Extending the Chemistry of [5.5.5.5]Fenestranes – Eightfold Peripheral Functionalization of Fenestrindanes

Jörg Tellenbröker[a] and Dietmar Kuck*[a]

Dedicated to Professor Henning Hopf on the occasion of his 60th birthday

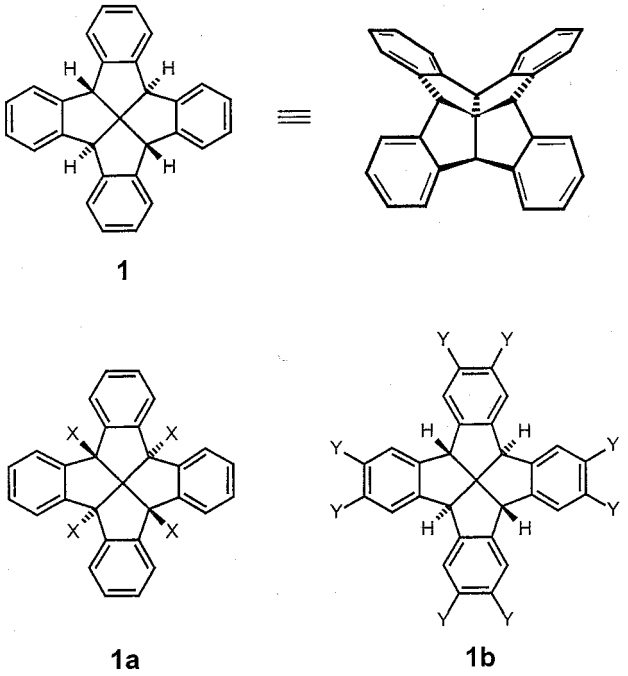
Keywords: Arenes / Aromatic substitution (multiple) / Fenestranes / Indane compounds / Polycycles (convex/concave)

Directed multiple functionalization of tetrabenzo[5.5.5.5]-fenestranes (fenestrindanes) at the molecular arene periphery has been achieved for the first time, starting from the fourfold bridgehead-methylated congener **2**. In particular, 2,3,6,7,10,11,14,15-octabromofenestrindane (**3**) and 2,3,6,7,10,11,14,15-octaiodofenestrindane (**7**) have been synthesized as key intermediates in excellent yields. Further eightfold functionalized analogs, such as the corresponding octa(*n*-butyl) thioether **5** and the octacyanofenestrindane **8**, are now accessible as well as other fenestrane hydrocarbons with an extended carbon framework, including the octakis-(phenylethynyl) and the octaphenyl derivatives **6** and **9**, respectively. The S_4-symmetrical conformation of these fenestranes is evident from their ^{1}H and ^{13}C NMR spectra. It is suggested that, owing to their uniquely curved convex/concave molecular shape, fenestrindanes with eightfold peripheral functionalization could serve as unusual motifs for liquid crystal engineering and dendrimer chemistry, and for the construction of graphite cuttings bearing a saddle-like, three-dimensionally distorted core.

Introduction

The unusual centrotetracyclic framework of fenestranes[1–3] has interested chemists mainly due to the strain and geometry of the tetracoordinate (carbon) atom at the central bridgehead position. This motif is now of interest not only in organic but also in metalorganic[4] and inorganic chemistry,[5] and inspiration from theoretical chemistry may lead to further developments in the organic chemistry of flattened or planar tetracoordinate carbon.[6] However, the synthetic utility of fenestranes as building blocks in organic chemistry has not been exploited to any great extent,[7] and only the facile access to benzoannelated derivatives of [5.5.5.5]- and [5.5.5.6]fenestranes has opened promising routes to extended molecular frameworks bearing the three-dimensional fenestrane core.[2,8–10] In a similar way to related aromatic hydrocarbons of the centropolyindane family,[10] and in particular the tribenzotriquinacenes,[11,12] the prototype of the benzoannelated fenestranes, fenestrindane **1**,[13] offers two different possibilities for the creation of novel molecular architectures: (i) Bridgehead functionalization, e.g. **1a**,[14] and (ii) directed functionalization at the aromatic rings, e.g. **1b** (Scheme 1). Besides a recent note on metal-carbonyl-mediated nucleophilic substitution of **1**,[15] the latter approach is reported here for the first time.

Recent investigations on the functionalization of tribenzotriquinacenes at the aromatic rings have revealed that exhaustive introduction of substituents at the six peripheral



Scheme 1. Fenestrindane (*all-cis*-tetrabenzo[5.5.5.5]fenestrane) **1** and its bridgehead-tetrasubstituted and peripherally octasubstituted derivatives (**1a** and **1b**, respectively)

arene positions can be achieved with high regioselectivity and efficiency.[12] The inner (*ortho*) positions were found to be inert in almost all cases studied to date.[15,16] This offers a variety of transformations for the construction of convex/concave molecules bearing both the curvature induced by the five-membered rings and the planar elements of the condensed aromatic nuclei.[17] In contrast to this bowl-shaped architecture, saddle-type molecular frameworks

[a] Fakultät für Chemie der Universität Bielefeld,
Universitätsstraße 25, 33501 Bielefeld, Germany
Fax: (internat.) + 49(0)-521/106-6417
E-mail: dietmar.kuck@uni-bielefeld.de

  1434–193X/01/0408–1483 $ 17.50+.50/0

should become accessible by introducing eight functional groups at the peripheral positions of fenestrindane, as shown in **1b**, and extending the highly symmetrical skeleton by appropriate C−C coupling, e.g. further benzoannelation reactions.[18] This approach would add a promising variant to the corresponding contrasting cases within the [*n*]circulene family, viz. to the bowl-shaped corannulene[19−21] and the saddle-shaped pleiadannulene.[22,23] A hypothetical saddle-like distorted graphite cutting fused around a fenestrindane core is illustrated schematically in Figure 1.[13,24]

