angles of the C4a and C8b atoms are somewhat distorted. Maximum deviations from the mean plane with C8b, C4a, C2, C3 atoms are –0.091(7) Å for **5** and 0.08(2) Å for **6**.

A mixture of **5** and **6** was subjected to dehydrobromination using *t*-BuOK. The reaction surprisingly gave tetrabromobenzocyclooctene **7** in nearly quantitative yield. The structure assignment of tetrabromide **7** is based on a correct elemental analysis, the parent ion peak in the MS, and a simple ^{1}H NMR spectra which exhibited two singlets for the olefinic protons at δ 6.76 and δ 6.36 and a multiplet for the aromatic protons at δ 7.35. The ^{13}C NMR spectrum consists of 12 lines,

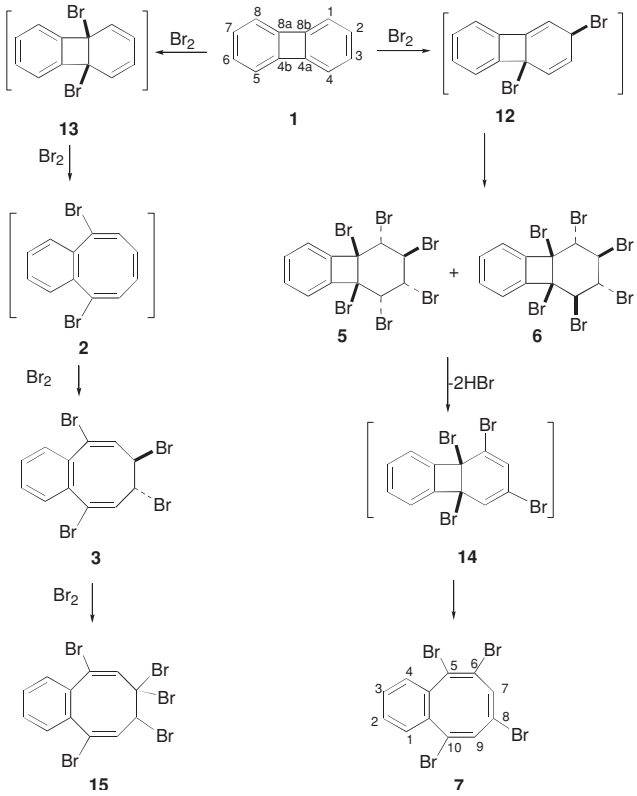


Scheme 3

six of which are quaternary, which supports the proposed tetrabromide structure and the low symmetry of the molecule.

Although the chemistry of [**8**]annulene (cyclooctatetraene, COT) has been extensively investigated, benzo[**8**]annulene (benzocyclooctene, **8)** has received little attention due to its inaccessibility.[9] The literature methods available for the synthesis of benzocyclooctene and its substituted derivatives are tedious or afford low yields. For instance, one of the drawback of the method[10] based on the addition of dimethyl acetylenedicarboxylate to 7,8-dimethylidenecycloocta-1,3, 5-triene (**9**) is the fact that **9** is not readily available, and the final decarboxylation proceeds in only 3% yield. The lead tetraacetate oxidation of a mixture of tricarbonylcyclobutadieneiron and tricarbonyl(cyclobuta-benzene)iron produces a 75% yield of the olefin **10**. On thermolysis by silver fluoroborate-catalysed ring-opening, compound **10** yields benzocyclooctene quantitatively.[11] However, tricarbonyl cyclobutadieneiron is not readily available since it is obtained from COT in a four-step sequence.[12] Another way to compound **8** is by the Diels–Alder addition of butadiene to 1,2-dehydro-COT (cycloocta-1,3,5-trien-7-yne, **11**), generated from a mixture of bromo-COT with potassium *tert*-butoxide (44.5% overall yield from COT).[13] Probably a more promising method is the reaction of biphenylene-dianion with H_2O to give 4a,8b-dihydrobiphenylene that opens thermally give benzocyclooctene in 80% yield.[14]

We have also investigated the bromination of biphenylene at elevated temperatures. A stirred solution of biphenylene in CCl_4 was heated to reflux (77 °C), and a solution of three equivalents of bromine in CCl_4 was added dropwise. Progress of the reaction was monitored by TLC or NMR. The reaction proceeded smoothly and conversion of biphenylene was complete. After repeated column chromatography on silica gel and recrystallisation, the tetrabromodihydrobenzocyclooctene **3**, hexabromides **5** and **6**, tetrabromobenzocyclooctene **7** and the pentabromide **15** were isolated in 7, 25, 30, 6 and 2% yields, respectively (Scheme 4).



