

Pentakis(phenylethynyl)benzene and Hexakis(phenylethynyl)benzene: A Revision Concerning Two Far Too Similar Prototype Hydrocarbons

Jens Nierle,^[a] Dieter Barth,^[a] and Dietmar Kuck*^[a]

Keywords: Alkynes / C–C coupling / Dehalogenation / Ethynylbenzenes / Palladium

A previously overlooked hydrodehalogenation reaction occurring during the multiple Pd⁰-catalysed C–C coupling reaction between phenylacetylene and hexaiodo- and hexabromobenzene was found to give pentakis(phenylethynyl)benzene ("pentatolane") as the major product, but no hexakis(phenylethynyl)benzene ("hexatolane") under conditions previously claimed to yield the latter hydrocarbon. As an alternative to a viable route to hexatolane described in the lit-

erature, an independent synthesis of this hydrocarbon through sixfold Sonogashira coupling of hexakis(ethynyl)benzene with iodobenzene has been developed. Some physical and spectroscopic properties of hexatolane and of the hitherto unknown pentatolane have been determined after thorough purification by HPLC.

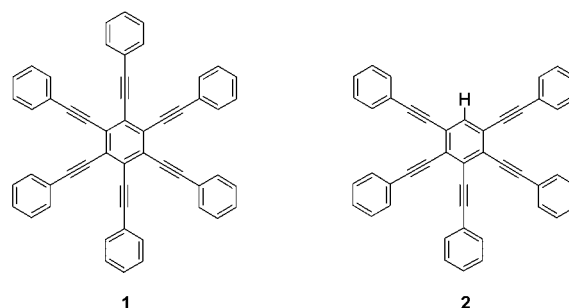
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

We would like to revise and update the synthesis and the properties of hexakis(phenylethynyl)benzene (**1**) and present for the first time a synthesis and complete characterization of its next-lower congener, pentakis(phenylethynyl)benzene (**2**). During investigations into the benzoannulation of stilbenes and tolans performed in the context of our research into the synthesis of benzoannulated spheriophanes,^[1,2] we obtained data on hydrocarbon **1** that were in conflict with reports in the literature. It turned out that, instead of the hexafold tolane **1** claimed to be formed under Pd⁰-catalysed C–C cross coupling conditions, the lower congener **2**, dubbed "pentatolane" here, was formed in some cases and that the properties of the latter hydrocarbon had erroneously been ascribed to the "hexatolane" (**1**).

In view of the importance of multiply phenylethynyl-substituted benzenes and the vast utilization of C–C coupling methodology in the field of material sciences, revision and completion of our knowledge on the parent compounds **1** and **2** appear appropriate.

The chemistry of oligo(phenylethynyl)-substituted benzenes has received increasing interest during recent years owing to their extended, previously unknown π -electron systems^[3,4] and their potential for the synthesis of liquid crystalline materials,^[5–10] dendritic structures,^[11] oligophenylenes^[12] and extremely large graphite cuttings far beyond the coronenes.^[13] Since the synthesis of hexaethynylbenzene (**6**) by Vollhardt et al. in 1986,^[4] many derivatives of this interesting family of fully conjugated, rigid, quasi two-dimensional hydrocarbons have been synthesized and



Scheme 1. Hexatolane **1** and pentatolane **2**

their properties studied. Hexatolane- and pentatolane-based compounds are most prominent among these. As a novel variant of this multifaceted theme,^[14–16] we have recently synthesized multiple tolans with convex-concave^[17] and saddle-shaped^[18] molecular frameworks.

Despite the elegance of the methodologies of Sonogashira^[19] and Heck^[20,21] for performing palladium(0)-catalysed ethynylation and ethenylation reactions, respectively, of multiply halogenated benzenes, experimental limitations to the "exhaustive" ethenylation of adjacent ring positions of such arenes have been noted.^[21,22] In general, ethynylation of bromo- and iodobenzenes tends to be more facile than ethenylation. However, the failure of a sixfold ethynylation of hexaiodobenzene (**4**) with trimethylsilylacetylene under Heck coupling conditions has been reported.^[4] Fortunately, use of hexabromobenzene (**3**) in place of **4** afforded sixfold C–C coupling, furnishing hexaethynylbenzene **6** in satisfactory yield on subsequent desilylation. Phenylethylation of hexaiodobenzene (**4**), in contrast to **3**, was found to yield pentasterylbenzene rather than hexasterylbenzene under Heck conditions.^[21] In further accord-

^[a] Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany

ance with this, recent studies on hexatolane-based dendrimers showed that Pd^0 -catalysed coupling between **4** and *N*-Boc-(4-ethynylphenyl)alanine methyl ester gave the corresponding pentaethynylbenzene derivative and that hexabromobenzene (**3**) was again required in order to furnish the corresponding hexatolane.^[11]