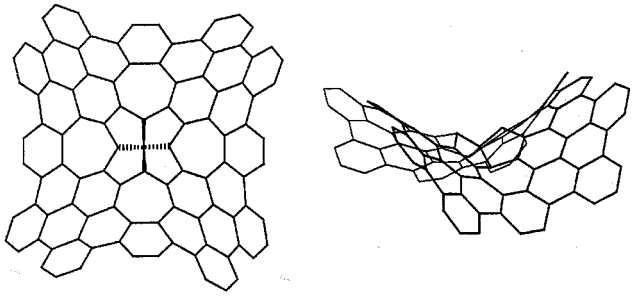
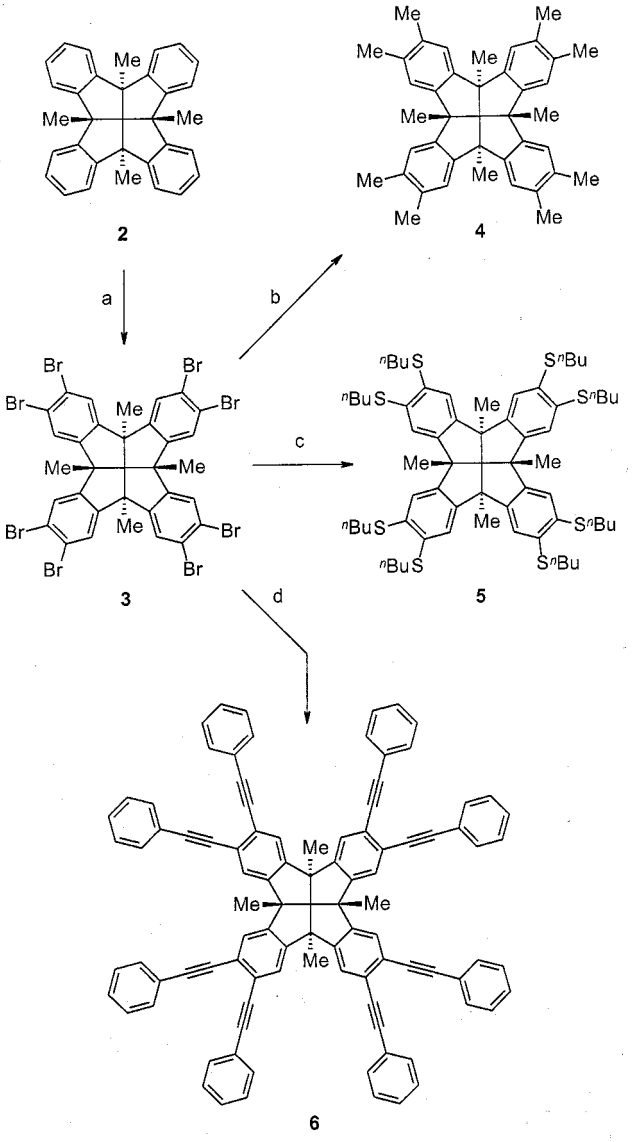


Figure 1. Schematic representation of a hypothetical saddle-type graphite cutting bearing a fenestrindane embedded into closed polycondensed arene framework, top view (left) and side view (right)

Results and Discussion

In this work, we present the results of our study on the exhaustive functionalization of the eight peripheral arene positions of fenestrindane.[25] We expect that the results presented here will give impetus to further investigations into the development of fenestrane chemistry in the context of other fields of contemporary organic chemistry. Our investigations represent model studies based on 4b,8b,12b,16b-tetramethylfenestrindane (**2**),[14a] a derivative of **1** that is advantageous because of its inertness at the otherwise very reactive benzhydrylic bridgehead positions. In a similar way to the corresponding tetramethyltribenzotriquinacene used in a previous study, we expected the *ortho* positions of **2** to be protected by steric shielding in the four three-dimensional bay regions of the diindane units within the tetrabenzo[5.5.5.5]fenestrane skeleton.[13]

When a solution of tetramethylfenestrindane **2** in tetrachloromethane was treated with ca. 10 equiv. of bromine in the presence of catalytic amounts of iron and iodine,[26] the 2,3,6,7,10,11,14,15-octabromo derivative **3** was formed and isolated in excellent yield (Scheme 2). This result confirmed our expectation that steric hindrance of the *ortho* positions of the fenestrindane framework would operate against electrophilic attack at the inner positions and restrict the substitution reaction to the eight peripheral positions of **2**. The identity and purity of **3** was determined unequivocally by mass spectrometry and NMR spectroscopy. A particularly noteworthy feature of the fenestrindanes bearing four methyl groups at the benzhydrylic bridgeheads is the fact that the eight *ortho* protons generate two clearly separated singlets ($\delta = 7.31$ and $\delta = 7.60$). This reflects our previous finding that the molecular framework of the fenestrindanes adopts two equivalent, distorted conformations of S_4 symmetry rather than a single D_{2d}-symmetrical one.[2,14a,14c,27] Accordingly, the ^{13}C NMR spectrum of **3** exhibits three pairs of resonances for the formally equivalent carbons at the indane junctions, those at the *ortho* positions and those at the molecular periphery.



Scheme 2. a) Br_2, Fe (cat.), I_2(cat.), CCl_4, 60 °C, 24 h, yield 90%; b) $AlMe_3$, $PdCl_2$, Ph_3P, THF, 70 °C, 20 h, yield 97%; c) Cu*n*Bu, pyridine, quinoline, 170 °C, 24 h, yield 75%; d) phenylacetylene, NEt_3, $(Ph_3P)_2PdCl_2$, CuI, Ph_3P, 120 °C, 48 h, yield 35%

Octabromofenestrindane **3** provides the basis for the synthesis of a series of novel eightfold functionalized derivates and [5.5.5.5]fenestranes with extended carbon frameworks (Scheme 2). As a striking example, dodecamethylfenestrindane **4** can be easily prepared in nearly quantitative yield by treating **3** with trimethylaluminum in toluene in the presence of palladium(0).[28] This eightfold Pd(0)-catalyzed methyl substitution of **3** represents a particularly interesting case since only a few examples have been described for the direct conversion of *ortho*-dihaloarenes into the corresponding *ortho*-dialkyarenes.[29] Functionalization of the eight benzylic methyl groups should open synthetic routes

to a number of highly interesting fenestrane derivatives and extended polycyclic frameworks bearing a [5.5.5.5]fenestrane core.

As another example, fenestrindanes bearing eight alkylthio groups at the peripheral positions, such as the octa(*n*-butyl) thioether **5**, can be synthesized in good yield by reacting **3** with copper(I) *n*-alkylmercaptides.[29] Fenestrane **5** was obtained in 75% yield after chromatographic purification as a colorless, glassy material that, as one would expect given the presence of the eight long thioether tentacula, was found to be highly soluble in organic solvents.

Dodecamethylfenestrindane **4** was obtained in high purity and products of the sevenfold substitution reaction or partial reduction were scarcely detectable by mass spectrometry. In the case of **5**, however, direct electron ionization (DEI) mass spectrometry revealed the presence of minor amounts (estimated $<5\%$) of the related hepta(*n*-butyl) thioether **10**, which proved impossible to separate. Partial reduction is known to accompany multiple coupling reactions of polyhaloarenes (see below).

However, ^{1}H NMR spectroscopy again revealed the apparently static conformation of the fenestrane framework of **4** and **5**. In the former case, the skeletal torsion gives rise to two separate singlets for the eight benzylic methyl groups at $\delta = 2.30$ and 2.21. The effect of the apparently static S_4-conformation of **4** and **5** is even more pronounced in the ^{13}C NMR spectra, which exhibit two sets of signals for the quaternary and tertiary arene carbon atoms and all of the methylene carbons of **5**. However, the effect is very small for the methyl groups of **4** (signals at $\delta = 19.9$ and 20.1).