Scheme 4

We assume that the initial attack occurs at the C-4a and C-2-positions in biphenylene to give the intermediate **12**. The addition of a further two molecules of bromine to the intermediate gives hexabromides **5** and **6** (Scheme 2). Isolation of only 2-substituted biphenylenes in qualitative studies of acylation, halogenation and nitration indicates that initial attack takes place at the C-2 position of biphenylene. It has been reported that NMR data at low temperatures provides evidence for biphenylene endoperoxide resulting from cycloaddition across the C-4a and C-2 position in biphenylene.[15]

The location of bromine atoms in positions 2 and 4a of **5** and **6**, as assigned by X-ray studies (Fig. 1), is consistent with the intermediacy of **12**. On the other hand, syn-addition of bromine to the four-membered ring of 1 results in the formation of 5, 10-dibromobenzocyclooctene (**2**), which is formed spontaneously by ring opening through the C8b–C4a bond cleavage in **5**. Further addition of bromine to **2** gives tetrabromide **3**. The trapping[14] of a 4a,8b-dihydrobiphenylene intermediate with maleic anhydride from the reaction of biphenylene dianion with H_2O is evidence that the cis-addition occurs to the 4a–8b bond in biphenylene and the formed intermediates undergo spontaneous ring opening to give benzocyclooctenes as suggested by Ebine[16] and Barton[17]. Our failure to detect an intermediate 4a,8b-dihydrobiphenylene is unsurprising since such a structure is reported to have a half-life of the order of a minute at 0 °C.[14]

^{1}H and ^{13}C NMR spectra of the tetrabromide **3** show an unsymmetrical structure, presumably as a result of puckering of the larger ring. In the ^{1}H NMR spectra, the chemical shifts of olefinic (δ 6.58 and 6.75) and allylic protons (δ 4.25 and 4.58) are consistent with the proposed structure. The dihedral angle of H5 and H6 (28.68°) as assigned by MM3 force-field calculations is sufficiently large to be revealed from the magnitude of the spin–spin interaction (J_{56} = 11.36 Hz). Twelve ^{13}C NMR signals are in accord with the structure of tetrabromide **3**, in a rigid puckered conformation.

In order to clarify the formation of the benzocyclooctene **7** we examined the stability of the hexabromides **6** and **7** under the reaction conditions. The hexabromide mixture was heated under reflux in CCl_4 in the presence of bromine. However, no observable change occurred. We assume that compound **7** is produced from hexabromide **5** and **6** by dehydrobromination through valence isomer **14** during column chromatography (Scheme 4)

The mass spectrum of pentabromide **15** gave a molecular ion group at about *m/z* 551 (M^+) corresponding to $C_{12}H_7Br_5$ and principal fragments 472, 391, 311, 230 and 150; a satisfactory elemental analysis was obtained. The ^{1}H NMR spectrum of pentabromide **15** consists of two olefinic (δ 7.45 s, 6.65 d), one saturated aliphatic (δ 4.65, d, J 9.03 Hz) and aromatic signals. ^{13}C NMR spectrum gave two saturated aliphatic (δ 64.65, s; 58.43, d) and ten olefinic signals. Finally, The X-ray analysis[18] of its structure showed the precise picture, in which the eight-membered ring is folded to form a boat-like conformation bonded to five bromine atoms. It appears likely that compound **15** arose from further reaction of tetrabromide **3** (Scheme 4).