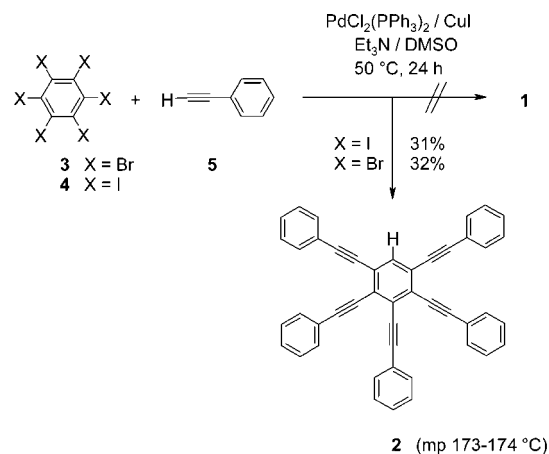
The first synthesis of the parent hexatolane **1** was described in 1987 by Praefcke et al.^[6] Hexabromobenzene (**3**) was treated with phenylacetylene (**5**) in triethylamine in the presence of palladium(0) catalyst, and a product of m.p. about 310 °C (dec.) was isolated as lemon yellow needles in 65% yield. The constitution of **1** was assigned to the product on the basis of electron ionization (EI) mass spectrometry.^[6] The UV/Vis spectrum of the product showed a strong absorption at $\lambda = 348$ nm ($\epsilon = 106000$), but no ^1H and ^{13}C NMR spectroscopic data were provided. Three years later, the multiple C–C cross coupling reaction between hexaiodobenzene (**4**) and phenylacetylene (**5**) under Pd^0 catalysis conditions in a triethylamine/dimethyl sulfoxide mixture was reported.^[22] The product of m.p. 169–170 °C was isolated as yellow needles and the structure of hexatolane **1** was assigned to it on the basis of ^1H NMR spectroscopic and combustion analytical data, which were also in agreement with the elemental constitution of **1**.^[22,23] In 1995, still another paper reported on the reaction between hexabromobenzene (**3**) and phenylacetylene (**5**) in *N,N,N',N'*-tetramethylethylenediamine and the product of m.p. 169 °C was characterized by ^1H NMR (270 MHz) and IR spectroscopy and again claimed as hexatolane **1**.^[7] The authors also provided a UV/Vis spectrum of this product, which appears similar but not identical to that published in 1987 by Praefcke.^[6,24]

In the course of our studies,^[1] we performed the Pd^0 -catalysed phenylethynylation of hexahalobenzenes **3** and **4** under the different previously described conditions.^[6,22] In one of these cases we also obtained the lower-melting product, the physical and spectroscopic properties of which turned out to be in conflict with those of hexatolane **1**. To clarify this situation, we developed an independent synthesis of **1** and performed a careful purification and characterization of the far too closely related hydrocarbons **1** and **2**.

Results and Discussion

Pentakis(phenylethynyl)benzene (2) through C–C Cross Coupling Reactions with Hexahalobenzenes 3 and 4: When hexaiodobenzene (**4**) was treated at 50 °C for 24 h in a mixture of phenylacetylene (**5**), bis(triphenylphosphane)palladium(II) dichloride, copper(I) iodide, DMSO and triethylamine, *fivefold* C–C coupling with concomitant single hydrodeiodination occurred, giving *pentakis*(phenylethynyl)benzene (**2**) as the major product (Scheme 2). The material was isolated in 31–54% yield as a yellow solid of m.p. 170–171 °C after repeated recrystallization. Examination of the product by ^1H and ^{13}C NMR spectroscopy, as well as by standard electron ionization (EI) and also by direct

electron ionization (DEI) mass spectrometry, unequivocally confirmed the identity of the reduction product **2**, a hitherto unknown hydrocarbon. Combustion analysis was also performed and found to be in agreement with the structure of **2**.^[23b] Notably, analysis of the crude product mixture by mass spectrometry on careful fractional evaporation gave no hint of the presence of **1**, but indicated the formation of considerable amounts of a tetrakis(phenylethynyl)benzene or several such isomeric “tetratolanes” as by-products.^[22] Repetition of the experiment with hexabromobenzene (**3**) in place of hexaiodobenzene (**4**) gave virtually the same results.



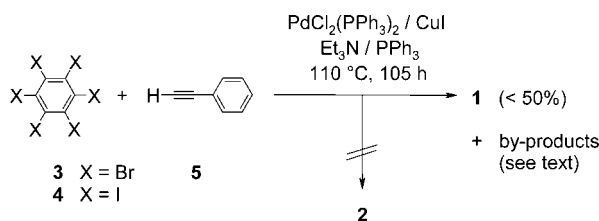
Scheme 2. Formation of pentatolane **2** instead of hexatolane **1**

To remove any doubts about the purity of pentatolane **2**, and in view of the notorious difficulties encountered in our attempts to purify hexatolane **1** (see below), we subjected the former hydrocarbon to careful semi-preparative high-pressure liquid chromatography (HPLC). The yellow solid obtained from this purification procedure was found to melt at 173–174 °C, significantly above but still close to the melting points twice mentioned in the literature for hexatolane **1**.^[7,22] However, the identity of pentatolane **2** was evident from the base peak at $m/z = 578$ in its EI and DEI mass spectra, which, in line with expectation, reflects the resistance of the molecular ion $\text{2}^{+\cdot}$ towards fragmentation.^[26] Losses of H_2 and of C_6H_6 gives rise to peaks in the 1–10% range only.^[27] Sequential losses of several molecules of dihydrogen (H_2 up to 5 H_2) and of ($\text{H}_2 + \text{C}_6\text{H}_6$) along with the formation of doubly and even triply charged ions were also observed in minor relative abundances. ^1H NMR spectra of **2** measured at 500 MHz in CDCl_3 exhibit a narrow composite signal in the $\delta = 7.33$ –7.38 ppm range, another composite signal at $\delta = 7.57$ –7.83 ppm and, notably, a sharp and well separated singlet at $\delta = 7.70$ ppm. The integral ratios observed for these three resonances are 15:10:1, in full accordance with the assumption that the *meta* and *para* protons of pentatolane **2** are almost isochronous and that magnetic deshielding of the three sets of *ortho* protons of **2** is also very similar.

