DOI: 10.1002/chem.200600498

Phane Properties of [2.2]Paracyclophane/Dehydrobenzoannulene Hybrids

Heino Hinrichs,[a] Andrew J. Boydston,[b] Peter G. Jones,[c] Kirsten Hess,[d] Rainer Herges,[d] Michael M. Haley,*[b] and Henning Hopf*[a]

Dedicated to Professor Siegfried Hünig on the occasion of his 85th birthday

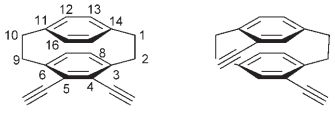
Abstract: A series of [2.2]paracyclophane/dehydrobenzo[14]annulene (PC/DBA) hybrids (hydrocarbons **5**, **6**, **9**, **10b**, and **10c**), [2.2]paracyclophane/dehydro[14]annulene (PC/DA) hybrids (**7** and **8**) and suitable model systems (**11**, **12**, and **33**) has been synthesized. Comparison of the electronic absorption spectra in each series of compounds provides further insight into the global communication between the decks in the [2.2]paracyclophane unit.

Keywords: annulenes · coupling reactions · cyclophanes · electronic interactions · electronic spectra

Introduction

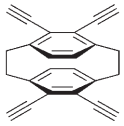
Highly conjugated organic compounds are now used in materials science for a variety of electronic and photonic applications, such as liquid crystal displays, organic LEDs, solar cells and optical storage devices.[1] Nonetheless, the rational design of unsaturated organic molecules with specific properties is still a challenging task. The chemical and physical properties of a conjugated organic molecule can be controlled by a multitude of factors, such as conjugation length, planarity versus non-planarity, double versus triple bonds as building units or introduction of electron donating and/or withdrawing groups.[2] With such possible variation of structures, there is still considerable room for exploration and development of new π-electron-rich systems targeted for materials uses.

In our opinion, the [2.2]paracyclophane unit (PC unit) represents a particularly valuable core for studying the effect of electronic "gaps" on the delocalization in highly conjugated molecules. We recently reported the synthesis of ethynylated [2.2]paracyclophanes **1**, **2**, and **4**.[3] Together with **3**,[4] these compounds represent unique building blocks for the construction of extended π-electron-rich hydrocarbons. Starting from **1** and **2**, we have synthesized and compared the paracyclophane/dehydrobenzoannulene (PC/DBA) systems **5** and **6** and their dehydroannulene analogues **7** and **8**, respectively. Using **3** and **4**, the larger hybrids "step" **9** and "propeller" **10** were prepared. All new paracyclophane-containing systems (**5**–**10**) were compared with a number of model compounds (e.g. **11** and **12**) to determine

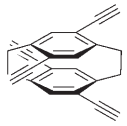


1

2



3



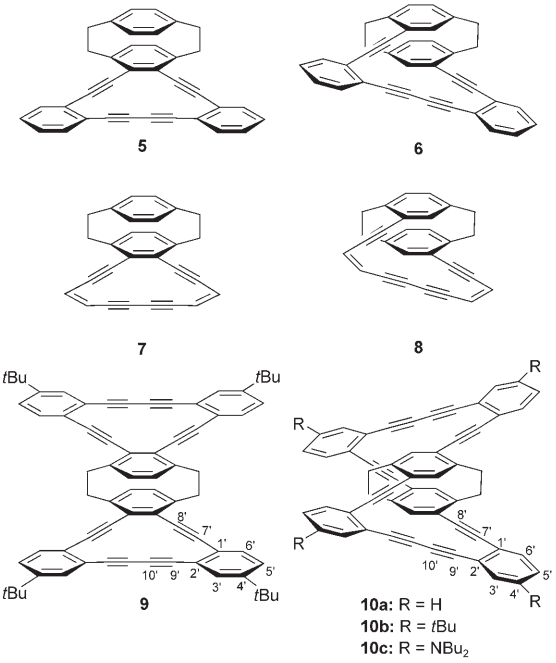
4

[a] Dr. H. Hinrichs, Prof. Dr. H. Hopf
Institut für Organische Chemie
Technische Universität Braunschweig
Hagenring 30, 38106 Braunschweig (Germany)
Fax: (+49) 531-391-5388
E-mail: h.hopf@tu-bs.de

[b] A. J. Boydston, Prof. Dr. M. M. Haley
Department of Chemistry, University of Oregon
Eugene, OR 97403-1253 (USA)
Fax: (+1) 541-346-0487
E-mail: haley@uoregon.edu

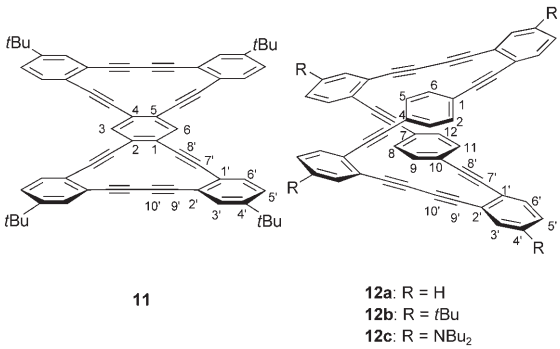
[c] Prof. Dr. P. G. Jones
Institut für Anorganische und Analytische Chemie
Technische Universität Braunschweig
Hagenring 30, 38106 Braunschweig (Germany)

[d] K. Hess, Prof. Dr. R. Herges
Otto-Diels-Institut für Organische Chemie
Universität Kiel
Otto-Hahn-Platz 4, 24118 Kiel (Germany)



the effect of PC incorporation on the delocalization in the overall π system.

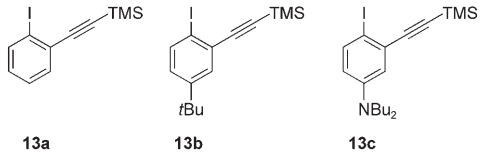
Another type of molecule that can be used to study the effects of π–π interactions between aromatic decks and their effect on the delocalization in annulenes are the fascinating acetylenic cyclophane macrocycles (e.g. **12a**) synthesized by Fallis and co-workers.[5] An X-ray study of **12a** has shown a propeller-type orientation in the solid state. The two benzene rings are aligned in a slightly offset but overlapping manner with an inter-ring distance of 3.57 Å, which is appreciably greater than the typical 3.09 Å found in most [2.2]paracyclophane derivatives. To study the electronic effect in annulenic systems, we have additionally synthesized **12b** and **12c**, which are related to Fallis' systems, and compared them with their [2.2]paracyclophane derivatives **10b** and **10c**.



From a formal point of view, structures **10** and **12** are doubly twisted (360° twist of the π nodal plane) annulenes which should be antiaromatic with 32 ($4n$) electrons, in contrast to annulenes with an odd number of twists (Möbius annulenes), which are aromatic with $4n$ electrons. The benzoannelation confers remarkable kinetic stability on the highly unsaturated dehydroannulene ring. However, the tropicity of the annulene ring is dramatically reduced because delocalization of the π electrons in the annulene ring competes with that of the annelated benzene rings.[6] To study this effect, alkene hybrids **7** and **8** have been synthesized and compared with benzoannulenes **5** and **6**. ACID calculations were performed with **10a** and **12a** to investigate the induced ring currents.

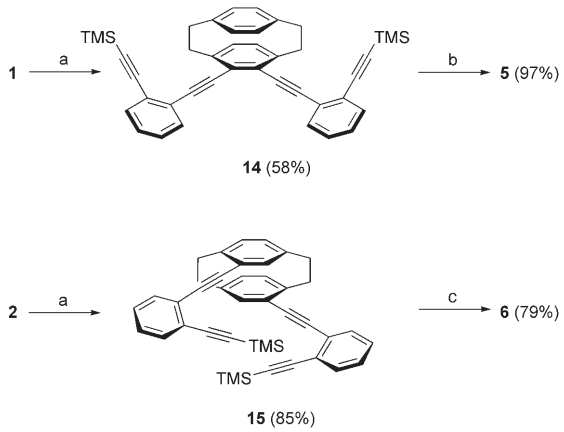
Results and Discussion

Synthesis: The straightforward syntheses of PC/DBAs **5** and **6** using the building block **13a** is shown in Scheme 1.



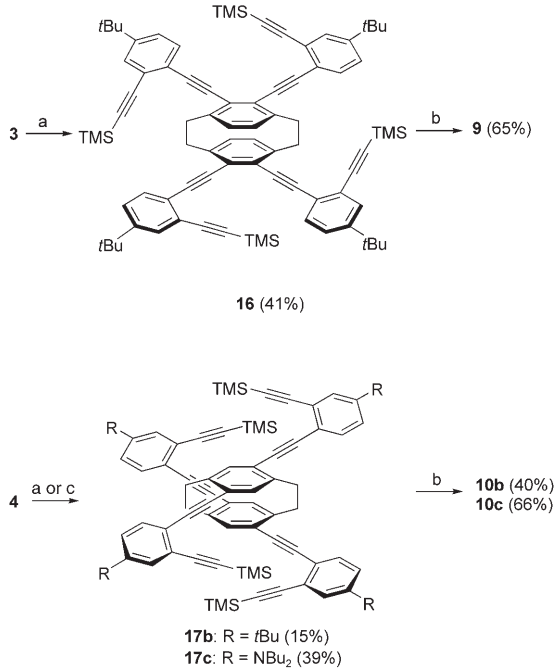
Pd-catalyzed cross-coupling of 4,5-diethynyl-[2.2]paracyclophane[3] (**1**) with 1-iodo-2-(trimethylsilylethynyl)benzene[7] (**13a**) provided tetrayne **14**, which was desilylated and cyclized using a one-pot procedure[8] to give *ortho*-PC/DBA **5** in 56% overall yield. The pseudo-*ortho* derivative **6** was synthesized in the same manner in 67% overall yield, starting from 4,15-diethynyl[2.2]paracyclophane[3] (**2**) and **13a**.