Another approach along these lines became viable by reacting octabromofenestrindane **3** with phenylacetylene under Heck conditions.[30,31] Recently, a similar sixfold reaction was carried out successfully starting from a hexabromotribenzotriquinacene.[12] On using the same conditions, the reaction of **3** furnished octa(phenylethynyl)fenestrindane **6** as a yellow, amorphous solid in moderate yield (35%). In contrast to the derivatives described above, EI or DEI mass spectrometry proved unsuccessful but matrix-assisted laser desorption ionization (MALDI) mass spectrometry gave the expected peak clusters centered around $m/z = 1225.5$ ($[M + H]^+$) and $m/z = 1210.4$ ($[M + H - CH_3]^{+\cdot}$. ^{1}H and ^{13}C NMR spectroscopy also confirmed the identity of this fenestrane-based octatolane, again reflecting the apparently static S_4-symmetrical conformation of the fenestrane core. In a similar way to the thioether **5**, the presence of the corresponding hepta(phenylethynyl)fenestrindane **11**, formed in minor amounts ($< 5\%$) as a product of partial protiodepalladation of an (aryl)palladium intermediate,[32,33] was detected by mass spectrometry. This contamination could not be removed either by chromatography or by recrystallization. Despite this limitation, eightfold C−C coupling at the periphery of fenestrindanes may nevertheless add new perspectives to the growing fields of tolane-based liquid crystals and dendritic structures.[34,35] The three-dimensional shape of octatolane **6** is illustrated in Figure 2.

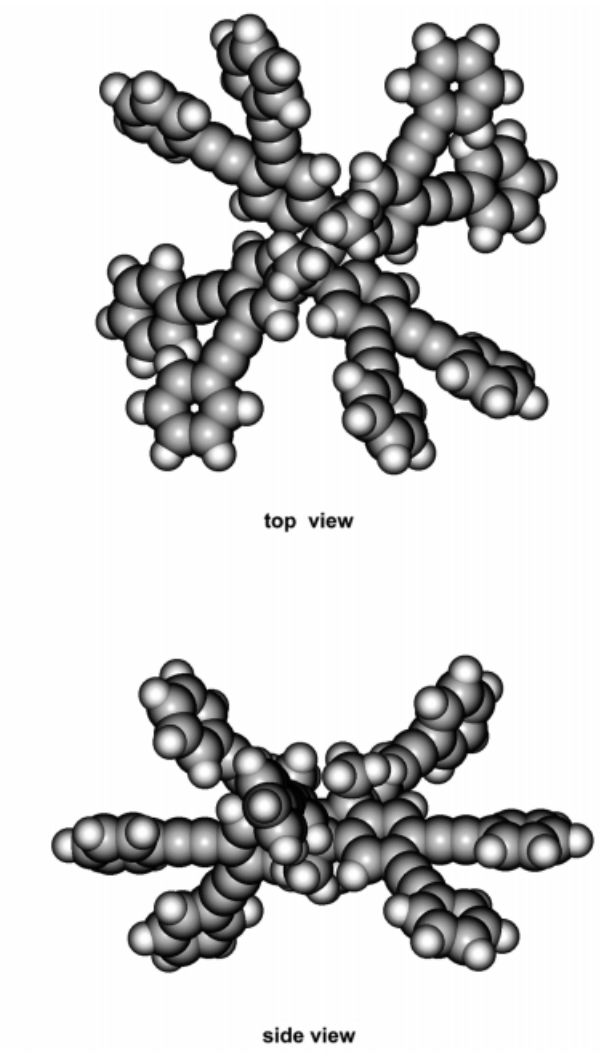
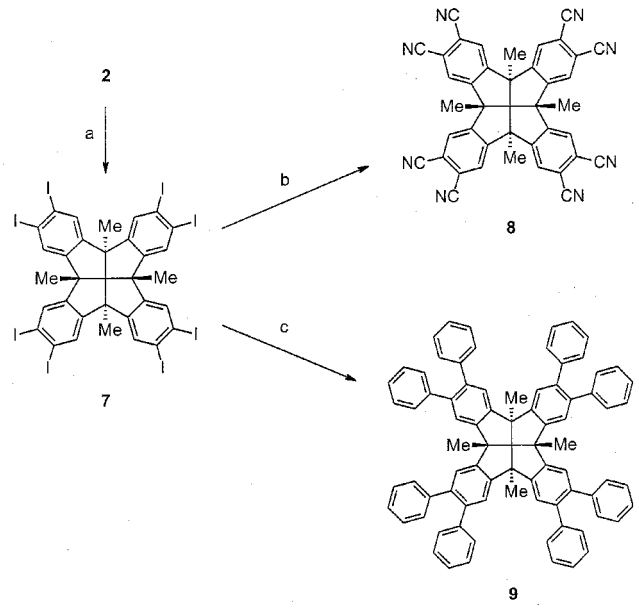


Figure 2. Molecular shape of octa(phenylethynyl)fenestrindane **6** [by force-field (MM+) calculations]; top view along the fenestrane axis showing two interacting methyl groups in the center (left), and side view showing the saddle with two methyl groups above and another one below (right)

In analogy to bromination, iodination of **2** using potassium iodide and periodic acid[36] gave octaiodofenestrindane **7** in surprisingly good yield (Scheme 3). The solubility of the compound is extremely poor and the ^{1}H NMR spectroscopic characterization of **7** was only possible in [D$_6$]DMSO.[37] ^{13}C NMR spectroscopy in solution was impossible and EI or DEI mass spectrometry were also excluded because of the low volatility of **7**. However, positive atmospheric pressure chemical ionization (APCI+) mass spectrometry furnished the quasimolecular ion ($[M + H]^+$) peak at $m/z = 1432$ together with the $[M + H - CH_3]^{+\cdot}$ peak at $m/z = 1417$. Only traces of the heptaiodo analog were detected with this technique. As occurred with octabromofenestrindane **3**, octaiodofenestrindane **7** tends to incorporate solvent molecules. Thus, combustion analysis indicated the presence of one mol of water and also some elemental iodine, which again proved extremely difficult to remove. However, octaiodofenestrindane **7** represents an-

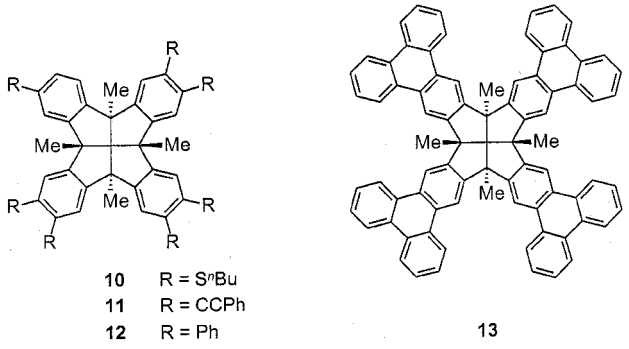
other useful key compound for the synthesis of unusual fenestranes with an extended carbon framework (Scheme 3).