Closer inspection of **2** by ^1H NMR spectroscopy at 600 MHz in $[\text{D}_8]\text{THF}$ revealed three doublets of doublets

centred at $\delta = 7.58, 7.61$ and 7.63 in a 2:2:1 ratio, reflecting three slightly magnetically different sets of *ortho* protons and thus the C_{2v} molecular symmetry of **2**. The ^{13}C NMR spectrum (150.9 MHz) of **2** exhibits all six non-equivalent acetylene resonances in two distinct groups at $\delta = 86.68, 86.91$ and 87.03 ppm (intensity ratio ca. 1:2:2) and at $\delta = 95.52, 98.42$ and 99.46 ppm (ca. 2:1:2). At high field, all of the six possible resonances of non-equivalent quaternary carbon nuclei of the pendant rings are also observable, as are six of the nine non-equivalent tertiary carbons at these rings. The unique CH group of the central ring appears at lowest field ($\delta = 133.80$ ppm). Unlike in the lower-resolution NMR spectra, which reflect an apparent equivalence of the five phenylethynyl groups, the formal C_{2v} symmetry of **2** is also confirmed by ^{13}C NMR at high resolution. Finally, both accurate mass measurements and combustion analysis were found to be in accordance with the elemental composition ($\text{C}_{46}\text{H}_{26}$) of pentatolane **2**.

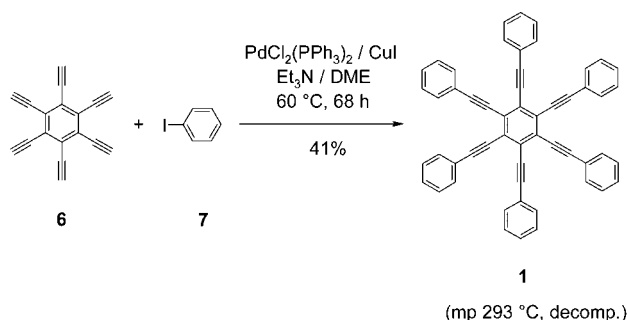
Hexakis(phenylethynyl)benzene (1) by Sonogashira Cross Coupling of Hexabromo- and Hexaiodobenzene with Phenylacetylene: Repetition of the sixfold C–C coupling of hexabromobenzene (**3**) with phenylacetylene (**5**) under the conditions described by Praefcke et al.^[6] (that is, in the absence of DMSO but in the presence of an excess of triphenylphosphane) was also performed several times. In accordance with the results reported by these authors, hexatolane **1** was found to be the major product (Scheme 3). The crude product, obtained in 67–70% yield after a single recrystallization, did not contain pentatolane **2** or any tetratolanes, as found by DEI mass spectrometry and ^1H NMR spectroscopy. However, contamination with partially chlorinated products was inferred from characteristic peaks above $m/z = 678$. In spite of repeated attempts, recrystallization did not enable us to remove these impurities completely.^[28] The corresponding experiments starting from hexaiodobenzene **2** furnished similar product mixtures in 70–73% yields.



Scheme 3. Synthesis of hexatolane **1** without formation of pentatolane **2** under conditions described by Praefcke et al. for the case of X = Br^[6]

Hexakis(phenylethynyl)benzene (1) by Cross Coupling of Hexaethynylbenzene and Iodobenzene – an Independent Synthesis: Because of the difficulties involved in obtaining hexatolane **1** in a pure state by the published procedures, we attempted to synthesize this hydrocarbon in an independent way. To this end, hexaethynylbenzene (**6**), obtained from hexabromobenzene (**3**) via hexakis(trimethylsilylethynyl)benzene according to the procedure published by Vollhardt et al.,^[4] was treated with iodobenzene (**7**) in the presence of

$[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI in dimethoxyethane/triethylamine at 60°C (Scheme 4). Flash chromatography of the product mixture again gave a yellow solid, which, in contrast to **2** (see above), melted at 293°C , somewhat lower than the approximate melting temperature published earlier.^[6] The same melting point was determined for the yellow solid isolated by careful semi-preparative HPLC purification of the crude product mixture obtained from hexahalobenzenes **3** and **4** and phenylacetylene (**5**) under the reaction conditions described in the previous section. Mass spectra and ^1H and ^{13}C NMR spectra of the hexatolane products obtained from these independent syntheses and purification procedures were found to be identical.