Because of anticipated solubility problems, the bis(dehydrobenzoannuleno)[2.2]paracyclophanes **9** and **10b** were synthesized with solubilizing *tert*-butyl substituents by cross-coupling of the tetraethynyl[2.2]paracyclophanes **3**[4] and **4**[3] with iodobenzene **13b** (formation of **16** and **17b**, re-



Scheme 1. a) **13a**, $[Pd(PPh_3)_4]$, CuI, Et_3N, THF; b) K_2CO_3, $Cu(OAc)_2$, CH_3CN, CH_3OH; c) K_2CO_3, CuCl, $Cu(OAc)_2$, pyridine, CH_3OH.

spectively), followed by in situ deprotection/cyclization as described for the PC/DBAs **5** and **6**. Since **10b** shows strong delocalization through the alkyne units (see below), the donor-substituted *N*,*N*-dibutylamino derivative **10c** was prepared by cross-coupling of **4** with iodobenzene **13c** (formation of **17c**) followed by in situ deprotection/homocoupling (Scheme 2).

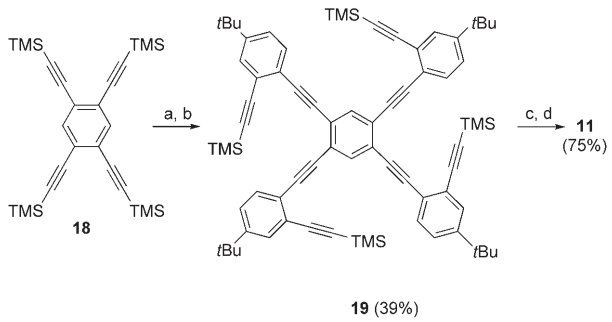


Scheme 2. a) **13b**, $[Pd(PPh_3)_4]$, CuI, iPr_2NH, THF; b) K_2CO_3, $Cu(OAc)_2$, CH_3CN, CH_3OH, CH_2Cl_2; c) **13c**, $[Pd(PPh_3)_4]$, CuI, iPr_2NH, THF.

The synthesis of functionalized bis(dehydrobenzoannuleno)benzenes has recently been reported.[9] In the case of the neutral derivative, the decyl group was chosen to increase the solubility. Since we have used the *tert*-butyl group in the PC/DBA systems, the unknown tetrakis(*tert*-butyl)bis(dehydrobenzo[14]annulene) (**11**) was synthesized here as a model compound.

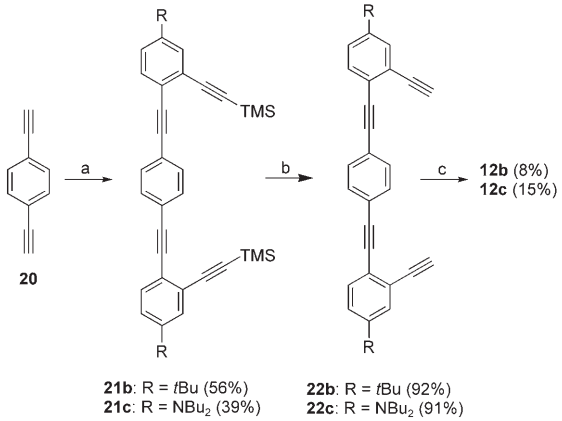
Treatment of 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene (**18**)[10] with KOH in methanol/Et_2O provided the deprotected tetrayne which, because of its instability, was used directly in the following cross-coupling step to give **19** in 39% yield (Scheme 3). Deprotection of **19** was accomplished by treatment with K_2CO_3 in methanol/CH_2Cl_2. Since intramolecular homocoupling under Eglinton conditions with Cu salts/pyridine gave exclusively the bis(dehydrobenzo[15]annulene) in 39% yield,[9c] oxidative homocoupling using $[Pd(dppe)Cl_2]$,[9a] a Pd complex with a *cis*-bidentate ligand, was applied to give bis(dehydrobenzo[14]annulene) **11** in 75% yield.

The ^1H NMR spectrum of **11** shows a downfield shift of the annulene protons relative to precursor **19** ($\Delta\delta = +0.40$, $+0.16$, $+0.26$). Comparable downfield shifts were observed for decyl- and dibutylamino-substituted bis(dehydrobenzo[14]annulenes) ($\Delta\delta = +0.48$, $+0.12$, $+0.30$ for R = decyl; $\Delta\delta = +0.37$, $+0.02$, $+0.23$ for $R = NBu_2$) whereas the spectra of the bis(dehydrobenzo[15]annulenes) display no significant shift differences ($\Delta\delta = +0.08$, $+0.08$, $+0.15$ for R = decyl; $\Delta\delta = +0.01$, $+0.03$, $+0.08$ for $R = NBu_2$).[9]



Scheme 3. a) KOH, CH_3OH, Et_2O; b) **13b**, $[Pd(PPh_3)_4]$, CuI, iPr_2NH, THF; c) K_2CO_3, CH_3OH, CH_2Cl_2; d) $[Pd(dppe)Cl_2]$, CuI, I_2, iPr_2NH, THF.

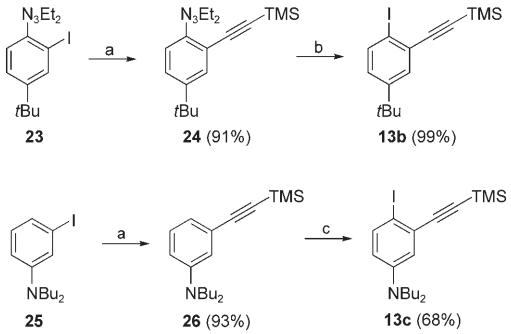
The syntheses of the non-ethano-bridged cyclophynes **12b** and **c** were carried out in a slightly different manner than reported by Fallis for **12a**.[5] Pd-catalyzed cross-coupling of iodobenzenes **13b** or **c** with 1,4-diethynylbenzene (**20**)[11] furnished the tetraynes **21b** and **c**, which were deprotected to the terminal alkynes **22b** and **c** with K_2CO_3 in CH_3OH under standard conditions. The final dimerization to **12b** and **c**, respectively, was accomplished by using $Cu(OAc)_2$ in a 3:1 mixture of pyridine/Et_2O under high dilution conditions (Scheme 4).



Scheme 4. a) **13b** or **13c**, $[Pd(PPh_3)_4]$, CuI, iPr_2NH, THF; b) K_2CO_3, CH_3OH, CH_2Cl_2; c) $Cu(OAc)_2$, pyridine, Et_2O.

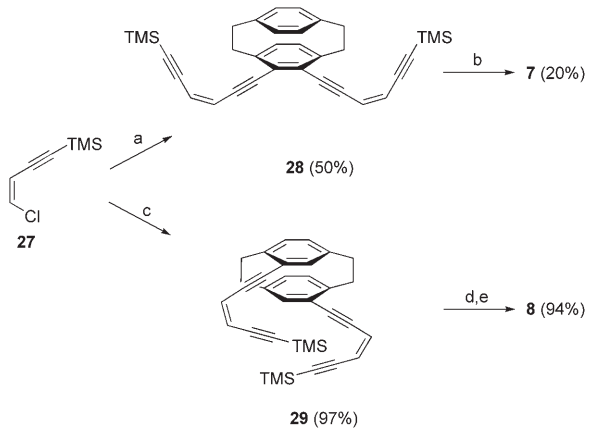
Even though the required iodobenzenes **13b** and **c** have been widely used by the Bunz group,[12] their synthesis and characterization has not been described to date. The synthesis of the neutral *tert*-butyl derivative **13b** starts from known triazene **23**,[13] which was treated with trimethylsilylacetylene (TMSA) in a Pd-catalyzed cross-coupling reaction. Triazene **24** was converted to the iodo compound **13b** by heating in CH_3I at 120°C in a sealed ampoule.[14] To obtain iodoben-

zene **13c**, *N*,*N*-dibutyl-3-iodoaniline (**25**)[15] was treated with TMSA under Pd catalysis. The final iodination was performed employing the mild reagent $BnNMe_3ICl_2$ (Scheme 5).[16]



Scheme 5. a) TMSA, $[Pd(PPh_3)_4]$, CuI, iPr_2NH, THF; b) CH_3I, 120 °C; c) $BnNMe_3^+ICl_2^-$, $CaCO_3$, CH_3OH, CH_2Cl_2.

As mentioned above, we have also prepared PC/DA systems to study the ring currents in dehydroannulenic systems. The *ortho* derivative **7**, which proved to be stable only in dilute solutions, was obtained in about 10% yield by cross-coupling of 4,5-diethynyl[2.2]paracyclophane (**1**) with (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane (**27**)[17] to tetrayne **28**, followed by an in situ deprotection/homocoupling protocol (Scheme 6).