Conclusion

It was previously reported that bromination of biphenylene in the presence of pyridine resulted in formation of monobromobiphenylene (substitution product) in a yield of 49%,[5] whereas photo-induced bromination of biphenylene in CCl_4 gave benzocyclooctene derivatives (ring-opening products) as the main product.[6] However, our one-pot photochemical procedure has led to complete formation of normal-addition products in 80% yield (hexabromides **5** and **6**), whose dehydrobromination affords synthetically valuable tetrabromobenzocyclooctene **7** as the sole product in nearly quantitative yield. Hexabromides **5** and **6** and tetrabromide **7** are starting compounds for polyfunctionalisation of biphenylene and benzocyclooctene, due to their ready conversion into other derivatives. The tetrabromide **7** is a promising intermediate for the synthesis of substituted derivatives of benzocyclooctene (**8**) as shown for bromocyclooctene which has been converted into organometallic compounds, undergo replacement of its vinyl halogen.[19] Thus, we have opened an access to tetrasubstituted benzocyclooctenes with various functionality.

Experimental

Thin layer chromatography was carried out on Merck silica F_{254} 0.255 mm plates, and spots were visualised by UV fluorescence at 254 nm. Classic column chromatography was performed using Merck 60 (70–230 Mesh) silica gel. Photobromination was carried out in a borosilicate-glass two-neck vessel with a dropping funnel, into which a tube was immersed. For irradiation, this tube containing a 150W projector lamp was cooled with circulating water. Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Solvents were concentrated at reduced pressure. IR spectra were recorded on a Perkin Elmer 980 instrument. Mass spectra were recorded on a VG Zab Spec GC-MS spectrometer under electron-impact (EI) and chemical ionisation conditions. The most intense member of each mass signal group is quoted for the intensitites. NMR spectra were recorded on a Bruker AC 200 L instrument at 200 MHz for ^{1}H and at 50 MHz for ^{13}C NMR.

*Preparation of biphenylene (**1**)*

The reported yield of biphenylene by the literature[20] method is in the range 21–30 %. As a result of our minor modifications, its preparation became more practical and the yield increased to 33–36 %.

Benzenediazonium-2-carboxylate

CAUTION! Dry benzene-1-diazonium-2-carboxylate detonates violently when scraped or heated, and it is strongly recommended that it be kept in solvent all the time. It should be prepared and used in a hood behind a safety screen. A wet towel or sponge should be kept within easy reach for deactivation of any spilled material, which should then be disposed of by flooding with water.

Anthranilic acid (17.1 g, 125 mmol) and trichloroacetic acid (0.15 g) were dissolved in THF (125 ml) in a 250 ml beaker. To the magnetically stirred solution, cooled in an ice-water bath, was added isopentyl nitrite (28 ml, freshly prepared) over a few minutes. Since the reaction is mildly exothermic, the reaction temperature was kept at 20–25 °C. After *ca* 1 h, an orange to brick-red precipitate appeared, indicating completion of the reaction. The mixture was cooled to 5–10 °C, and the product was first collected by suction filtration on a plastic Buchner funnel and then washed with cold THF until the washings are colourless.

CAUTION! The filter cake should not be allowed to become dry.) Then, the product was washed with 1,2-dichloroethane (3 × 25 ml) until THF was completely removed. The product should be used immediately because it deteriorates slowly at room temperature.

Biphenylene: The solvent-moist benzenediazonium-2-carboxylate was washed from the Buchner funnel into a 200 ml beaker with 1, 2-dichloroethane (150 ml) and dispensed with a plastic spatula. The resulting slurry was added during 2–3 minutes to gently boiling and stirred 1,2-dichloroethane (550 ml) in a 1l two-necked flask over a magnetic stirrer-hot plate. Frothing ceased in a few minutes after completion of the addition, and the mixture acquired a clear dark-brown colour, indicating the end of the reaction. After 10 min at reflux under a water-cooled condenser, the dichloroethane was distilled off until *ca* 50 ml of a dark residue remained in the flask. After addition of ethylene glycol (200 ml) to the reaction flask, simple distillation was performed using an air condenser. The fraction up to 197 °C was collected. The distillate was cooled to 5–10 °C and the precipitated product was separated by suction filtration. The filtrate was extracted with 1,2-dichloroethane (2 × 100 ml). The extracts were evaporated in vacuo. The residue (a pale yellow oil) and the precipitated material were combined and purified on a short silica gel column (20 g) by elution with hexane pure biphenylene

(3.0–3.3 g, 33–36%) was obtained. The material was recrystallised (1:7 CH_2Cl_2 : hexane, 20 ml) in a frezeer (–10 °C) to yield pale yellow needles; m.p. 110–111 °C (lit.,[20] 109–112 °C).