Scheme 4. Independent synthesis of hexatolane **1** from hexaethynylbenzene (**6**)

EI and, in particular, DEI mass spectrometry, as well as ^1H and ^{13}C NMR spectroscopy, clearly confirmed the isolation of pure hexatolane **1**. In line with expectations, the EI and DEI mass spectra of **1** exhibit the molecular ion signals at $m/z = 678$ as the base peaks, with fragmentation occurring only to a very minor extent. Losses of up to five H_2 molecules in low relative abundances ($\leq 5\%$) and of C_6H_6 , as well as the combined loss of H_2 and C_6H_6 (ca. 10% each) were observed, together with the formation of doubly charged fragment ions in the $m/z = 298\text{--}300$ range, corresponding mainly to ions $[\mathbf{1} - (\text{H}_2, \text{C}_6\text{H}_6)]^{2+}$ (ca. 10%). Triply charged ions were also generated in very minor relative abundances. Thus, not surprisingly, the gas-phase fragmentation behaviour of the radical cations of hexatolane ($\mathbf{1}^{\cdot+}$) and of pentatolane ($\mathbf{5}^{\cdot+}$) is very similar.

The ^1H NMR spectra (500 and 600 MHz) of **1** exhibit only two slightly broadened singlets at $\delta = 7.40$ and 7.67 , with an integral ratio of 3:2, in accordance with 18 protons at the *meta* and *para* positions and twelve protons at the *ortho* positions of the six phenyl rings. In comparison with the spectrum of pentatolane **2**, additional magnetic deshielding due to the presence of the sixth phenyl group in **1** is almost negligible ($\Delta\delta = \delta_{\text{H}(1)} - \delta_{\text{H}(2)} \leq +0.05$ ppm).

The ^{13}C NMR spectrum (150.9 MHz) of hexatolane **1** dissolved in $[\text{D}_8]\text{tetrahydrofuran}$ ^[28] reflects the effective (formal) D_{6h} symmetry of the molecule in solution. It exhibits only seven different resonances, three of them ($\delta = 128.5, 129.0$ and 131.7 ppm, in an approximate intensity ratio of 2:1:2) attributable to the carbon nuclei in the tertiary positions. The quaternary carbon atoms of the central ring

Table 1. ^{13}C chemical shifts (δ) of hexatolane **1** and pentatolane **2**

Compound ^[a]	1	2			
Position	(all)	[C-1(5)–CCPh]	[C-2(4)–CCPh]	[C-3–CCPh]	C-6
C ^{central}	127.39	125.44	127.37	128.54	133.80
C ^{α}	86.79	87.0 ^[b]	87.0 ^[b]	86.68 ^[b]	—
C ^{β}	99.51	95.52	99.46	98.42	—
C-1'	122.93	122.80	123.04	123.02	—
C-2', C-6'	131.65	131.65	131.60 ^[b]	131.65	—
C-3', C-5'	128.47	128.44	128.44	128.44	—
C-4'	129.01	128.87 ^[b]	128.90 ^[b]	128.90 ^[b]	—

^[a] Measured at 125.9 MHz in $[\text{D}_8]\text{THF}$. ^[b] No more specific assignment achieved.

resonate at significantly lower field ($\delta = 127.4$ ppm) than those of the pendant phenyl groups ($\delta = 122.9$ ppm) and the lines for the inner (α) and outer (β) acetylene carbon nuclei appear at $\delta = 86.8$ and $\delta = 99.5$ ppm, respectively, as confirmed by correlation (HMQC and HMBC) measurements. The acetylenic carbon atoms of hexatolane derivatives such as the dendritic phenylalanine analogues of **1**^[11] were found to resonate at similar fields but no assignment was made. Thus, as expected, all four ^{13}C resonances of the pendant phenyl rings of **1** and **2** are found to be very similar (Table 1). However, significant differences are found between the chemical shifts of the acetylene groups and the central carbon atoms of **1** and some of the corresponding positions of **2**. The resonances of the C ^{β} nuclei of **1** are almost identical with the resonances of those C ^{β} nuclei of **2** that are incorporated in the phenylacetylene groups at C-2 and C-4 ($\delta = 99.5$ ppm) but slightly and even drastically different from those of the C ^{β} nuclei present in the phenylacetylene groups at C-3 ($\delta = 98.4$ ppm) and at C-1 and C-5 of **2** ($\delta = 95.5$ ppm), respectively. Similar differences are noted for the chemical shifts of the quaternary carbon centres in the central rings of **1** and **2** (Table 1). In turn, however, the resonances of the C ^{α} nuclei of **1** and **2** are all within a very small range ($\delta = 86.7$ – 87.0).

UV/Vis Spectra of Hexatolane (1) and Pentatolane (2): In view of the broad interest in the optical properties of the multiply phenylethynyl-substituted benzenes and in particular of the discrepancies encountered with the identity and purification of the parent hydrocarbon **1**, the electronic spectra of **1** and **2** were measured (Figure 1).