Scheme 6. a) **1**, $[Pd(PPh_3)_4]$, CuI, $PrNH_2$, THF; b) K_2CO_3, $Cu(OAc)_2$, CH_3OH, CH_3CN; c) **2**, $[Pd(PPh_3)_4]$, CuI, $PrNH_2$, THF; d) K_2CO_3, CH_3OH, THF; e) $Cu(OAc)_2$, CH_3CN.

Cross-coupling of 4,15-diethynyl[2.2]paracyclophane (**2**) with **27** gave tetrayne **29** in quantitative yield. Initial attempts using the method described above for the annulene formation resulted in a disappointing 16% yield. However, stepwise deprotection with K_2CO_3 in CH_3OH/THF followed by Cu-catalyzed homocoupling with $Cu(OAc)_2$ in CH_3CN furnished the pseudo-*ortho* PC/DA **8** in 91% overall yield.

X-ray structure analysis: Single crystals of **12b** were prepared by slow diffusion of CH_3OH into a CH_2Cl_2 solution. The structure of **12b** is shown in Figure 1. The molecule possesses crystallographic twofold symmetry. The central rings (C13–C18 and its symmetry equivalent) subtend a surprisingly large interplanar angle of 10°, with an interplanar distance of about 3.7 Å and an offset of about 0.95 Å (note that the latter two quantities are strictly only defined for parallel rings). Some of the angles at triply bonded atoms deviate appreciably from linearity, notably those of 172° at C11 and C12. The structure of **12a**[5] is more regular than that of **12b**, with parallel rings at a distance of 3.56 Å.

Compound **4** (Figure 2) displays an essentially typical [2.2]paracyclophane geometry. The rings have a flattened boat conformation, with the bridgehead atoms displaced by 0.16–0.17 Å from the plane of the other four atoms of the relevant ring. The interplanar angle is 0.4° and the distance between ring centroids (calculated without bridgehead atoms) is 3.08 Å. The rings are mutually rotated by about 9°. The packing shows one short C-H···π contact, from C2–H2b to the centroid of C12,13,15,16: C-H 1.08, H···π 2.60 Å, angle 141°, via the 2_1 operator.

NMR Spectroscopy: The PC/DBA and PC/DA systems, in which the [14]annulene framework is *ortho*-fused to one of the benzene decks of the [2.2]paracyclophane unit, can be used to detect an induced ring current in the annulene core. In these systems, the cyclophane protons 15-H/16-H lie above the annulene ring and thus can function as an anisotropy probe.

The aromatic region of the ^1H NMR spectra of PC/DBA **5** and its precursor **14** is shown in Figure 3. Upon cyclization, 15-H and 16-H show a distinct upfield shift ($\Delta\delta = -0.37$ ppm) when compared with the analogous resonances in **14**, indicative of a diatropic ring current in the [14]annulene unit. The upfield shift is considerably more pronounced in going from **28** to **7** ($\Delta\delta = -0.92$ ppm). Because of ring current competition between annulene and benzene rings, the cyclophane protons 7-H and 8-H experience a slight downfield shift ($\Delta\delta = 0.19$–0.25 ppm). These two effects cause problems in analyzing the ring currents in "step" PC/bis-DBA **9**. Even though the expected upfield shift in going from **16** to **9** is observed ($\Delta\delta = -0.24$ ppm), one has to consider that the same protons experience a downfield shift due to a competing ring current.

The stronger aromaticity in the [14]annulene unit of **7** as compared to **5** is corroborated by ACID (anisotropy of the induced current density) calculations.[19] The ACID scalar field is interpreted as the density of delocalized electrons and is plotted (very much the same way as the total electron density) as an isosurface (yellow "bulges" in Figure 4). Current density vectors plotted onto the ACID isosurface indicate that in **5** all benzene rings are included in the diatropic ring current, except the benzene in the upper deck of the cyclophane unit. Thus, the perimeter includes 26 rather than 14 electrons (both $4n+2$). However, the conjugation is reduced by benzoannelation. A qualitative inspection of the

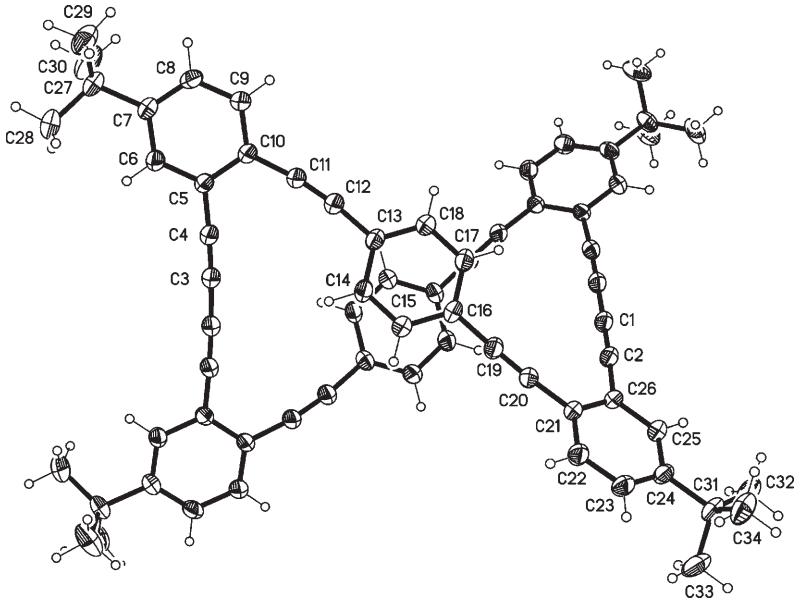


Figure 1. Molecular structure of **12b**; ellipsoids are drawn with 50% probability.

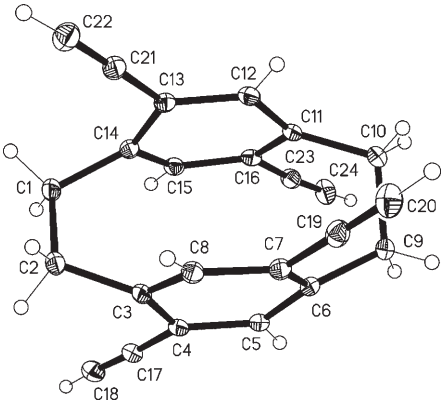


Figure 2. Molecular structure of **4**; ellipsoids are drawn with 50% probability.

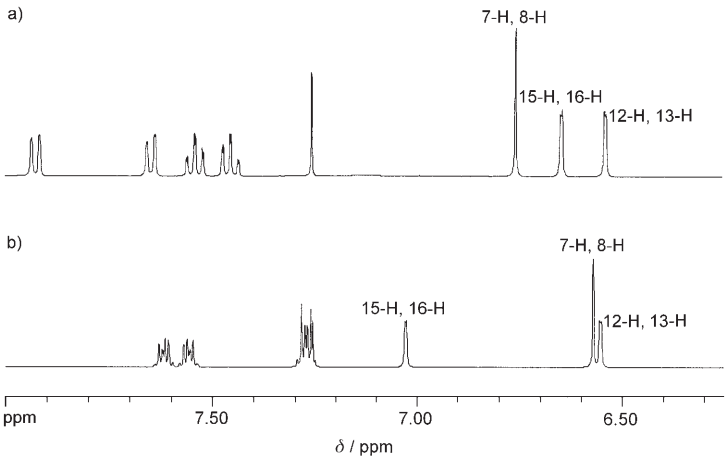


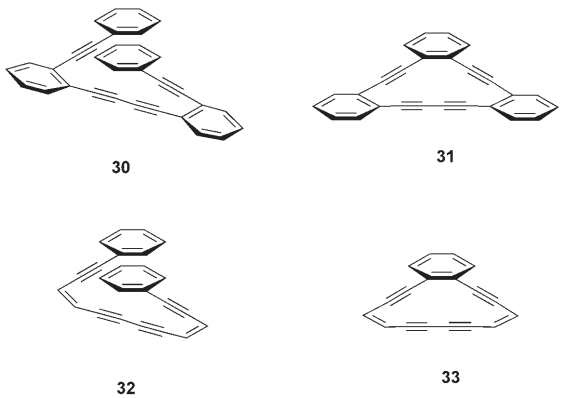
Figure 3. Aromatic region of the ^{1}H NMR spectra of a) dibenzo-[2.2]paracyclophanotetradehydro[14]annulene (**5**) and b) its open precursor **14**.

(yellow) ACID isosurface in Figure 4 already palpably demonstrates the different degree of conjugation in **5** and **7**. We use the critical isosurface values (CIV) to quantify the strength of conjugation. CIVs are consistently higher in **7** compared with **5** (Figure 4). The weakest point of conjugation is the central C–C bond in the 1,3-diyne unit with CIV = 0.023 in **5** and 0.068 in **7**. Our ACID results thus predict a much stronger aromaticity in **7** and explain the higher upfield shift of 15-H and 16-H in **7** compared with **5**. Since one of the benzene rings of the [2.2]cyclophane unit is included in the perimeter of the diatropic ring current, the protons 15-H and 16-H are close to the ring center and therefore are sensitive probes for "measuring" the aromaticity of the tetrayne ring.

We could not detect a distinct ring current in the periphery of **6** and **8**.

Electronic absorption spectra: The absorption of ultraviolet or visible light by a molecule causes the excitation of an electron from an initially occupied orbital with lower energy to a previously unoccupied orbital with higher energy. Delocalization of the π electrons results in a lower energy of the π* orbital, causing a bathochromic shift of the absorption maxima. To gain a deeper insight into the electronic structures of the PC/DBA systems, we have compared their UV/Vis spectra with the spectra of their silyl-protected precursors and with the model systems **30**–**33**.