Scheme 3. a) KI, H_5IO_6, conc. H_2SO_4, 0 → 20 °C,12 h, yield 87%; b) CuCN, pyridine, 115 °C, 20 h, yield 41%; c) $PhB(OH)_2$, $[Pd(dba)_2]$, KOH, PPh_3,$PhNO_2/H_2O$, 100 °C, 24h, yield 29%

Reaction of **7** with copper(I) cyanide[38] gave the fenestrindane-2,3,6,7,10,11,14,15-octacarbonitrile **8** in 41% yield. Despite its extremely low solubility in common organic solvents, the identity of the compound was documented unequivocally by NMR spectrometry in $[D_8]$THF. Again, two singlets in the ^{1}H NMR spectrum at $\delta = 8.05$ and 8.40 reflect two sets of *ortho* protons and thus the apparently static conformation of **8**. Likewise, the ^{13}C NMR spectrum exhibits two resonances for two sets of cyano groups at $\delta = 150.1$ and 155.5, as well as two sets of arene resonances. As an alternative to fenestrindane **4** bearing four *ortho*-xylene units at the fenestrane core, the octacarbonitrile **8** may provide an independent access to various eightfold C_1-functionalized fenestrindanes.

Finally, the octaiodofenestrane **7** was also used to perform an eightfold phenylation of the fenestrindane framework under Suzuki conditions.[39] Recently, a similar sixfold transformation of a corresponding hexiodotribenzotriquinacene was carried out with high efficiency.[13] In fact, Pd(0)-catalyzed reaction of **7** with phenylboronic acid affords multiple C−C bond formation that leads to the octaphenyl derivative **9**, but yields are only moderate in this case (Scheme 3). In comparison to **8**, both the solubility and volatility of **9** are increased owing to the absence of polar groups at the molecular periphery, and complete spectroscopic characterization was achieved. In particular, the ^{1}H NMR spectrum again reflects the apparently static S_4-symmetrical conformation of **9**. The DEI mass spectrum of **9** also confirms its identity, showing the molecular ion peak at $m/z = 1032$ and the $[M - CH_3]^+$ peak at $m/z = 1017$. However, limitations of the synthetic approach also became evident since DEI mass spectrometry revealed the presence of minor amounts of the corresponding heptaphenylfenestrindane **12** as a by-product. Thus, in a similar way to the ethynylation of **3** to **6** under Heck conditions, partial protiodepalladation competes with multiple C−C bond formation. Another limitation encountered here arose when several attempts to perform a fourfold photocyclodehydrogenation of **9** to give the hypothetical tetra(triphenyleno)[5.5.5.5]fenestrane **13** turned out to be unsuccessful.



Conclusion

The results presented here demonstrate for the first time that fenestrindanes are suitable building blocks for the construction of novel extended molecular frameworks bearing the [5.5.5.5]fenestrane core. Besides the previously demonstrated[15] variability of the bridgehead chemistry of fenestrindane **1**, this particular centropolyindane may develop a rich chemistry by functionalization and extension of the molecular periphery. Thus, dendrimers, liquid crystals and polycondensed ring systems with saddle-like molecular structures may become available in this way. Experimental restrictions, which are clearly due to the low solubility of some of the octafunctionalized fenestrindanes, appear to be a more important parameter than with the related tribenzotriquinacenes studied recently,[13] but the problems may be overcome by introducing lyophilizing substituents, particularly at the bridgehead positions of **1** and/or along with the synthons to be attached at the arene periphery. Investigations towards these aims are underway.

Experimental Section

General: Melting points were determined using an Electrothermal Melting Point Apparatus and were not corrected. − Infrared spectra were recorded on a Perkin−Elmer 841 spectrophotometer. − The ^{1}H NMR spectra were recorded on Bruker AM 250 (250 MHz) and Bruker DRX 500 (500 MHz) spectrometers. The ^{13}C NMR measurements were obtained using the same instruments at 62.9 and 125.8 MHz, respectively, using broad-band decoupling, with *J*-modulated spinecho and DEPT techniques. Spectra measured at 62.9 MHz refer to tetramethylsilane (TMS), while those measured at 125.8 MHz refer to the solvent as a standard resonance. − Electron ionization (EI) mass spectra and exact mass measurements were obtained using a Fisons Autospec double focusing instrument at 70 eV electron energy. The peak intensities are given relative to

the base peak. − UV/Vis spectra were recorded on Beckman model 25 and Perkin−Elmer Lambda 40 spectrophometers. − Combustion analyses were performed on a Perkin−Elmer model 240 elemental analyzer. − Column chromatography was performed using silica gel (0.063−0.200 mm); solvents were distilled before use. Thin layer chromatography (TLC): Aluminum foil, Kieselgel 60 F_{254} (Merck); detection: MinUVis (Desaga). Compositions of solvents are given as ratios of volumes.

2,3,6,7,10,11,14,15-Octabromo-4b,8b,12b,16b-tetramethyl-4bα,8bβ,12bα,16bβ-tetrahydrodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno-[1,6-*cd*]pentalene (2,3,6,7,10,11,14,15-Octabromo-4b,8b,12b,16b-tetramethylfenestrindane, 3): Iron powder (30 mg) and several crystals of iodine were added to a stirred solution of tetramethylfenestrindane **2** (200 mg, 471 μmol) in 50 mL of tetrachloromethane at 60 °C. Subsequently, a solution of bromine (213 μL, 4.15 mmol) in 25 mL of the same solvent was added dropwise and the mixture was stirred for 24 h at the same temperature. The suspension formed was completely dissolved in trichloromethane and the solution was washed with water and dried with sodium sulfate. Filtration and removal of the solvent under reduced pressure gave a residue, which was recrystallized from tetrahydrofuran, yielding octabromofenestrinane **3** (450 mg, 90%) as a colorless, amorphous solid, m.p. >360 °C. − IR (KBr): $\tilde{\nu}$ = 3001 cm^{-1}, 2973, 2941, 2928, 1449, 1377, 1371, 1350, 1282, 1235, 1213, 1102, 1072, 1057, 1040, 984, 888, 858, 817, 790, 737. − ^1H NMR (500 MHz, $C_2D_2Cl_4$): δ = 7.60 (s, 4 H, H^{ortho}), 7.31 (s, 4 H, H^{ortho}), 1.15 (s, 12 H, CH_3). − ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): δ = 151.1, 146.1 (C), 129.1, 127.0 (CH), 124.7, 124.3 (C), 77.5 (C), 58.3 (C), 27.9 (CH_3). − MS (EI, 70 eV); *m*/*z* (%): 1056 (13) [$M^{+\cdot}$], 1041 (58), 976 (11), 961 (47), 898 (3), 883 (16), 803 (6), 80 (100). − $C_{33}H_{20}Br_8 \cdot CH_2Cl_2$ H_2O (1158.7): calcd. C 35.24, H 2.09; found C 35.28, H 1.96.