The UV/Vis spectrum of hexatolane (**1**) measured on the HPLC-purified material exhibits the maximum absorption at $\lambda = 349$ nm ($\epsilon = 155000$) and a shoulder at $\lambda \approx 371$ nm ($\epsilon = 81000$). The former absorption is in good agreement with the maximum absorption published for hexatolane **1** by Praefcke et al. ($\lambda = 348$)^[6] and also by Kondo et al. ($\lambda = 350$ nm).^[7] It is interesting to mention that the low-energy shoulder has also been noted (at $\lambda \approx 370$ nm) by one of these groups.^[7] The UV/Vis spectrum of pentatolane **2** exhibits the maximum absorption at $\lambda = 333$ nm ($\epsilon = 93000$) and a shoulder at $\lambda \approx 368$ nm ($\epsilon = 36000$). Notably, these bands fit well in between those observed in the spectra of hexatolane **1** and the D_{2h} -symmetrical next-lower analogue, 1,2,4,5-tetrakis(phenylethynyl)benzene, published by Kondo et al. ($\lambda = 315$ nm and $\lambda \approx 350$ nm).^[7]

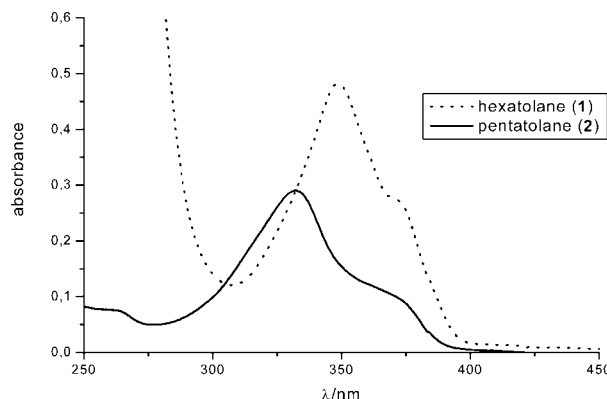


Figure 1. UV/Vis spectra of hexatolane **1** and pentatolane **2** (CH_2Cl_2 , $3.1 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$)

In summary, a new synthesis of hexakis(phenylethynyl)benzene (“hexatolane”, **1**) together with careful HPLC purification has enabled us to determine and correct the physical properties of this prototypical hydrocarbon in detail. Its syntheses from hexabromo- and hexaiodobenzene and phenylacetylene under Pd^0 catalysis conditions, claimed in the literature, were found to be incorrect or dubious. In one of the procedures, pentakis(phenylethynyl)benzene (“pentatolane”, **2**) is formed instead of hexatolane as the major coupling product, together with even lower analogues. Also, purification of hexatolane **1**, once obtained, is difficult, and tedious HPLC purification has to be performed to remove contaminants of similarly low solubility. By employment of a complementary synthesis strategy using Pd^0 cross coupling of hexaethynylbenzene and iodobenzene, these complicating factors can be largely circumvented.

Experimental Section

General: Melting points (uncorrected): Electrothermal, Melting point apparatus. HPLC purification of compounds **1** and **2** was performed with a Merck–Hitachi instrument equipped with an L-6250 Intelligent Pump, an L-7420 UV/Vis detector and a Hibar column packed with LiChrosorb Si 60 (\varnothing , 7 μm). The isocratic runs (cyclohexane/ CHCl_3 , 2:1 v/v) were monitored at $\lambda = 280$ nm. IR spectroscopy: Perkin–Elmer, Model 841. NMR spectroscopy: Bruker DRX 500 (^1H , 500 MHz, ^{13}C : 125.7) and Bruker Avance

600 (^1H , 600 MHz, ^{13}C : 150.9 MHz). UV/Vis spectroscopy: Perkin–Elmer UV Lambda 40. Mass spectrometry: Fisons VG, Autospec; accurate mass measurements (HRMS) was performed with use of the peak-matching method at a resolution of $m/\Delta m = 8000$ (10% valley). Combustion analysis: Perkin–Elmer, Model 240.

Hexakis(phenylethynyl)benzene (1): A solution of hexaethynylbenzene (**6**,^[4] 40.0 mg, 0.18 mmol) in DME (10 mL), bis(triphenylphosphane)palladium(II) chloride (7.5 mg, 10 μmol), copper(I) iodide (1.0 mg, 5.0 μmol) and triethylamine (10 mL) was prepared, and iodobenzene (**7**, 322.0 mg, 1.58 mmol) was added. The mixture was stirred at 60 °C for 68 h under argon and then cooled to ambient temperature. The solvent was evaporated and the residue was subjected to flash chromatography through silica gel with $\text{CHCl}_3/n\text{-hexane}$ (1:1). Hexatolane (**1**, 50.0 mg, 41%) was obtained as a yellow solid, m.p. 293 °C (dec.). ^1H NMR (500 MHz, CDCl_3): $\delta = 7.67$ (m_c , 12 H), 7.40 (m_c , 18 H) ppm. IR (KBr): $\tilde{\nu} = 3055\text{ cm}^{-1}$, 2926, 2855, 1598, 1493, 1067, 1024, 749, 687. MS (EI, 70 eV): m/z (rel. int., %) = 680 (18) [$^{13}\text{C}_2\text{M}^+$], 679 (57) [$\{^{13}\text{C}_1\}\text{M}^+$], 678 (100) [M^+], 677 (5) [$\text{M} - \text{H}$] $^+$, 676 (5) [$\text{M} - \text{H}_2$] $^+$, 675 (3) [$\text{M} - (\text{H}, \text{H}_2)$] $^+$, 674 (3) [$\text{M} - 2\text{H}_2$] $^+$, 599 (11), 598 (13), 597 (6), 299 (15). After purification by HPLC (silica gel, $c\text{-C}_6\text{H}_{12}/\text{CHCl}_3$, 2:1), the following data were obtained for **1**: M.p. 293 °C (dec.). ^1H NMR (600 MHz, $[\text{D}_8]\text{THF}$): $\delta = 7.699$ (m_c , 12 H^{ortho}), 7.433 (m_c , 18 H^{meta} and H^{para}) ppm. ^{13}C NMR, HMBC (150.9 MHz, $[\text{D}_8]\text{THF}$): $\delta = 131.65$ (t, $\text{C}^{\text{ph,ortho}}$), 129.01 (t, $\text{C}^{\text{ph,para}}$), 128.47 (t, $\text{C}^{\text{ph,meta}}$), 127.39 (q, C-1 to C-6), 122.93 (q, $\text{C}^{\text{ph,ipso}}$), 99.51 (q, $\text{C}^{\beta/\text{C}}$), 86.79 (q, C/ C^{α}) ppm. MS (DEI, 70 eV): $m/z = 680$ (22) [$\{^{13}\text{C}_2\}\text{M}^+$], 679 (59) [$\{^{13}\text{C}_1\}\text{M}^+$], 678 (100) [M^+], 677 (6) in part [$\text{M} - \text{H}$] $^+$, 676 (6) in part [$\text{M} - \text{H}_2$] $^+$, 675 (5) in part [$\text{M} - (\text{H}, \text{H}_2)$] $^+$, 674 (6) in part [$\text{M} - 2\text{H}_2$] $^+$, 673 (4) in part [$\text{M} - (\text{H}, 2\text{H}_2)$] $^+$, 672 (5) [$\text{M} - 3\text{H}_2$] $^+$, 600 (14) [$\text{M} - \text{C}_6\text{H}_6$] $^+$, 599 (11), 598 (15), 597 (7), 596 (9), 594 (3), 298 (10). UV/Vis (CH_2Cl_2 , $3.1 \times 10^{-6}\text{ mol}\cdot\text{L}^{-1}$): λ (ϵ) = 348 (155000), 370 nm (s, 81000). Accurate mass by EI-MS ($\text{C}_{54}\text{H}_{30}$): calcd. 678.2347; found 678.2340. $\text{C}_{54}\text{H}_{30}$ (678.84): calcd. C 95.55, H 4.45; found C 94.43, H 4.62.