Photobromination of biphenylene

Biphenylene (0.54 g, 3.54 mmol) was dissolved in CCl_4 (30 ml) in a 60 ml immersion type photochemical reactor, and the solution was cooled to 10 °C (ice bath). The magnetically stirred solution was irradiated with light from a 150 W projector lamp cooled with circulating water, and bromine (1.8 g, 11.30 mmol) in CCl_4 (20 ml) was added dropwise over 30 min. The reaction mixture was irradiated for a further 30 min (total 1 h). The reaction progress was monitored by ^{1}H NMR and TLC. After consumption of biphenylene, the solvent and excess of bromine were removed *in vacuo*. The residue was filtered with using a short silica gel (15 g) column, eluting with hexane (300 ml). The precipitated reaction product was allowed to crystallise from ether–petroleum ether (20 ml) overnight at room temperature. The precipitated material consisted of the hexabromides **5** and **6** (1.81 g, 80%) in 7 : 3 ratio (by ^{1}H NMR). Fractional crystallisation (chloroform–hexane) combined with repeated silica gel column chromatography (R_f 0.76, 0.62 hexane) eluted with chloroform–hexane (1 : 9) gave 1,2,3,4,4a,8b-hexabromo-1,2,3,4, 4a,8b-tetrahydrobiphenylenes **5** and **6** were isolated in yields of 1.01 g (45%) and 0.56 g (25%), respectively and recrystallised from chloroform.

1,2,3,4,4a,8b-hexabromo-1,2,3,4,4a,8b-hexahydrobiphenylene 5: colourless needles ($CHCl_3$), m.p.180–181 °C (lit.,[7]: 183–185 °C); IR: ν_{max} (KBr)/cm^{-1} 3010, 1360, 1320, 1250, 1160, 920, 760; NMR: δ_H (200 MHz; $CDCl_3$) 7.35 (m, 4H, arom.), 5.19 (d, J_{34} = 5.13 Hz, 1H, H_4) 5.01 (d, J_{12} 9.04 Hz, H_1) 4.87 (dd, J_{23} 3.69 Hz, 1H, H_3) 4.63 (dd, 1H, H_2); δ_C (50 MHz; $CDCl_3$) 144.2 (s), 143.7 (s), 133.55 (s) 133.4 (s), 125.8 (d), 124.0 (d), 74.4 (s), 74.1 (s) 61.2 (d), 57.5 (d), 57.2 (d) 54.9 (d); MS (EI): *m/z* 624/626/628/630/632/634/636 (M^+, 3) 547/549/551/553/555/557 (M^+–Br, 83) 467/469/471/473/475 (M^+–Br–HBr, 50) 387/389/391/393/395 (M^+–3Br/M^+–Br–2HBr 73), 305/307/309/311/313/315/317 (M^+–3Br–HBr, 83), 297/299/301 (13), 284/286/288 (65), 230/231/233 (M^+–5Br/M^+–4Br–HBr, 86), 206/208 (8), 195 (12) 150, 151,152 (M^+–6Br, 100), 153, 156, 125/126/127 (68), 115/116 (54), 98/99/100/101/102 (30), 86/87 (30), 74/75 (88). Found: C, 23.30; H, 1.29. $C_{12}H_8Br_6$ requires C, 23.22, H, 1.28 %.

1,2,3,4,4a,8b-hexabromo-1,2,3,4,4a,8b-hexahydrobiphenylene 6: colourles needles ($CHCl_3$), m.p. 150–151 °C (lit.,[6] 150–151 °C); IR: ν_{max} (KBr)/cm^{-1} 2980, 2930, 2910, 1440, 1320, 1260, 1230, 1150, 950, 920, 820, 780; NMR: δ_H (200 MHz; $CDCl_3$): 7.40–7.60 (m, 4H, arom.), 5.75 (d, J_{34} 11.67), H_4) 5.35 (m, 2H, H_1 and H_2), 3.71 (dd, J_{32} 6.1, H_3); δ_C (50 MHz; $CDCl_3$): 142.52 (s) 140.87 (s) 132.10 (d), 132.04 (d), 124.61 (d), 134.23 (d), 70.40 (s) 61.46 (d), 58.43 (d), 54.41 (d), 52.21 (d); MS (EI): *m/z* 626.5/628.8/630.5/632.5/634.5 (M^+, 3), 548.6/550.6/552.6/554.6 (M^+–Br,70), 466.7/468.7/470.7/ 472.7/474.7 (M^+–Br–HBr, 51) 386.8/388.8/390.8/392.8 (M^+–Br–2HBr, 73) 306.8/308.8/310.8/312.8/312.8/314.8 (M^+–4Br, 75), 229.9/230.9/231.9/232.9 (M^+–5Br, 94), 150, 151, 152/153(M^+-6Br,100), 126 (40), 115 (55), 74, 76 (92), 61, 63 (38).