2,3,4b,6,7,8b,10,11,12b,14,15,16b-Dodecamethyl-4bα,8bβ,12bα,16bβ-tetrahydrodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (2,3,4b,6,7,8b,10,11,12b,14,15,16b-Dodecamethylfenestrindane, 4): A mixture of octabromofenestrindane **3** (200 mg, 189 μmol), palladium(II) chloride (13 mg, 74 μmol) and triphenylphosphane (40 mg, 152 μmol) in 20 mL of anhydrous tetrahydrofuran was stirred under argon at 50 °C for 30 min. Trimethylaluminum (291 μL, 219 mg, 3.03 mmol) was added and the mixture was heated under reflux for 20 h. The mixture was allowed to cool, diluted by the cautious addition of THF and hydrochloric acid (10%) and then extracted with trichloromethane. The combined organic extracts were dried with sodium sulfate and the solvent was removed under reduced pressure to leave a crude material, which was recrystallized from dichloromethane to give dodecamethylfenestrindane **4** (98 mg, 97%) as a colorless, amorphous solid, m.p. >360 °C. − IR (KBr): $\tilde{\nu}$ = 3004 cm^{-1}, 2969, 2932, 2873, 1482, 1449, 1311, 991, 883, 872. − ^1H NMR (500 MHz, $CDCl_3$): δ = 7.21 (s, 4 H, H^{ortho}), 6.96 (s, 4 H, H^{ortho}), 2.30 (s, 12 H), 2.21 (s, 12 H, arene-CH_3), 1.23 (s, 12 H, bridgehead-CH_3). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.7, 144.6, 135.6, 134.9 (C), 124.7, 122.7 (CH), 89.2 (C), 58.4 (C), 28.5, 20.1, 19.9 (CH_3). − MS (EI, 70 eV); *m*/*z* (%): 537 (9) [$M^{+\cdot}$], 521 (100), 507 (20), 491 (4), 476 (3), 461 (2), 268 (5), 261 (6), 253 (23). − HRMS: calcd. for $C_{41}H_{44}$ 536.3443; found 536.3443.

2,3,6,7,10,11,14,15-Octa(*n*-butylthio)-4b,8b,12b,16b-tetramethyl-4bα,8bβ,12bα,16bβ-tetrahydrodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno-[1,6-*cd*]pentalene [2,3,6,7,10,11,14,15-Octa(*n*-butylthio)-4b,8b,12b,16b-tetramethylfenestrindane, 5]: To a suspension of octabromofenestrindane **3** (150 mg, 142 μmol) in 3.70 mL of quinoline and 1.19 mL of pyridine was added copper *n*-butylmercaptide (191 mg, 1.25 mmol). The mixture was stirred and heated at 170 °C for 24 h. After cooling to room temperature, the deep brown solution was poured into a mixture of 100 g of ice and 30 mL of conc. hydrochloric acid. This mixture was extracted with diethyl ether and the combined extracts were washed with hydrochloric acid (10%), water, conc. aqueous ammonia and again with water. After drying with sodium sulfate, the solvents were removed under reduced pressure and the residual brown oil was purified by column chromatography (silica gel, $CHCl_3$/hexane 1:1) to give octa(*n*-butylthio)fenestrindane **5** (120 mg, 75%) as a colorless, glassy oil; R_f ($CHCl_3$/hexane 1:1) = 0.63. − IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2959, 2874, 1459, 1378, 1368, 1277, 1073. − ^1H NMR (500 MHz, $CDCl_3$): δ = 7.33 (s, 4 H, H^{ortho}), 7.02 (s, 4 H, H^{ortho}), 2.95 (m, 8 H, ^3J = 7.1 Hz), 2.87 (m, 8 H, ^3J = 9.7 Hz), 1.66 (m, 8 H), 1.61 (m, 8 H), 1.46 (m, 16 H), 1.22 (s, 12 H, bridgehead-CH_3), 0.90 (dt, 24 H, ω-CH_3). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.3, 144.8, 137.2, 135.7 (C), 124.8, 121.9 (CH), 89.1 (C), 58.5 (C), 33.4, 33.0 (CH_2), 30.9, 30.7 (CH_2), 28.0 (CH_3), 22.05, 21.98 (CH_2), 13.7 (CH_3). − MS (DEI, 70 eV); *m*/*z* (%): 1129 (67) [$M^{+\cdot}$], 1114 (24), 1074 (33), 1059 (12), 1020 (10), 986 (7), 971 (5), 564 (8) [M^{2+}], 537 (3), 56 (100). − HRMS: calcd. for $C_{65}H_{92}S_8$ 1128.4965; found 1128.4955.

4b,8b,12b,16b-Tetramethyl-2,3,6,7,10,11,14,15-octa(phenylethynyl)-4bα,8bβ,12bα,16bβ-tetrahydrodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno-[1,6-*cd*]pentalene [4b,8b,12b,16b-Tetramethyl-2,3,6,7,10,11,14,15-octa(phenylethynyl)fenestrindane, 6]: A mixture of octabromotetramethylfenestrindane **3** (200 mg, 189 μmol), bis(triphenylphosphane)-palladium(II) chloride (36 mg, 50.6 μmol), phenylacetylene (499 μL, 4.55 mmol), copper(II) iodide (36 mg, 189 μmol) and triphenylphosphane (72 mg, 274 μmol) in 20 mL of triethylamine was heated under argon at 120 °C for 48 h. The mixture was allowed to cool and then poured into ice-cold hydrochloric acid (10%) and extracted with dichloromethane. The combined extracts were dried with magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, $CHCl_3$/hexane 1:2) to give octatolane **6** (81 mg, 35%) as a slightly yellow, amorphous solid, m.p. >360 °C, R_f ($CHCl_3$/hexane 1:2) = 0.16. − IR (KBr): $\tilde{\nu}$ = 2999 cm^{-1}, 1597, 1492, 1472, 1442, 1068, 1000, 993, 895, 749, 687. − ^1H NMR (500 MHz, $CDCl_3$): δ = 7.74 (s, 4 H, H^{ortho}), 7.59 (m, 16 H), 7.47 (s, 4 H, H^{ortho}), 7.34 (m, 24 H), 1.37 (s, 12 H, CH_3). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.2, 145.9 (C), 131.7, 128.41, 128.37, 127.4 (CH), 125.9, 125.4, 125.1, 123.3, 123.2 (C), 93.8, 93.6, 88.6, 88.4 (C), 58.9 (C), 27.8 (CH_3); the resonance of the central C atom was not observed. − MS (MALDI, DHB matrix with Ag^+ and vasopressin added); *m*/*z* (%): 1225.5 (11) [M + H]$^{+\cdot}$, 1210 (100); peaks for **10**: *m*/*z* (%): 1125.4 (6) [M + H]$^+$, 1110.4 (33). − HRMS: calcd. for $C_{97}H_{60}$ 1224.4695; found 1224.4921. − UV/Vis (CH_2Cl_2, $c = 1.63 \times 10^{-6}$ mol L^{-1}): λ_{max} (lg ε) = 280 (5.32), 287 (5.43), 310 (5.06), 325 (4.97), 3.43 (4.51) nm.