Pentakis(phenylethynyl)benzene (2): A mixture of hexaiodobenzene (**4**, 2.08 g, 2.50 mmol), phenylacetylene (**5**, 3.37 g, 33.0 mmol), bis(triphenylphosphane)palladium(II) chloride (0.12 g, 0.17 mmol), copper(I) iodide (0.07 g, 0.37 mmol) and triethylamine (15 mL) and DMSO (3 mL) was heated at 50 °C under argon for 24 h. The reaction mixture was cooled to ambient temperature and then filtered, and the filtrate was concentrated in vacuo to yield a yellow solid, which was recrystallized from ethanol/dichloromethane (1:1). Pentatolane **2** (0.45 g, 31%), containing some residual tetratolane(s) (see above), was obtained as a yellow solid, m.p. 170 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 7.70$ (s, 1 H), 7.63 (m_c , 10 H), 7.35 (m_c , 15 H) ppm. ^{13}C NMR (125.7 MHz, CDCl_3): $\delta = 133.84$ (t), 131.78 (t), 128.81 (t), 128.62 (q), 128.45 (t), 127.53 (q), 125.34 (q), 123.19 (q), 122.88 (q), 99.39 (q), 98.31 (q), 95.49 (q), 87.46 (q), 87.32 (q), 87.09 (q). IR (KBr): $\tilde{\nu} = 3055\text{ cm}^{-1}$, 2925, 1796, 1781, 1773, 1701, 1596, 1492, 1442, 1407, 1145, 1067, 1025, 998, 906, 884, 757, 748, 725, 689, 621. MS (EI, 70 eV): $m/z = 580$ (17) [$\{^{13}\text{C}_2\}\text{M}^+$], 579 (50) [$\{^{13}\text{C}_1\}\text{M}^+$], 578 (100) [M^+], 577 (12) [$\text{M} - \text{H}$] $^+$, 576 (13) [$\text{M} - \text{H}_2$] $^+$, 575 (8) [$\text{M} - (\text{H}, \text{H}_2)$] $^+$, 574 (11) [$\text{M} - 2\text{H}_2$] $^+$, 573 (5) [$\text{M} - (\text{H}, 2\text{H}_2)$] $^+$, 572 (7) [$\text{M} - 3\text{H}_2$] $^+$, 500 (16), 498 (14), 496 (5), 286 (12), 249 (17). After purification by HPLC (silica gel, $c\text{-C}_6\text{H}_{12}/\text{CHCl}_3$, 2:1), the following data were obtained for **2**: M.p. 173–174 °C. ^1H NMR, HMQC, HMBC (600 MHz, $[\text{D}_8]\text{THF}$): $\delta = 7.804$ (s, 1 H, 6-H), 7.695 (m_c , 2 H, $\text{H}^{\text{ortho(para-ph)}}$), 7.678 (m_c , 4 H, $\text{H}^{\text{ortho(meta-ph)}}$), 7.647 (m_c , 4 H, $\text{H}^{\text{ortho(ortho-ph)}}$), 7.420 (m_c , 15 H, H^{meta} and H^{para}) ppm. ^{13}C NMR, ^{13}C DEPT, HMQC, HMBC