Figure 5 compares the electronic absorption spectra of *ortho* PC/DBA **5**, its precursor **14** and dehydrobenzo[14]annulene (**31**).[20] A significant bathochromic shift ($\Delta\lambda \approx 60$ nm) is observed relative to **14**, indicating conjugation in



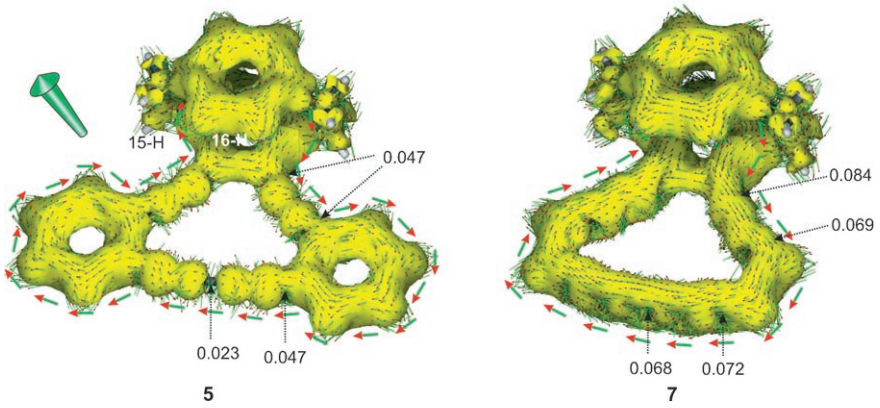


Figure 4. ACID plot of **5** and **7** (B3LYP/6-31G* optimized geometry, isosurface value 0.03). Current density vectors are plotted onto the isosurface (small green arrows with red arrow head, length is proportional to the current, magnetic field is orthogonal with respect to the 14-membered ring, large green arrow). The green arrows with red arrow head around the periphery indicate qualitatively the flow of the current. The diatropic ring current (clockwise) in **7** is distinctively stronger than in **5**. Critical isosurface values (CIV) which indicate the degree of conjugation are given for selected bonds. The CIVs are also consistently higher in **7** compared with **5**. Both the ring current and the CIVs indicate a much stronger aromaticity of the [14]annulene unit in **7**.

question to answer was whether **9** behaves more like a bis[14]DBA with communication between the annulene decks or more like two independent [14]annulene systems.

The electronic absorption spectra (Figure 7) show for both systems the expected bathochromic shift relative to the silyl-protected precursor. Comparing **9** with bisDBA **4** gives evidence for stronger delocalization in the unbridged system **4**, indicating no or only weak π–π interactions between the annulene decks in PC/bisDBA **9**. A comparison of the electronic absorption spectra of the [14]annulenes (Figure 8) supports the previous assumption. "Step" PC/bisDBA **9** shows nearly the same shift as PC/DBA **5**, indicating that the annulenes in **9** behave more like two independent [14]annulene units.

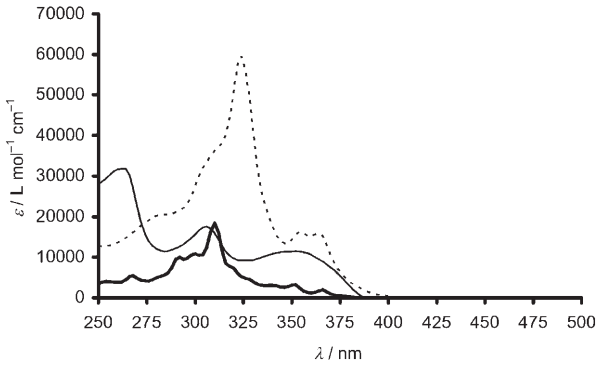


Figure 5. Electronic absorption spectra of **5** (•••••), **14** (——), and **31** (——).

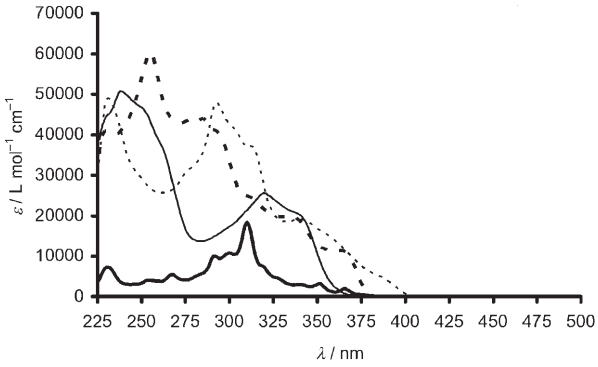


Figure 6. Electronic absorption spectra of **6** (-----), **15** (——), **30** (•••••), and **31** (——).

the [14]annulene unit. Compared with **31**, PC/DBA **5** shows a bathochromic shift of ≈15 nm, which can be explained by through-space interactions in the cyclophane moiety.

A comparison of the electronic absorption spectra of pseudo-*ortho* PC/DBA **6**, "open" precursor **15**, model system **30** (which contains the same chromophores as **6** but lacks the bridging ethylene units) and dehydrobenzo[14]annulene (**31**) is shown in Figure 6.

In the pseudo-*ortho* derivative **6**, a significant bathochromic shift ($\Delta\lambda \approx 25$–40 nm) is observed relative to the precursor **15** and model system **30**. Interestingly, **6** shows nearly the same shift as **31** but with greater absorption intensity. Furthermore, **6** has an extended absorption cut-off relative to the other compounds. Both observations are most probably a result of delocalization throughout the fully conjugated macrocycle by through-space interactions in the cyclophane unit.

To gain a deeper insight into the π–π interactions between the cyclophane decks, "step" PC/bisDBA **9** was synthesized and compared with flat bisDBA **11** (Figure 7). The main

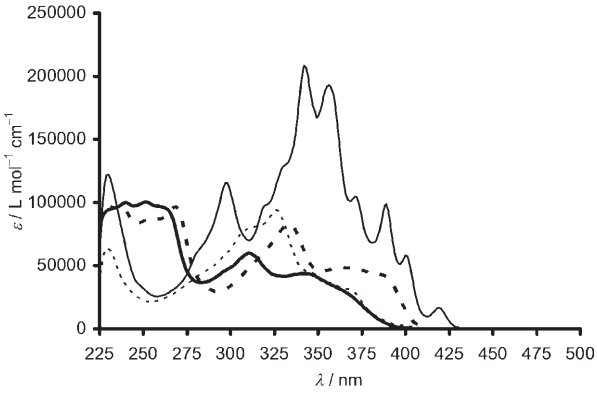


Figure 7. Electronic absorption spectra of **9** (-----), **11** (——), **16** (——), and **19** (•••••).

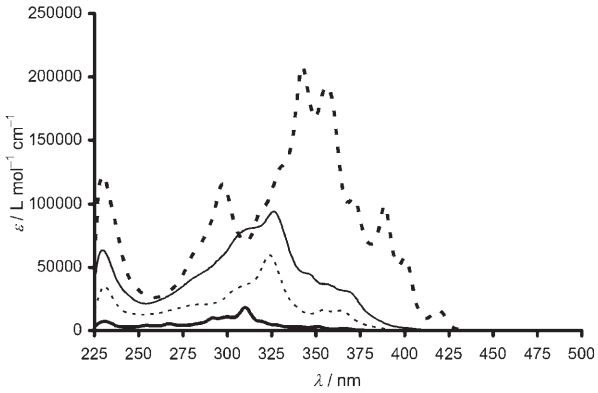


Figure 8. Electronic absorption spectra of **5** (-----), **9** (——), **11** (•••••), and **31** (——).

The neutral propeller-type PC/DBA **10b** displays the same three band pattern as seen in hydrocarbon **6**, but with a red shift of about 20–25 nm for the first two bands and about 55 nm for the low energy band. With the added electron density of four NBu_2 groups, the bands are further red shifted by about 35 nm for the first two bands and about 60 nm for the low energy band (Figure 9).

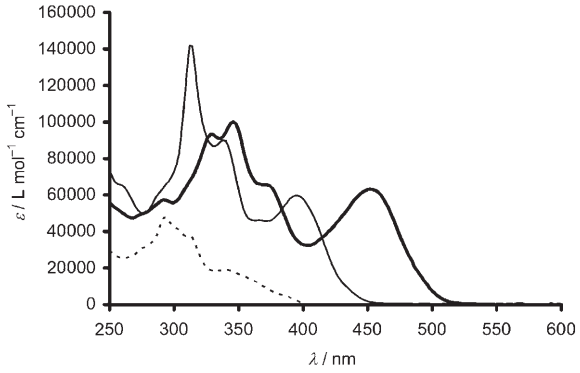


Figure 9. Electronic absorption spectra of **6** (•••••), **10b** (——), and **10c** (——).

To study the effect of the distance between the cyclophane decks on the delocalization in the PC/DBA, we have compared the electronic absorption spectra of the PC/DBAs **10** with their silyl-protected precursors **17** and the non-ethano-bridged systems **12**.

For the neutral systems (Figure 10), the [2.2]paracyclophane derivative **10b** shows a small bathochromic shift of the low energy band by about 10 nm relative to precursor **17b**. Compared with **12b**, the low energy band of **12b** is red shifted by about 35 nm, the higher energy bands display a red shift of about 8 nm. In case of the tetra-donor systems (Figure 11), a bathochromic shift of the low energy band (ca. 30 nm) is observed for the [2.2]paracyclophane system **10c** relative to precursor **17c** and non-ethano-bridged derivative **12c**.