2,3,6,7,10,11,14,15-Octaiodo-4b,8b,12b,16b-tetramethyl-4bα,8bβ,12bα,16bβ-tetrahydrodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]-pentalene (2,3,6,7,10,11,14,15-Octaiodo-4b,8b,12b,16b-tetramethylfenestrindane, 7): Periodic acid (859 mg, 3.77 mmol) was dissolved under cooling in an ice/water bath in 40 mL of conc. sulfuric acid. Potassium iodide (1.88 g, 11.3 mmol) was added in small portions followed by tetramethylfenestrindane **2** (200 mg, 471 μmol). The mixture was allowed to warm up to ambient temperature and stirred for 12 h. The deep violet mixture was poured into ice and the liquid component was removed under reduced pressure. The residual brown solid was repeatedly boiled with methanol (20 mL each) and separated by filtration to give octaiodofenestrindane **7** (588 mg, 87%) as a slightly rose-colored, amorphous solid, m.p. >360 °C. − IR (KBr): $\tilde{\nu}$ = 3003 cm^{-1}, 2968, 1445, 1377, 1369, 1333, 1274, 1083, 1034, 983, 884. − ^1H NMR (500 MHz,

[D_6]DMSO): δ = 8.25 (s, 4 H, H^{ortho}), 7.81 (s, 4 H, H^{ortho}), 1.12 (s, 12 H, CH_3); a ^{13}C NMR spectrum could not been measured due to the extremely poor solubility of **7**. − MS (APCI+); *m/z* (%): 1432.1 (32) $[M + H]^+$, 1416.8 (23) $[M + H - CH_3]^{+\cdot}$; the compound tends to enclose additional iodine. − $C_{33}H_{20}I_8 \cdot 0.5\ I_2 \cdot H_2O$ (1576.68): calcd. C 25.14, H 1.41; found C 25.05, H 1.57.

2,3,6,7,10,11,14,15-Octacyano-4b,8b,12b,16b-tetramethyl-4bα,8bβ,12bα,16bβ-tetrahydrodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]-pentalene (2,3,6,7,10,11,14,15-Octacyano-4b,8b,12b,16b-tetramethyl-fenestrindane, 8): Octaiodofenestrindane **7** (250 mg, 175 μmol) and copper(I) cyanide (1.38 g, 15.4 mmol) were mixed with 100 mL of pyridine and the mixture was heated at 115 °C for 20 h. The reaction mixture was allowed to cool and poured into conc. aqueous ammonia. Extraction with ethyl acetate, drying of the combined extracts with sodium sulfate and removal of the solvent under reduced pressure gave a crude product, which was purified by column chromatography (silica gel, $CHCl_3$/EtOAc 2:1) to give octacyanofenestrindane **8** (45 mg, 41%) as a colorless, amorphous solid; m.p. >360 °C; R_f ($CHCl_3$/EtOAc 2:1) = 0.67. − IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1}, 2852, 2238, 1701, 1449, 1376, 1120, 1082, 665. − ^1H NMR (500 MHz, [D_8]THF): δ = 8.40 (s, 4 H, H^{ortho}), 8.05 (s, 4 H, H^{ortho}), 1.40 (s, 12 H, CH_3). − ^{13}C NMR (125 MHz, [D_8]THF): δ = 155.5, 150.1 (C), 131.6, 128.5 (CH), 117.6, 117.3, 116.2, 116.0 (C), 60.9 (C), 27.7 (C); the signal for the central C atom was not observed. − MS (DEI, 70 eV); *m/z* (%): 609 (40) $[M - CH_3]^+$, 294 (10). − HRMS: calcd. for $C_{40}H_{17}N_8$ ($[C_{41}H_{20}N_8 - CH_3]^+$) 609.1576; found 609.1587. The compound tends to include solvent molecules.

4b,8b,12b,16b-Tetramethyl-2,3,6,7,10,11,14,15-octaphenyl-4bα,8bβ,12bα,16bβ-tetrahydrodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno-[1,6-*cd*]pentalene (4b,8b,12b,16b-Tetramethyl-2,3,6,7,10,11,14,15-octa-phenylfenestrindane, 9): Octaiodotetramethylfenestrindane **7** (100 mg, 69.8 μmol), phenylboronic acid (409 mg, 3.35 mmol), bis(dibenzylidenacetone)palladium (10 mg, 16.8 μmol), potassium hydroxide (768 mg, 13.7 mmol) and triphenylphosphane (103 mg, 391 μmol) were suspended in nitrobenzene (20 mL) and water (6 mL) and the mixture was heated under argon to 100 °C for 24 h. The reaction mixture was allowed to cool, diluted with 250 mL of diethyl ether and washed twice with 100 mL of 2 M aqueous potassium hydroxide, hydrochloric acid (10%) and water. The organic solution was dried with sodium sulfate and the solvent was removed under reduced pressure to give a residue, which was purified by column chromatography (silica gel, $CHCl_3$/hexane 1:2). Octaphenylfenestrindane **9** (21 mg, 29%) was obtained as a colorless, amorphous solid; R_f ($CHCl_3$/hexane 1:2) = 0.35; m.p. >360 °C. − IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1}, 3028, 2967, 2928, 1600, 1474, 1446, 1232, 1073, 1043, 1026, 895, 768, 703. − ^1H NMR (500 MHz, $CDCl_3$): δ = 7.56 (s, 4 H, H^{ortho}), 7.32 (s, 4 H, H^{ortho}), 7.19 (m, 40 H, H^{phenyl}), 1.57 (s, 12 H, CH_3). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.0, 146.1, 141.9, 140.3, 139.8 (C), 130.0, 127.8, 126.3, 125.8, 123.8 (CH), 59.1 (C), 28.8 (CH_3); the signal for the central C atom was not observed. − MS (DEI, 70 eV); *m/z* (%): 1032 (26) $[M^{+\cdot}]$, 1017 (57), 509 (3); peaks of heptaphenylfenestrindane **11**: *m/z* (%) 957 (43) $[M^{+\cdot}]$, 942 (100), 471 (13). − HRMS: calcd. for $C_{81}H_{60}$ (**9**) 1032.4695; found 1032.4705. − HRMS: calcd. for $C_{75}H_{56}$ (**11**) 956.4382; found 956.4427. − UV/Vis (CH_2Cl_2, $c = 4.26 \times 10^{-6}$ mol L^{-1}): λ_{max} (lg ε) = 242 (5.09) nm.