(150.9 MHz, $[\text{D}_8]\text{THF}$): $\delta = 133.80$ (t, C-6), 131.65, 131.61 and 131.60 (all t, $\text{C}^{\text{ph,ortho}}$, rel. intensities ca. 1:2:2), 128.90 and 128.87 (both t, $\text{C}^{\text{ph,para}}$, rel. intensities ca. 1.5:1), 128.54 (q, C-3), 128.44 (t, $\text{C}^{\text{ph,meta}}$), 127.37 (q, C-2 and C-4), 125.44 (q, C-1 and C-5), 123.04, 123.02 and 122.80 (all q, $\text{C}^{\text{ph,ipso}}$, rel. intensities ca. 2:1:2), 99.46, 98.42, 95.52 (all q, $\text{C}^{\beta=\text{C}}$, rel. intensities ca. 2:1:2, assignment based on rel. intensities and HMBC: $\text{C}^{\beta(\text{meta})}$, $\text{C}^{\beta(\text{para})}$, $\text{C}^{\beta(\text{ortho})}$, respectively), 87.03, 86.91, 86.68 (all q, $\text{C}\equiv\text{C}^{\alpha}$, rel. intensities 2:2:1) ppm. MS (DEI, 70 eV): $m/z = 580$ (17) [$\{^{13}\text{C}_2\}\text{M}^+$], 579 (50) [$\{^{13}\text{C}_1\}\text{M}^+$], 578 (100) [$\{^{13}\text{C}_0\}\text{M}^+$], 577 (10) in part [$\text{M} - \text{H}$] $^+$, 576 (12) in part [$\text{M} - \text{H}_2$] $^+$, 575 (8) in part [$\text{M} - (\text{H}, \text{H}_2)$] $^+$, 574 (10) in part [$\text{M} - 2\text{H}_2$] $^+$, 573 (5) in part [$\text{M} - (\text{H}, 2\text{H}_2)$] $^+$, 572 (6, [$\text{M} - 3\text{H}_2$] $^+$), 500 (13, [$\text{M} - \text{C}_6\text{H}_6$] $^+$), 499 (7), 498 (11), 497 (3), 496 (4), 250 (5), 249.5 (5), 249.0 (9). UV/Vis (CH_2Cl_2 , $3.1 \times 10^{-6}\text{ mol}\cdot\text{L}^{-1}$): λ (ϵ) = 333 (93000), 368 nm (s, 36000). Accurate mass by EI-MS ($\text{C}_{46}\text{H}_{26}$): calcd. 578.2034; found 578.2037. $\text{C}_{46}\text{H}_{26}$ (578.72): calcd. C 95.47, H 4.53; found C 95.28, H 4.71.

When the reaction was carried out by starting from hexabromobenzene (**3**, 1.38 g, 2.50 mmol) instead of **4** with the same components in the same amounts and under the same conditions as described above, recrystallization from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ furnished pentatolane **2** in virtually the same yield (460 mg, 32%), and with identical properties.

Acknowledgments

We are grateful to Dr. Mathias Letzel and Dr. Andreas Mix for their assistance in spectroscopic analyses.

- [1] [1a] J. Nierle, D. Kuck, in *Threefold ortho-Terphenyls as Intermediates to Spherical C₆₀-Hydrocarbons*, 8th International Symposium on Novel Aromatic Compounds (ISNA-8), Braunschweig, Germany, July 30 to August 04, **1995**, Poster No. 10. [1b] J. Nierle, *Doctoral thesis*, University of Bielefeld, **1998**.
- [2] For the chemistry of non-benzoannelated spheriphanes, see: J. Groß, G. Harder, A. Siepen, J. Harren, F. Vögtle, H. Stefan, K. Gloe, B. Ahlers, K. Cammann, K. Rissanen, *Chem. Eur. J.* **1996**, 2, 1585–1595, and previous papers cited therein.
- [3] J. Zhang, D. J. Pesak, J. L. Ludwick, J. S. Moore, *J. Am. Chem. Soc.* **1994**, 116, 4227–4239.
- [4] R. Diercks, J. C. Armstrong, R. Boese, K. P. C. Vollhardt, *Angew. Chem.* **1986**, 98, 270–271; *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 268–269.
- [5] [5a] M. Ebert, D. A. Jungbauer, R. Kleppinger, J. H. Wendorff, B. Kohne, K. Praefcke, *Liq. Cryst.* **1989**, 4, 53–67. [5b] K. Praefcke, B. Kohne, D. Singer, *Angew. Chem.* **1990**, 102, 200–202; *Angew. Chem. Int. Ed. Engl.* **1990**, 29, 177–179. [5c] K. Praefcke, B. Kohne, D. Singer, D. Demus, G. Pelzl, S. Diele, *Liq. Cryst.* **1990**, 7, 589–594. [5d] K. Praefcke, B. Kohne, D. Singer, M. Ebert, A. Liebmman, J. H. Wendorff, *Liq. Cryst.* **1991**, 10, 147–159.
- [6] B. Kohne, K. Praefcke, *Chimia* **1987**, 41, 196–198.
- [7] K. Kondo, S. Yasuda, T. Sakaguchi, M. Miya, *J. Chem. Soc., Chem. Commun.* **1995**, 55–56.
- [8] [8a] S. Marguet, A. Germain, P. Millie, *Chem. Phys.* **1996**, 208, 351–373. [8b] S. Marguet, D. Markovitsi, D. Goldmann, D. Janietz, K. Praefcke, D. Singer, *J. Chem. Soc., Faraday Trans.* **1997**, 93, 147–155.
- [9] C. J. Booth, D. Krüerke, G. Heppke, *J. Mater. Chem.* **1996**, 6, 927–934.
- [10] S. Kumar, S. K. Varshney, *Angew. Chem.* **2000**, 112, 3270–3272; *Angew. Chem. Int. Ed.* **2000**, 39, 3140–3142.
- [11] [11a] B. Kayser, J. Altman, W. Beck, *Chem. Eur. J.* **1999**, 5,