The propeller-type structures **10** and **12** can be viewed as doubly twisted annulenes.[21] It seems paradoxical at a first glance that an annulene in which the p orbitals are almost parallel should exhibit a 360° twist of the nodal π plane. The twist becomes apparent if the "Figure 8-shaped" system is transformed into a planar ring (Figure 12).

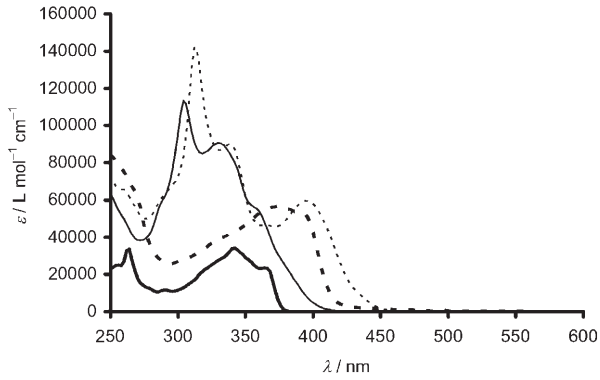


Figure 10. Electronic absorption spectra of **10b** (-----), **12b** (——), **17b** (•••••), and **21b** (——).

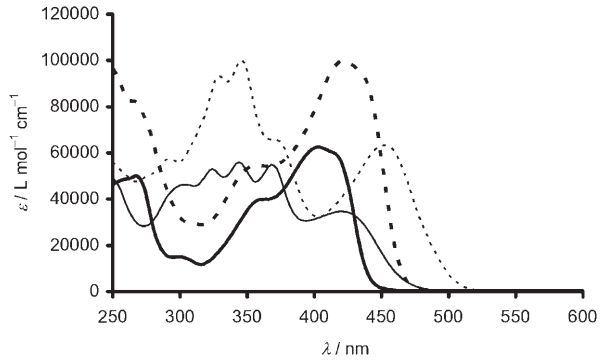


Figure 11. Electronic absorption spectra of **10c** (-----), **12c** (——), **17c** (•••••), and **21c** (——).

Annulenes with an even number (including 0) of 180° twists follow the Hückel rule (aromatic with $4n+2$ electrons). Möbius annulenes with an odd number of twists are aromatic with $4n$ electrons.[22] The propeller annulenes **10**

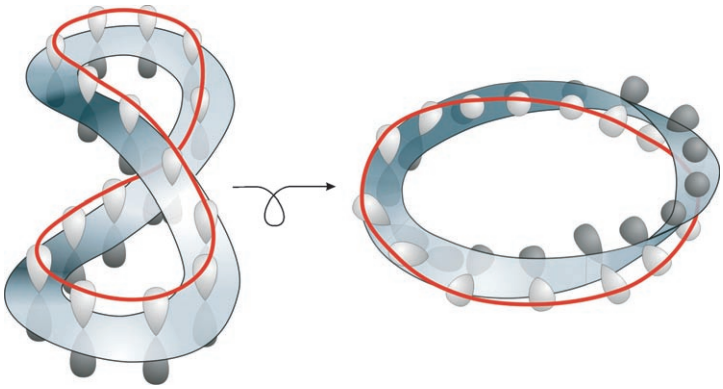


Figure 12. Transformation of number 8 shaped structure **12a** to a planar ring (keeping the mutual overlap of the p orbitals) results in a double twist of the π system.

and **12**, with 32 electrons in the perimeter, should thus be antiaromatic. To investigate the electronic and magnetic properties, we performed ACID[19] calculations (B3LYP/6-31G*) and plotted the current density vectors onto the ACID isosurface of **10a** and **12a** (Figure 13).

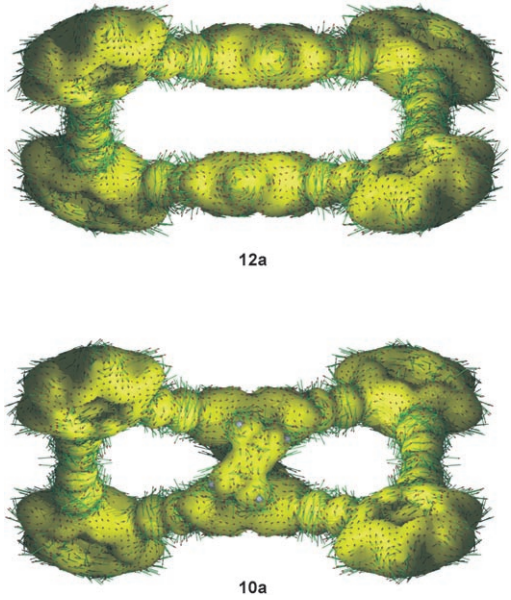


Figure 13. ACID plot of the propeller-type annulenes **10a** and **12a** (B3LYP/6-31G* optimized geometry, isosurface value 0.02). Current density vectors are plotted onto the isosurface (magnetic field parallel to the C_2 axis, pointing towards the viewer). There are strong ring currents induced in the benzene rings and in the cylinder shaped acetylene units; however, there is no distinct ring current including the total 32 π perimeter.

The orientation of the magnetic field with respect to the molecule was chosen in such a way as to induce a maximum ring current (magnetic field parallel to the C_2 axis). There is no distinct ring current including the 32 π electron periphery. Obviously, the benzene rings within the perimeter reduce the contiguous 32 π conjugation.

A comparison of the UV/Vis spectra of **8** with precursor **29**, model compound **32** and annulene **33**[17] is given in Figure 14. For PC/DA **8** no bathochromic shift relative to the corresponding model systems is observed. However, the extended cut-off point ($\Delta\lambda \approx 50$–75 nm), together with the greater absorption intensity at higher wavelength relative to PC/DBA **6**, indicates increased effective conjugation in **8**, because of the presence of the alkene units instead of benzene rings.

Conclusion

We have synthesized a series of dehydrobenzoannulenes and [2.2]paracyclophane/dehydrobenzoannulene hybrids and compared their electronic properties in order to study the through-space interactions in the [2.2]paracyclophane unit.

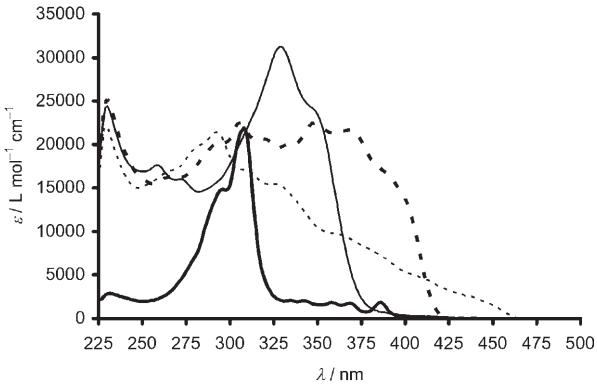


Figure 14. Electronic absorption spectra of **6** (-----), **15** (——), **32** (•••••), and **33** (——).

A comparison of "step" PC/bisDBA with *ortho*-PC/DBA and bisDBA gave no evidence for π-π-interactions between the cyclophane decks, whereas the "propeller" type PC/DBA systems show stronger delocalization than Fallis' unbridged propeller type molecules.

Experimental Section

General procedure A: In a tube with screw cap, a solution of the iodoarene in THF and iPr$_2$NH was deoxygenated by bubbling argon through it. [Pd(PPh$_3$)$_4$], CuI and TMSA were added and the reaction mixture was heated to 60 °C in the closed tube. The solvents were evaporated and the residue purified by column chromatography.

General procedure B: A solution of the iodoarene in THF and iPr$_2$NH was deoxygenated by bubbling Ar through it. To this solution, [Pd(PPh$_3$)$_4$] and CuI were added. A deoxygenated solution of the terminal acetylene in THF was added with a syringe pump at 60 °C. After 1 d, the reaction mixture was concentrated in vacuo and purified by column chromatography.

General procedure C: K_2CO_3 (2.5–3 equiv per TMS group) was added to a solution of the TMS protected alkyne in CH_2Cl_2/MeOH 1:1. After stirring for 1 d at room temperature, the reaction mixture was diluted with CH_2Cl_2 and washed with NH_4Cl solution and water. The aqueous phase was re-extracted with CH_2Cl_2 and the combined organic phases were dried with Na_2SO_4 or $MgSO_4$.

General procedure D: K_2CO_3 and $Cu(OAc)_2 \cdot H_2O$ were added to a solution of the TMS-protected alkyne in MeOH/CH_3CN. The mixture was heated to reflux for 24 h, cooled, diluted with CH_2Cl_2 and washed with brine. The organic phase was dried with Na_2SO_4 and the solvent removed in vacuo.

General procedure E: A solution of the terminal acetylene in pyridine/Et_2O was added with a syringe pump to a solution of $Cu(OAc)_2$ in pyridine/Et_2O at room temp. Upon completion, the mixture was diluted with Et_2O and washed with brine. The solvents were removed in vacuo, the residue dissolved in CH_2Cl_2 and dried with Na_2SO_4.