Acknowledgments

We would like to thank the Deutsche Forschungsgemeinschaft, Bonn, and the Fonds der Chemischen Industrie, Frankfurt/Main, for financial support. We are also grateful to Dr. H. Luftmann, Universität Münster, and Dr. M. Letzel, Universität Bielefeld, for MALDI mass spectrometric measurements of **6** and Mr. St. John Skilton, Micromass Ltd., Manchester/UK, for performing the APCI(+) measurements of **7**.

[1] Reviews on mainly alicyclic fenestranes: [1a] H . Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2000**; pp. 81−102. − [1b] M. Thommen, R. Keese, *Synlett* **1997**, 231−240. − [1c] W. Luef, R. Keese in *Advances in Strain in Organic Chemistry, Vol. 3* (Ed.: B. Halton), JAI Press, Greenwich, CT, **1993**, pp. 229−267. − [1d] W. C. Agosta in *The Chemistry of Alkanes and Cycloalkanes* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1992**; pp. 927−962. − [1e]A. K. Gupta, X. Fu, J. P. Snyder, J. M. Cook, *Tetrahedron* **1991**, *47*, 3665−3710. − [1f] K. Krohn in *Organic Synthesis Highlights* (Eds.: J. Mulzer, H.-J. Altenbach, M. Braun, K. Krohn, H.-U. Reissig), VCH, Weinheim, **1991**, pp. 371−377. − [1g] B. R. Venepalli, W. C. Agosta, *Chem. Rev.* **1987**, *87*, 399−410.

[2] For a review on benzoannelated fenestranes, see: D. Kuck in *Advances in Theoretically Interesting Molecules, Vol. 4* (Ed.: R. P. Thummel), JAI Press, Greenwich, CT, **1998**, pp. 81−155.

[3] [3a] H. J. Monkhorst, *J. Chem. Soc., Chem. Commun.* **1968**, 1111−1112. − [3b] R. Hoffmann, R. W. Alder, C. F. Wilcox, Jr., *J. Am. Chem. Soc.* **1970**, *92*, 4992−4993. − [3c] R. Hoffmann, *Pure Appl. Chem.* **1971**, *28*, 181−194. − [3d] K. B. Wiberg, G. B. Ellison, J. J. Wendelowski, *J. Am. Chem. Soc.* **1976**, *98*, 1212−1218. − [3e] J. B. Collins, J. D. Hill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, J. A. Pople, *J. Am. Chem. Soc.* **1976**, *98*, 5419−5427.

[4] D. Röttger, G. Erker, *Angew. Chem.* **1997**, *109*, 840−856; *Angew. Chem. Int. Ed.* **1997**, *36*, 812−827.

[5] W. Siebert, A. Gunale, *Chem. Soc. Rev.* **1999**, *28*, 367−371.

[6] [6a] D. R. Rasmussen, L. Radom, *Angew. Chem.* **1999**, *111*, 3052−3054; *Angew. Chem. Int. Ed.* **1999**, *38*, 2876−2878. − [6b] L. Radom, D. R. Rasmussen, *Pure Appl. Chem.* **1998**, *70*, 1977−1984.

[7] B. Ding, R. Keese, H. Stoeckli-Evans, *Angew. Chem.* **1999**, *111*, 387−388; *Angew. Chem. Int. Ed.* **1999**, *38*, 375−376.

[8] Selected recent papers: [8a] D. Kuck, R. A. Krause, D. Gestmann, F. Posteher, A. Schuster, *Tetrahedron* **1998**, *54*, 5247−5258. − [8b] D. Kuck, A. Schuster, D. Gestmann, F. Posteher, H. Pritzkow, *Chem. Eur. J.* **1996**, *2*, 58−67. − [8c] D. Kuck, A. Schuster, B. Paisdor, D. Gestmann, *J. Chem. Soc., Perkin Trans. 1* **1995**, 721−732.

[9] For a recent review on advances in the synthesis of indane derivatives, see: B. C. Hong, S. Sarshar, *Org. Prep. Proc. Int.* **1999**, *31*, 1−86.

[10] [10a] D. Kuck in *Carbon-rich Organic Compounds I* (Ed.: A. de Meijere), *Top. Curr. Chem.* **1998**, *196*, 167−220. − [10b] D. Kuck, *Synlett* **1996**, 949−965. − [10c] D. Kuck, *Liebigs Ann./Rec.* **1997**, 1043−1057.

[11] D. Kuck, T. Lindenthal, A. Schuster, *Chem. Ber.* **1992**, *125*, 1449−1460.

[12] [12a] J. Tellenbröker, D. Kuck, *Angew. Chem.* **1999**, *111*, 1000−1004; *Angew. Chem. Int. Ed.* **1999**, *38*, 919−922. − [12b] D. Kuck, A. Schuster, R. A. Krause, J. Tellenbröker, C. P. Exner, M. Penk, H. Bögge, A. Müller, *Tetrahedron*, in press.

[13] [13a] D. Kuck, *Chem. Ber.* **1994**, *127*, 409−425. − [13b] D. Kuck, H. Bögge, *J. Am. Chem. Soc.* **1986**, *108*, 8107−8109.

[14] [14a] D. Kuck, A. Schuster, R. A. Krause, *J. Org. Chem.* **1991**, *56*, 3472−3475. − [14b] D. Kuck, A. Schuster, C. Fusco, M. Fiorentino, R. Curci, *J. Am. Chem. Soc.* **1994**, *116*, 2375−2381. − [14c] C. Fusco, M. Fiorentino, A. Dinoi, R. Curci, R. A. Krause, D. Kuck, *J. Org. Chem.* **1996**, *61*, 8681−8684.

[15] C. A. Dullaghan, G. B. Carpenter, D. Kuck, C. Fusco, R. Curci, D. A. Sweigart, *Organometallics* **2000**, *19*, 2233−2236.

[16] J. Tellenbröker, D. Barth, D. Kuck, unpublished results.

[17] [17a] H. W. Kroto, *Nature* **1987**, *329*, 529−531. − [17b] D'Arcy W. Thompson, *On Growth and Form, Vol. 2*; Cambridge University Press, Cambridge, 2nd edn. **1942**, and Ysel Press, Deventer, **1972**; pp. 732−740.

[18] M. Müller, C. Kübel, K. Müllen, *Chem. Eur. J.* **1998**, *4*, 2099−2109.

[19] [19a] W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1966**, *88*, 380−381. − [19b] R. G. Lawton, W. E. Barth, *J. Am. Chem. Soc.* **1971**, *93*, 1730−1745. − [19c] J. C. Hanson, C. E. Nordman, *Acta Crystallogr. Sect. B* **1976**, *32*, 1147−1153.