- 754–758. ^[11b] B. Kayser, J. Altman, W. Beck, *Tetrahedron* **1997**, *53*, 2475–2484. ^[11c] B. Kayser, J. Altman, H. Nöth, J. Knizek, W. Beck, *Eur. J. Inorg. Chem.* **1998**, 1791–1798.
- ^[12] ^[12a] R. Boese, A. J. Matzger, D. L. Mohler, K. P. C. Vollhardt, *Angew. Chem.* **1995**, *107*, 1630–1633; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1478–1481. ^[12b] K. P. C. Vollhardt, D. L. Mohler, in *Advances in Strain in Organic Chemistry*, (Ed.: B. Halton), JAI Press, Greenwich, CT, **1996**; Vol. 5, pp 121–160.
- ^[13] ^[13a] A. J. Berresheim, M. Müller, K. Müllen, *Chem. Rev.* **1999**, *99*, 1747–1785. ^[13b] S. V. Iyer, M. Wehmeier, J. D. Brand, M. A. Keegstra, K. Müllen, *Angew. Chem.* **1997**, *109*, 1676–1679; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1604–1607. ^[13c] M. Müller, V. S. Iyer, C. Kübel, V. Enkelmann, K. Müllen, *Angew. Chem.* **1997**, *109*, 1679–1682; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1607–1610.
- ^[14] F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, *104*, 1123–1146; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1101–1123.
- ^[15] ^[15a] U. H. F. Bunz, *Synlett* **1997**, 1117–1127. ^[15b] U. H. F. Bunz, *Top. Curr. Chem.* **1999**, *201*, 131–161.
- ^[16] M. M. Haley, J. J. Pak, S. C. Brand, *Top. Curr. Chem.* **1999**, *201*, 81–130.
- ^[17] ^[17a] J. Tellenbröcker, D. Kuck, *Angew. Chem.* **1999**, *111*, 1000–1004; *Angew. Chem. Int. Ed.* **1999**, *38*, 919–922. ^[17b] D. Kuck, A. Schuster, R. A. Krause, J. Tellenbröcker, C. P. Exner, M. Penk, H. Bögge, A. Müller, *Tetrahedron* **2001**, *57*, 3587–3613.
- ^[18] J. Tellenbröcker, D. Kuck, *Eur. J. Org. Chem.* **2001**, 1483–1489.
- ^[19] ^[19a] K. Sonogashira, Y. Thoda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467–4470. ^[19b] For some recent applications, see: R. G. Heidenreich, K. Köhler, J. G. E. Krauter, J. Pietsch, *Synlett* **2002**, 1118–1122, and work quoted therein.
- ^[20] ^[20a] H. A. Dieck, F. R. Heck, *J. Organomet. Chem.* **1975**, *93*, 259–263. ^[20b] R. F. Heck, *Acc. Chem. Res.* **1979**, *12*, 146–151.
- ^[21] A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, *106*, 2473–2506; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379.
- ^[22] W. Tao, S. Nesbitt, R. F. Heck, *J. Org. Chem.* **1990**, *55*, 63–69.
- ^[23] ^[23a] Apparently, the ¹H NMR spectrum reported in ref.^[22] consisted of a multiplet at $\delta = 7.34$ –7.67 ppm, the magnetic field strength not being mentioned. ^[23b] It should be noted here that the combustion analytical data calculated for compounds **1** and **2** are not distinguishable within the limits of experimental error (see Exp. Sect.).
- ^[24] For discussions on the electronic absorption spectra of **1** and related compounds, see refs.^[8]
- ^[25] The ¹H NMR spectra of crude and even of singly recrystallized **2** exhibit a small singlet at $\delta = 7.76$ ppm (i.e., ca. 55 ppb downfield of the H-6 singlet of **2**), which is attributed to the protons at the central ring of a tetratolane. The EI mass spectra of some samples exhibit a peak of medium relative intensity at $m/z = 478$, indicating the molecular ions of (isomeric) tetratolanes.
- ^[26] For reviews on mass spectrometry of alkylbenzenes, see: ^[26a] D. Kuck, *Mass Spectrom. Rev.* **1990**, *9*, 181–233. ^[26b] D. Kuck, *Mass Spectrom. Rev.* **1990**, *9*, 583–630.
- ^[27] For reviews on the loss of arenes from gaseous ions, see: ^[27a] D. Kuck, *Int. J. Mass Spectrom.* **2002**, *213*, 101–144. ^[27b] D. Kuck, *J. Mass Spectrom.*, in preparation.
- ^[28] The solubility of hexatolane **1** in organic solvents (including THF) is very low, much lower than that of pentatolane **2**.

Received October 10, 2003