***N*,*N*-Diethyl-*N'*-[4-*tert*-butyl-2-(trimethylsilylethynyl)phenyl]triazene (24)**: Triazene **23**[13] (1.44 g, 4 mmol) was subjected to general procedure A (40 mL THF; 40 mL iPr$_2$NH; 46 mg, 0.04 mmol [Pd(PPh$_3$)$_4$]; 15 mg, 0.08 mmol CuI; 0.85 mL, 6 mmol TMSA). Purification by column chromatography on silica gel (20 % CH_2Cl_2 in pentane, $R_f = 0.3$) gave **24** (1.21 g, 3.6 mmol, 91 %) as a pale yellow solid. M.p. 38 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.25$ (s, 9H, Si(CH_3)$_3$), 1.29 (s, 9H, C(CH_3)$_3$), 1.32 (t, $^3J = 7.1$ Hz, 6H, N(CH_2CH_3)$_2$), 3.77 (q, $^3J = 7.1$ Hz, 4H, N(CH_2CH_3)$_2$), 7.27 (dd, $^3J_{5,6} = 8.9$, $^4J_{5,3} = 2.4$ Hz, 1H, 5-H), 7.30 (d, $^3J_{6,5} = 8.9$ Hz, 1H, 6-H), 7.50 (d, $^4J_{3,5} = 2.4$ Hz, 1H, 3-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 0.1$

(q), 11.2, 14.3 (br q), 31.3 (q), 34.3 (s), 41.9, 49.0 (br t), 97.0 (s), 104.2 (s), 116.4 (d), 117.3 (s), 126.5 (d), 129.9 (d), 147.5 (s), 150.5 (s); IR (ATR): $\tilde{\nu}$ = 2969 (m), 2961 (m), 2902 (w), 2868 (w), 2156 (m), 1485 (w), 1465 (m), 1450 (m), 1431 (w), 1416 (w), 1385 (m), 1331 (m), 1248 (m), 1204 (m), 1109 (m), 1090 (m), 927 (m), 885 (w), 831 (vs), 756 cm^{-1} (s); MS (EI): *m/z* (%): 329 (11) [M^+], 230 (26), 229 (100) [M^+], 215 (41), 214 (20), 190 (25), 173 (24), 145 (37), 70 (76), 57 (74); elemental analysis calcd (%) for $C_{19}H_{31}N_3Si$ (329.56): C 69.25, H 9.48, N 12.75, Si 8.52; found C 69.42, H 9.59, N 12.88.

4-*tert*-Butyl-2-[(trimethylsilyl)ethynyl]iodobenzene (13b): In a pressure tube with Teflon screw cap, a solution of **24** (3.58 g, 10.8 mmol) in freshly distilled CH_3I (19 mL) was heated for 24 h at 120 °C. The reaction mixture was cooled to room temperature and the solvent was removed. Column chromatography on silica gel (20% CH_2Cl_2 in pentane, R_f = 0.74) gave **13b** (3.81 g, 10.7 mmol, 99%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.29 (s, 9H, Si(CH_3)$_3$), 1.28 (s, 9H, C(CH_3)$_3$), 7.02 (dd, $^3J_{5,6}$ = 8.4, $^4J_{5,3}$ = 2.5 Hz, 1H, 5-H), 7.49 (d, $^4J_{3,5}$ = 2.5 Hz, 1H, 3-H), 7.73 (d, $^3J_{6,5}$ = 8.4 Hz, 1H, 6-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.1 (q), 31.0 (q), 34.5 (s), 97.5 (s), 97.9 (s), 107.1 (s), 127.3 (d), 129.1 (s), 130.0 (d), 138.3 (d), 151.1 (s); IR (ATR): $\tilde{\nu}$ = 2960 (m), 2901 (w), 2867 (w), 2160 (m), 1459 (m), 1382 (m), 1248 (m), 1113 (m), 1014 (m), 919 (m), 838 (vs), 817 (s), 757 (s), 706 cm^{-1} (m); MS (GC-MS): *m/z* (%): 356 (54) [M^+], 341 (100), 229 (4), 199 (16), 149 (22); elemental analysis calcd (%) for $C_{15}H_{21}ISi$ (356.29): C 50.56, H 5.94, I 35.61, Si 7.88; found C 50.58, H 5.92.

***N*,*N*-Dibutyl-3-[(trimethylsilyl)ethynyl]aniline (26)**: *N*,*N*-Dibutyl-3-iodoaniline (**25**,[15] 1.69 g, 5 mmol) was subjected to general procedure A (40 mL THF; 40 mL *i*Pr_2NH; 58 mg, 0.05 mmol [$Pd(PPh_3)_4$]; 19 mg, 0.1 mmol CuI; 1.1 mL, 7.5 mmol TMSA). Purification by column chromatography on silica gel (5% CH_2Cl_2 in pentane, R_f = 0.15) gave **26** (1.4 g, 4.6 mmol, 93%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.29 (s, 9H, Si(CH_3)$_3$), 0.99 (t, ^3J = 7.4 Hz, 6H, $NCH_2CH_2CH_2CH_3$), 1.38 (sextet, ^3J = 7.4 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 1.54–1.61 (m, 4H, $NCH_2CH_2CH_2CH_3$), 3.25–3.28 (m, 4H, $NCH_2CH_2CH_2CH_3$), 6.62–6.64 (m, 1H, 6-H), 6.75–6.78 (m, 2H, 2-H, 4-H), 7.13 (t, ^3J = 7.9 Hz, 1H, 5-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.0 (q), 14.0 (q), 20.3 (t), 29.3 (t), 50.6 (t), 92.3 (s), 106.5 (s), 112.4 (d), 114.9 (d), 119.1 (d), 123.5 (s), 128.9 (d), 147.9 (s); IR (ATR): $\tilde{\nu}$ = 2957 (m), 2930 (m), 2898 (w), 2871 (m), 2155 (m), 1592 (m), 1566 (m), 1493 (m), 1463 (m), 1367 (m), 1288 (w), 1248 (m), 1189 (m), 1145 (m), 1108 (w), 1025 (w), 937 (w), 889 (m), 839 cm^{-1} (vs), 761 (m); MS (GC-MS): *m/z* (%): 301 (22) [M^+], 259 (18), 258 (100), 216 (43), 202 (16), 186 (19).

***N*,*N*-Dibutyl-4-iodo-3-[(trimethylsilyl)ethynyl]aniline (13c)**: *N*,*N*-Dibutyl-3-[(trimethylsilyl)ethynyl]aniline (**26**, 2.81 g, 9.3 mmol) in CH_2Cl_2 (170 mL) and CH_3OH (30 mL) was treated with $(BnNMe_3)^+ICl_2^-$ (3.24 g, 9.3 mmol) and $CaCO_3$ (1.33 g, 13.3 mmol). The reaction mixture was stirred for 2 h and filtered. The filtrate was washed with $NaHSO_3$ solution (200 mL, 5%) which was subsequently extracted with Et_2O. The combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. Chromatography on silica gel (pentane, R_f = 0.27) gave **13c** (2.70 g, 6.3 mmol, 68%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.28 (s, 9H, Si(CH_3)$_3$), 0.94 (t, ^3J = 7.4 Hz, 6H, $NCH_2CH_2CH_2CH_3$), 1.33 (sextet, ^3J = 7.4 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 1.48–1.56 (m, 4H, $NCH_2CH_2CH_2CH_3$), 3.18–3.22 (m, 4H, $NCH_2CH_2CH_2CH_3$), 6.32 (dd, $^3J_{6,5}$ = 8.9, $^4J_{6,2}$ = 3.1 Hz, 1H, 6-H), 6.75 (d, $^4J_{2,6}$ = 3.1 Hz, 1H, 2-H), 7.51 (d, $^3J_{5,6}$ = 8.9 Hz, 1H, 5-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.0 (q), 14.0 (q), 20.3 (t), 29.2 (t), 50.6 (t), 82.5 (s), 96.8 (s), 107.6 (s), 114.3 (d), 116.0 (d), 129.4 (s), 138.7 (d), 147.8 (s); IR (ATR): $\tilde{\nu}$ = 2958 (s), 2927 (s), 2871 (m), 2857 (m), 2361 (s), 1583 (s), 1482 (m), 1464 (m), 1369 (m), 1249 (m), 1028 (m), 949 (s), 844 cm^{-1} (vs); MS (GC-MS): *m/z* (%): 427 (45) [M^+], 385 (20), 383 (100), 341 (49), 184 (42), 163 (54), 73 (18).

4,16-Bis(2′-(trimethylsilylethynyl)phenylethynyl)[2.2]paracyclophane (15): A solution of 1-iodo-2-(trimethylsilylethynyl)benzene[7] (**13a**, 878 mg, 2.93 mmol) in Et_3N (30 mL) was deoxygenated by bubbling N_2 through it. To this solution was added [$Pd(PPh_3)_4$] (176 mg, 0.15 mmol) and CuI (85 mg, 0.44 mmol). A deoxygenated solution of 4,16-diethynyl-[2.2]paracyclophane[3] (**2**, 300 mg, 1.17 mmol) in THF (5 mL) was added with a syringe. The reaction was stirred at 40 °C for 18 h. The cooled reaction mixture was concentrated and the residue was redissolved in CH_2Cl_2 and filtered through a pad of silica gel. Column chromatography on silica gel (10% CH_2Cl_2 in hexanes) gave **15** (600 mg, 85%) as a bright yellow solid. M.p. 62–63 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.93 (ddd, ^2J = 12.6, ^3J = 10.5, ^3J = 5.4 Hz, 2H), 3.12 (ddd, ^2J = 12.7, ^3J = 10.5, ^3J = 2.1 Hz, 2H), 3.38 (ddd, ^2J = 12.7, ^3J = 10.5, ^3J = 5.4 Hz, 2H), 3.93 (ddd, ^2J = 12.6, ^3J = 10.5, ^3J = 2.1 Hz, 2H), 6.56–6.57 (m, 4H), 7.22 (br s, 2H), 7.27–7.30 (m, 4H), 7.54–7.57 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$); δ = 0.0, 33.7, 34.6, 91.8, 93.5, 98.2, 104.0, 124.9, 125.0, 126.4, 127.5, 128.2, 132.4, 132.9, 133.3, 133.4, 134.7, 139.7, 142.3; IR (neat): $\tilde{\nu}$ = 3088, 3060, 3028, 3012, 2958, 2930, 2896, 2854, 2204, 2156, 1590, 1488, 1475, 1441, 1250, 862, 843, 758 cm^{-1}; UV (CH_2Cl_2): λ_{max} (log ε) = 238 (4.71), 320 (4.41), 339 nm (4.31); MS (FAB): *m/z* (%): 600 (25) [M^+], 585 (25), 527 (65), 285 (80), 239 (100).