5,6,8,10-tetrabromobenzocyclooctene (7): To a stirred solution of a mixture of hexabromides 5 and 6 or pure 5 or 6 (2.528 g, 4 mmol) in dry THF (60 ml) was added 1.12 g (10 mmol) of potassium *t*-butoxide in dry THF (40 ml). The resulting mixture was stirred for 8 h at room temperature. Reaction progress was monitored by TLC. The mixture was diluted with water (60 ml), extracted with diethyl ether (50 × 3 ml) and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue (a pale yellow oil) was passed through a short silica gel column (10 g) using n-hexane as eluent to give 1.85 g (98%) of **7**.

5,6,8,10-Tetrabromobenzocyclooctene (7): IR: ν_{max} (neat)/cm^{-1} 3065, 2925, 2850, 1622, 1600, 1580, 1480, 1450, 1415, 1380, 1340, 1300, 1260, 1240, 1220, 1200; NMR (200 MHz; $CDCl_3$): δ_H 7.35 (m, 4H, arom.), 6.76 (s, 1H, H_5), 6.36 (s, 1H, H_3), 6.36 (s); NMR (50 MHz; $CDCl_3$) δ_C 138.4 (s), 135.9 (s), 133.4 (d), 132.4(d), 129.8(d), 129.8 (d), 129.2 (d), 126.1 (s), 123.9 (s), 121.9 (s), 121.3 (s). MS (EI): *m/z* 467/469/471/473/475 (M^+, 16) 389/391/393/394 (M^+–Br, 46) 365/367/369/371 (M^+–Br–2C, 46) 309/310/31/,312/313/314 (M^+–2Br, 90) 286/288 (65), 232 (67) 153 (100) 126 (M^+–4Br–2C, 95). (Found: C, 30.11; H, 1.35. $C_{12}H_6Br_4$ requires C, 30.48; H, 1.29 %)

High temperature bromination of biphenylene

Biphenylene (**1**) (0.5 g, 3.28 mmol) was dissolved in CCl_4 (40 ml) in a round-bottomed flask (100 ml) equipped with a reflux condenser. The solution was heated under magnetic stirring until the CCl_4 began to reflux. To the refluxing solution bromine (1.76 g, 11 mmol) was added dropwise in the dark over 20 min. The reaction progress was monitored by TLC or ^{1}H NMR. The starting material was completely converted into products in 3 h. After cooling to room temperature the solvent was evaporated, providing 2.0 g of crude material. TLC (hexane) of the residue indicated five spots (R_f 0.76, 0.62, 0.51, 0.42, 0.29). The product mixture (2.0 g) was chromatographed on silica gel (170 g) eluting with hexane. First, 5,6,8,10-tetrabromobenzo-cyclooctene (**7**) (93 mg, 6%) was isolated as an oil. The second component was 5,7,7,8,10-pentabromo-7, 8-dihydrobenzocyclo-octene (**15**) (51 mg, 2 %). Further elution yielded *trans*-5,7,8,10-tetrabromo-7,8-dihydrobenzocyclooctene (**3**) (109 mg, 7%). Lastly, 1,2,3,4,4a,8b-hexabromo-1,2,3,4,4a,8b tetrahydro-biphenylenes 5 and **6** were isolated on increasing the polarity of the eluent (chloroform-hexane 1 : 9). The eluates containing the mixture of hexabromides **5** and **6** were further chromatographed (70 g silica gel, chloroform–hexane (1 : 9), whereby the hexabromides **5** (520 mg, 25%) and **6** (620 mg, 30%)were separately isolated as colourless crystals.