[20] [20a] L. T. Scott, M. M. Hashemi, D. T. Meyer, H. B. Warren, *J. Am. Chem. Soc.* **1991**, *113*, 7082−7084. − [20b] L. T. Scott, M. M. Hashemi, M. S. Bratcher, *J. Am. Chem. Soc.* **1992**, *114*, 1920−1921. − [20c] T. Kiyobayashi, Y. Nagano, M. Sakiyama, K. Yamamoto, P. C. Cheng, L. T. Scott, *J. Am. Chem. Soc.* **1995**, *117*, 3270−3271. − [20d] L. T. Scott, M. S. Bratcher, S. Hagen, *J. Am. Chem. Soc.* **1996**, *118*, 8743−8744. − [20e] L. T. Scott, *Pure Appl. Chem.* **1996**, *68*, 291−300.

[21] [21a] P. W. Rabideau, A. Sygula in *Advances in Theoretically Interesting Molecules, Vol. 3* (Ed.: R. P. Thummel), JAI Press, Greenwich CT, **1995**, pp 1−36. − [21b] P. W. Rabideau, A. Sygula, *Acc. Chem. Res.* **1996**, *29*, 235−242. − [21c] A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1998**, *120*, 12666−12667.

[22] [22a] K. Yamamoto, T. Harada, Y. Okamoto, H. Chikamatsu, M. Nakazaki, Y. Kai, T. Takano, M. Tanaka, S. Harada, N. Kasai, *J. Am. Chem. Soc.* **1988**, *110*, 3578−3584. − [22b] K. Yamamoto, Y. Saitoh, D. Iwaki, T. Ooka, *Angew. Chem.* **1991**, *103*, 1202−1203; *Angew. Chem. Int. Ed.* **1991**, *30*, 1173−1174. − [22c] K. Yamamoto, *Pure Appl. Chem.* **1993**, *65*, 157−163. − [22d] K. Yamamoto, H. Sonobe, H. Matsubara, M. Sato, S. Okamoto, K. Kitaura, *Angew. Chem.* **1996**, *108*, 69−70; *Angew. Chem. Int. Ed.* **1996**, *35*, 69−70.

[23] J. S. Siegel, T. J. Seiders, *Chem. Ber.* **1995**, 313−316.

[24] For recent reviews, see: [24a] Y. S. Anant, T. J. Seiders, J. S. Siegel, *Top. Curr. Chem.* **1998**, *196*, 1−43. − [24b] S. Hagen, H. Hopf, *Top. Curr. Chem.* **1998**, *196*, 47−89. − [24c] M. M Haley, J. J. Pak, S. C. Brand, *Top. Curr. Chem.* **1999**, *201*, 81−130. − [24d] U. Scherf, *Top. Curr. Chem.* **1999**, *201*, 163−222.

[25] J. Tellenbröker, Doctoral thesis, Universität Bielefeld, **1999**.

[26] E. Klingsberg, *Synthesis* **1972**, 29−30.

[27] A. Schuster, Doctoral thesis, Universität Bielefeld, **1991**.

[28] [28a] J. Blum, D. Gelman, W. Baidossi, E. Shakh, A. Rosenfeld, Z. Aizenshtat, B. C. Wassermann, M. Frick, B. Heymer, S. Schutte, S. Wernik, H. Schumann, *J. Org. Chem.* **1997**, *62*, 8681−8686. − [28b] K. Hirota, Y. Kitade, Y. Kanbe, Y. Isobe, Y. Maki, *Synthesis* **1993**, 213−215. − [28c] K. Hirota, Y. Kitade, Y. Kanbe, Y. Maki, *J. Org. Chem.* **1992**, *57*, 5268−5270.

[29] [29a] K. Tamao, K. Sumitani, M. Kumada, *J. Am. Chem. Soc.* **1972**, *94*, 4374−4376. − [29b] K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, M. Kumada, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958−1969. − [29c] B. Mohr, V. Enkelmann, G. Wegner, *J. Org. Chem.* **1994**, *59*, 635−638. − [29d] K. C. Eapen, S. S. Dua, C. Tamborski, *J. Org. Chem.* **1984**, *49*, 478−482. − [29e] T. J. Seiders, K. K. Baldridge, E. L. Elliot, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **1999**, *121*, 7439−7440. − [f] T. J. Seiders, E. L. Elliot, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **1999**, *121*, 7804−7813.

[30] R. Adams, W. Reifschneider, A. Ferretti, *Org. Synth.* **1962**, *42*, 22−25.

[31] K. Praefcke, B. Kohne, D. Singer, *Angew. Chem.* **1990**, *102*, 200−202; *Angew. Chem. Int. Ed.* **1990**, *29*, 177−179.

[32] A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, *106*, 2473−2506; *Angew. Chem. Int. Ed.* **1994**, *33*, 2379.

[33] For recent results concerning the apparent sixfold Heck reaction of hexaiodobenzene with phenylacetylene, see: J. Nierle, D. Kuck, to be published.

[34] [34a] R. Diercks, J. C. Armstrong, R. Boese, K. P. C. Vollhardt, *Angew. Chem.* **1986**, *98*, 270−271; *Angew. Chem. Int. Ed.* **1986**, *25*, 268−269. − [34b] B. Kohne, K. Praefcke, *Chimia* **1987**, *41*, 196−198. − [34c] K. Praefcke, B. Kohne, D. Singer, *Angew. Chem.* **1990**, *102*, 200−202; *Angew. Chem. Int. Ed.* **1990**, *29*, 177. − [34d] K. Praefcke, B. Kohne, D. Singer, M. Ebert, A. Liebmann, J. H. Wendorff, *Liq. Cryst.* **1991**, *10*, 147−159. − [34e] K. Kondo, S. Yasuda, T. Sakaguchi, M. Miya, *J. Chem. Soc., Chem. Commun.* **1995**, 55−56. − [34f] S. Marget, D. Markovitski, D. Goldmann, D. Janietz, K. Praefcke, D. Singer, *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 147−155.

[35] [35a] B. Kayser, J. Altman, W. Beck, *Chem. Eur. J.* **1999**, *5*, 754−758. − [35b] B. Kayser, J. Altman, W. Beck, *Tetrahedron* **1997**, *53*, 2475−2484. − [35c] B. Kayser, J. Altman, H. Nöth, J. Knizek, W. Beck, *Eur. J. Inorg. Chem.* **1998**, 1791−1798.

[36] D. L. Mattern, *J. Org. Chem.* **1983**, *48*, 4772−4773.

[37] [D_2]-1,1,2,2-tetrachloroethane (even at 120 °C) and [D_8]THF do not allow one to measure a ^{1}H NMR spectrum of **7**.

[38] R. G. R. Bacon, H. A. O. Hill, *J. Chem. Soc.* **1964**, 1097−1107.

[39] M. B. Goldfinger, K. B. Crawford, T. M. Swager, *J. Am. Chem. Soc.* **1997**, *119*, 4578−4593.

Received December 19, 2000
[O00648]