PC/DBA 6: CuCl (741 mg, 7.48 mmol) and K_2CO_3 (1.36 g, 7.48 mmol) were added to a solution of **15** (155 mg, 0.25 mmol) in pyridine (30 mL) and CH_3OH (30 mL). The dark blue-green slurry was stirred for 72 h. The reaction mixture was diluted with CH_2Cl_2 and washed successively with 5% HCl solution, saturated $NaHCO_3$, and water. The organic layer was dried ($MgSO_4$) and filtered. Column chromatography on silica gel (20% CH_2Cl_2 in hexanes) provided **6** (90 mg, 79%) as a yellow powder. M.p. 281.2 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.78–2.89 (m, 2H), 3.03–3.19 (m, 4H), 3.68–3.76 (m, 2H), 6.62 (m, 4H), 7.10 (br s, 2H), 7.39–7.27 (m, 4H), 7.57–7.50 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.3, 35.7, 78.6, 82.1, 91.0, 93.5, 123.5, 124.0, 127.8, 128.9, 129.0, 131.0, 132.4, 133.1, 133.8, 133.8, 139.8, 143,3, IR (KBr): $\tilde{\nu}$ = 3060, 3024, 3004, 2958, 2925, 2886, 2849, 2215, 2196, 1581, 1552, 1482, 1442, 752 cm^{-1}; UV (CH_2Cl_2): λ_{max} (log ε) = 231 (4.69), 293 (4.68), 312 (4.57), 340 nm (4.28); MS (FAB): *m/z* (%): 455 (19) [M^+], 242 (100), 136 (54).

4,16-Bis(6′-trimethylsilyl-1′,5′-hexadiyne-3′-ene)[2.2]paracyclophane (29): A mixture of THF (150 mL) and *n*$PrNH_2$ (20 mL) was deoxygenated by bubbling N_2 through it. To this solution was added (*Z*)-(4-chloro-3-buten-1-ynyl)-trimethylsilane[17] (390 mg, 2.46 mmol) [$Pd(PPh_3)_4$] (108 mg, 0.09 mmol), and CuI (223 mg, 1.17 mmol). A deoxygenated solution of 4,15-diethynyl[2.2]paracyclophane (**2**; 300 mg, 1.17 mmol) dissolved in THF (5 mL) was added. The reaction vessel was wrapped in aluminium foil and the reaction was stirred at room temperature for 24 h. The dark green solution was diluted with Et_2O and filtered through a pad of silica gel. Radial chromatography on silica gel (10% CH_2Cl_2 in hexanes) provided **29** (567 mg, 97%) as a yellow solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.26 (s, 18H), 2.85 (ddd, ^2J = 12.8, ^3J = 10.5, ^3J = 6.0 Hz, 2H), 3.08 (ddd, ^2J = 12.8, ^3J = 10.5, ^3J = 2.0 Hz, 2H), 3.29 (ddd, ^2J = 12.8, ^3J = 10.4, ^3J = 6.0 Hz, 2H), 3.79 (ddd, ^2J = 12.8, ^3J = 10.4, ^3J = 2.0 Hz, 2H), 5.94 (d, ^3J = 11.0 Hz, 2H), 6.17 (d, ^3J = 11.0 Hz, 2H), 6.57 (br s, 4H), 7.01 (br s, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 0.2, 33.9, 35.1, 91.2, 97.9, 103.1, 103.3, 118.8, 121.2, 124.8, 134.2, 134.3, 134.8, 140.5, 143.3; IR (neat): $\tilde{\nu}$ = 3034, 2956, 2931, 2896, 2855, 2190, 2139, 1589, 1578, 1412, 1249, 1043, 842, 760 cm^{-1}; UV (CH_2Cl_2): λ_{max} (log ε) = 230 (4.39), 258 (4.25), 329 (4.50), 349 nm (4.38); MS (FAB): *m/z* (%): 501 (55) [M^+], 427 (95), 353 (70), 235 (100), 136 (94).

PC/DA 8: K_2CO_3 (1 mL sat. solution) was added to a solution of **29** (120 mg, 0.24 mmol) in THF (20 mL) and CH_3OH (20 mL). The flask was wrapped with aluminum foil and the reaction mixture was stirred for 2 d at room temp. The mixture was diluted with Et_2O, washed with NH_4Cl, brine and water and dried with $MgSO_4$. The solution was concentrated and diluted with CH_3CN. The flask was wrapped with aluminium foil and $Cu(OAc)_2$ (654 mg, 3.6 mmol) was added. The mixture was stirred at 40 °C for 36 h, diluted with Et_2O and washed with brine and water. The organic phase was dried with $MgSO_4$ and purified by preparative TLC on silica (15% CH_2Cl_2 in hexanes) to provide **8** (80 mg, 0.23 mmol, 94%) as a bright yellow solid. M.p. 171–173 °C (decomp); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.74–2.84 (m, 2H), 2.94–3.04 (m, 2H), 3.10–3.18 (m, 2H), 3.54–3.64 (m, 2H), 5.91 (d, ^3J = 10.2, 2H), 6.38 (d, ^3J = 10.2, 2H), 6.60–6.61 (m, 4H), 6.96 (br s, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 33.7, 35.8, 84.6, 90.7, 98.6, 98.9, 117.8, 123.5, 126.6, 133.8, 134.1, 134.3, 140.4, 144.7; IR (neat): $\tilde{\nu}$ = 3042, 2954, 2925, 2887, 2849, 2165, 1540, 1449, 1432, 905, 869, 739 cm^{-1}; UV (CH_2Cl_2): λ_{max} (log ε) = 229 (4.35), 292

(4.33), 325 (4.19), 329 (4.18), 362 (3.99), 436 nm (3.42); MS (FAB): *m*/*z* (%): 354 (23) [M^+], 307 (30), 217 (60), 154 (100).

4,5,12,13-Tetrakis(4′-*tert*-butyl-2′-[trimethylsilyl]ethynylphenylethynyl)-[2.2]paracyclophane (16): 4,5,13,14-Tetraethynyl[2.2]paracyclophane[4] (**3**, 15 mg, 0.05 mmol) in THF (1.5 mL) was coupled with 4-*tert*-butyl-2-[(trimethylsilyl)ethynyl]iodobenzene (**13b**, 89 mg, 0.25 mmol) as described in general procedure B (14 mg, 0.013 mmol [$Pd(PPh_3)_4$]; 7 mg 0.038 mmol CuI; 6 mL THF; 7.5 mL *i*Pr_2NH). Column chromatography on silica gel (10% CH_2Cl_2 in pentane, R_f=0.07) gave **16** (25 mg, 0.02 mmol, 41%) as a colorless solid. M.p. 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.22 (s, 36H, Si(CH_3)$_3$), 1.34 (s, 36H, C(CH_3)$_3$), 3.15–3.22 (m, 4H, 1-, 2-, 9-, 10-H), 3.71–3.78 (m, 4H, 1-, 2-, 9-, 10-H), 7.08 (s, 4H, 7-, 8-, 15-, 16-H), 7.30 (dd, $^3J_{5',6'}$=8.2, $^4J_{5',3'}$=2.1 Hz, 4H, 5′-H), 7.55 (d, $^3J_{6',5'}$=8.2 Hz, 4H, 6′-H), 7.56 (d, $^4J_{3',5'}$=2.1 Hz, 4H, 3′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.1 (q, Si(CH_3)$_3$), 31.1 (q, C(CH_3)$_3$), 33.0 (t, C-1, -2, -9, -10), 34.8 (s, C(CH$_3$)$_3$), 92.1 (s, C-8′), 95.9 (s, C-7′), 97.5 (s, C-10′), 104.5 (s, C-9′), 123.5 (s, C-1′), 124.6 (s, C-2′), 125.7 (d, C-5′), 128.2 (s, C-4, -5, -12, -13), 129.9 (d, C-3′), 130.2 (d, C-7, -8, -15, -16), 132.7 (d, C-6′), 142.4 (s, C-3, -6, -11, -14), 151.1 (s, C-4′); IR (ATR): $\tilde{\nu}$=2961 (m), 2904 (w), 2869 (w), 2155 (w), 1494 (m), 1462 (m), 1393 (m), 1363 (w), 1248 (m), 1200 (w), 1126 (w), 1094 (w), 925 (m), 837 (vs), 757 (s), 700 cm^{-1} (m); UV (CH_2Cl_2): λ_{max} (lg ε)=240 (5.00), 251 (5.00), 310 (4.78), 343 nm (4.64); MS (ESI, Ag^+): *m*/*z* (%): 1324 (63), 1325 (69), 1326 (100), 1327 (84), 1328 (52), 1329 (25), 1330 (10).