5,7,8,10-tetrabromo-7,8-dihydrobenzocyclooctene (3): colourless crystals (dichloromethane-petroleum ether, 1 : 3), m.p. 139–140 °C (lit·[7b] 139–140 °C). IR: ν_{max} (KBr)/cm^{-1} 3050, 1620, 1590, 1560, 1470, 1430, 1350, 1330, 1280, 1230, 1200, 1140, 1060, 950, 900, 850, 780, 760, 650; NMR (200 MHz; $CDCl_3$): δ_H 7.64 (m, 1H, arom.) 7.48 (m, 3H,arom.) 6.75 (d, J_{67} 7.66, 1H, H_7), 6.58 (J_{45} 8.92, 1H, H_4), 4.58 (dd, J_{56}11.36, 1H, H_6), 4.29 (d, 1H, H_5); (50 MHz; $CDCl_3$): δ_C 139.9 (s) 136.2 (s) 136.1 (d) 134.4 (d) 132.4 (d) 132.0 (d) 131.6 (d) 130.3 (d) 124.5 (s) 123.0 (s) 54.3 (d) 53.8 (d); MS (EI): *m/z* 466/468/470/472/474 (M^+, 10), 387/389/391/393 (M^+–Br, 55), 308/310/312 (M^+ –2Br, 100), 230/232 (M^+–3Br, 56), 150 (M^+–4Br-2H, 56).

5,7,7,8,10-Pentabromo-7,8-dihydrobenzocyclooctene (15): colourless crystals (CH_2Cl_2–petroleum ether, 1 : 3), m.p. 120–121 °C. IR: ν_{max} (KBr)/cm^{-1} 3040, 2980, 1630, 1610, 1480, 1430, 1330, 1250, 1190, 950, 950, 900, 870, 860, 760; NMR (200 MHz; $CDCl_3$): δ_H 7.60 (m, 1H, aryl), 7.45 (m, 3H, aryl) 7.45 (s, 1H, H_1) 6.65 (d, J 9.03, 1H, H_4) 4.66 (d, 1H, H_3); (50 MHz; $CDCl_3$): δ_C 137.3 (d), 136.6 (d), 134.0 (s), 133.6 (d), 130.7 (d) 130.2 (d), 130.0 (d), 128. 7 (d), 121.6 (s), 118.6 (s), 58.4 (d), 64.65 (d); MS (EI): *m/z* 546/548/550/552/554/556 (M^+, 3) 467/469/471/473/475 (M^+–Br, 80) 387/389/391/393 (M^+–2Br, 5) 309/311/313 (M^+–3Br, 41) 230/232 (M^+–4Br, 100), 150 (M^+–5Br-H, 60). Found C, 26.38; H, 1.35. $C_{12}H_7Br_5$ (550.73) requires C, 26.17; H, 1.28 %.

X-Ray crystallographic study

Compound **5**: $C_{12}H_8Br_6$, M = 631.65, triclinic, a = 9.101(2), b = 9.307(2), c = 9.485(3) Å, β = 108.98(1)°, U = 746.45(3) Å^3, T = 19 (1) °C, space group $P\bar{1}$, Z =2, D_c = 2.810 g cm^{-3}, λ(Mo–K_α) = 0.71069 Å, μ (absorption coefficient)= 4.414 mm^{-1}, 3225 unique reflections measured, corrected for absorption (R_{int} 0.06), and used in all calculations. Final R_1 [2833 F>nσ(F)] = 0.0390 and *wR (all F^2)* was 0.040.

Compound **6**: $C_{12}H_8Br_6$, M = 631.65, monoclinic, a = 12.075(1), b = 9.820(1), c = 3.199(1) Å, β = 98.133°, U = 1549.3(2) Å^3, T = 20(1) °C, space group $P2_1/c$, Z = 4, D_c = 2.691 g cm^{-3}, λ(Mo–K_α) = 0.71069 Å, μ = 15.39 mm^{-1}, 2864 unique reflections measured, corrected for absorption (R_{int}– 0.03), and used in all calculations. Final R_1 [924 F>nσ(F)] = 0.03 and *wR(all F^2)* was 0.0423.

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