PC/bis-DBA 9: A solution of polyyne **16** (12 mg, 0.01 mmol) in CH_2Cl_2 (10 mL) was subjected to general procedure D (14 mg, 0.1 mmol K_2CO_3, 80 mg, 0.4 mmol $Cu(OAc)_2{\cdot}H_2O$, 20 mL CH_3OH, 20 mL CH_3CN). Column chromatography on silica gel (20% CH_2Cl_2 in pentane) yielded **9** (5 mg, 0.005 mmol, 50%) as a colorless solid. M.p. ≈180 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.41 (s, 36H, C(CH_3)$_3$), 3.21–3.49 (m, 4H, 1-, 2-, 9-, 10-H), 3.88–3.95 (m, 4H, 1-, 2-, 9-, 10-H), 6.84 (s, 4H, 7-, 8-, 15-, 16-H), 7.60 (dd, $^3J_{5',6'}$=8.3, $^4J_{5',3'}$=2.0 Hz, 4H, 5′-H), 7.69 (d, $^4J_{3',5'}$=2.0 Hz, 4H, 3′-H), 7.89 (d, $^3J_{6',5'}$=8.3 Hz, 4H, 6′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=31.2 (q, C(CH_3)$_3$), 33.7 (t, C-1, C-2, C-9, C-10), 35.0 (s, C(CH$_3$)$_3$), 80.2 (s, C-10′), 86.5 (s, C-9′), 93.2 (s, C-8′), 97.3 (s, C-7′), 122.4 (s, C-2′), 125.3 (s, C-4, -5, -12, -13), 126.2 (d, C-3′), 126.3 (d, C-5′), 127.3 (s, C-1′), 130.0 (d, C-7, -8, -15, -16), 132.6 (d, C-6′), 143.9 (s, C-3, -6, -11, -13), 151.4 (s, C-4′); IR (ATR): $\tilde{\nu}$=3281 (br), 2959 (s), 2927 (s), 2867 (m), 2167 (w), 1694 (m), 1596 (m), 1558 (m), 1484 (s), 1460 (m), 1436 (m), 1394 (w), 1363 (m), 1254 (m), 1198 (m), 1167 (m), 1129 (m), 1100 (m), 1027 (w), 903 (m), 866 (m), 823 (s), 796 (w), 730 cm^{-1} (vs); UV (CH_2Cl_2): λ_{max} (lg ε)=230 (4.80), 315 (4.91), 326 (4.97), 345 (4.65), 355 (4.56), 368 nm (4.50); MS (ESI, Ag^+): *m*/*z* (%): 1031 (78), 1032 (63), 1033 (100), 1034 (65), 1035 (24).

4,7,13,16-Tetrakis(4′-*tert*-butyl-2′-[trimethylsilyl]ethynyl-phenylethynyl)-[2.2]paracyclophane (17b): 4,7,13,16-Tetraethynyl[2.2]paracyclophane[3] (**4**, 61 mg, 0.2 mmol) in THF (2 mL) was coupled with 4-*tert*-butyl-2-[(trimethylsilyl)ethynyl]iodobenzene (**13b**, 257 mg, 1.0 mmol) as described in general procedure B (18 mg, 0.016 mmol [$Pd(PPh_3)_4$]; 3 mg 0.016 mmol CuI; 10 mL THF; 12 mL *i*Pr_2NH). Purification by preparative thick layer chromatography (10% CH_2Cl_2 in pentane, R_f=0.07) gave **17b** (40 mg, 0.03 mmol, 15%) as a pale yellow solid. M.p. 96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.22 (s, 36H, Si(CH_3)$_3$), 1.35 (s, 36H, C(CH_3)$_3$), 3.11–3.18 (m, 4H, 1-, 2-, 9-, 10-H), 3.67–3.74 (m, 4H, 1-, 2-, 9-, 10-H), 7.22 (s, 4H, 5-, 8-, 12-, 15-H), 7.33 (dd, $^3J_{5',6'}$=8.2, $^4J_{5',3'}$=2.0 Hz, 4H, 5′-H), 7.51 (d, $^3J_{6',5'}$=8.2 Hz, 4H, 6′-H), 7.55 (d, $^4J_{3',5'}$=2.0 Hz, 4H, 3′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.07 (q, Si(CH_3)$_3$), 31.1 (q, C(CH_3)$_3$), 32.7 (t, C-1, -2, -9, -10), 34.8 (s, C(CH$_3$)$_3$), 92.6 (s, C-8′), 93.3 (s, C-7′), 97.6 (s, C-10′), 104.3 (s, C-9′), 123.5 (s, C-1′), 124.8 (s, C-2′), 125.4 (s, C-4, C-7, C-13, C-16), 125.7 (d, C-5′), 129.7 (d, C-3′), 132.2 (d, C-6′), 135.0 (d, C-5, -8, -12, -15), 141.9 (s, C-3, -6, -11, -14), 151.1 (s, C-4′); IR (ATR): $\tilde{\nu}$=2958 (m), 2921 (m), 2900 (m), 2864 (m), 2153 (w), 2135 (w), 1587 (w), 1540 (w), 1498 (m), 1463 (m), 1431 (m), 1392 (m)1292 (w), 1247 (m), 1199 (w), 1102 (w), 926 (m), 856 (w), 832 (vs), 830 (vs), 810 (m), 757 (m), 722 cm^{-1} (m); UV (CH_2Cl_2): λ_{max} (lg ε)=240 (5.25), 250 (5.21), 268 (5.09), 312 (4.76), 332 (4.88), 374 (5.03), 386 nm (5.01); MS (EI): *m*/*z* (%): 1218 (22), 1219 (15), 1220 (8) [M^+], 1217 (20), 1144 (20), 1145 (20), 1146 (13), 1072 (17), 1000 (11), 73 (100).

PC/bis-DBA 10b: Polyyne **17b** (38 mg, 0.033 mmol) was subjected to general procedure D (46 mg, 0.33 mmol K_2CO_3; 265 mg, 1.32 mmol $Cu(OAc)_2{\cdot}H_2O$; 66 mL CH_3OH; 66 mL CH_3CN; 13 mL CH_2Cl_2). Purification by preparative thick layer chromatography (20% CH_2Cl_2 in pentane, R_f=0.49) yielded **10b** (12 mg, 0.013 mmol, 40%) as a pale yellow solid. M.p. ≈220 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.35 (s, 36H, C(CH_3)$_3$), 3.06–3.14 (m, 4H, 1-, 2-, 9-, 10-H), 3.48–3.56 (m, 4H, 1-, 2-, 9-, 10-H), 7.18 (s, 4H, 5-, 8-, 12-, 15-H), 7.40 (dd, $^3J_{5',6'}$=8.2, $^4J_{5',3'}$=2.0 Hz, 4H, 5′-H), 7.48 (d, $^3J_{6',5'}$=8.2 Hz, 4H, 6′-H), 7.55 (d, $^4J_{3',5'}$=2.0 Hz, 4H, 3′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=31.0 (q, C(CH_3)$_3$), 33.1 (t, C-1, -2, -9, -10), 34.9 (s, C(CH$_3$)$_3$), 78.2 (s, C-10′), 82.4 (s, C-9′), 92.7 (s, C-8′ or C-7′), 92.9 (s, C-7′ or C-8′), 123.9 (s, C-2′), 124.4 (s, C-4, -7, -13, -16), 125.7 (s, C-1′), 126.4 (d, C-5′), 128.1 (d, C-3′), 132.1 (d, C-6′), 133.8 (d, C-5, -8, -12, -15), 143.1 (s, C-3, -6, -11, -14), 151.6 (s, C-4′); IR (ATR): $\tilde{\nu}$=2959 (s), 2926 (m), 2902 (m), 2867 (m), 1594 (w), 1494 (s), 1462 (m), 1427 (m), 1394 (m), 1363 (m), 1255 (m), 1200 (m), 1127 (m), 1027 (m), 900 (m), 828 (s), 738 (m), 725 (m), 712 cm^{-1} (m); UV (CH_2Cl_2): λ_{max} (lg ε)=232 (5.11), 258 (4.82), 290 (4.8), 312 (5.15), 338 (4.95), 366 (4.67), 394 nm (4.78); MS (MALDI-TOF): *m*/*z*: 947.3, 948.4, 949.4 [M^++Na], 924.3, 925.4, 926.4 [M^+].

4,7,13,16-Tetrakis(4′-*N*,*N*-dibutylamino-2′-[trimethylsilyl]ethynylphenylethynyl)[2.2]paracyclophane (17c): 4,7,13,16-tetraethynyl[2.2]paracyclophane (**4**, 26 mg, 0.085 mmol) in THF (1 mL) was coupled with *N*,*N*-dibutyl-4-iodo-3-[(trimethylsilyl)ethynyl]aniline (**13c**, 172 mg, 0.425 mmol) as described in general procedure B (8 mg, 0.007 mmol [$Pd(PPh_3)_4$]; 1 mg, 0.007 mmol CuI; 5 mL THF; 6 mL *i*Pr_2NH). Purification by preparative thick layer chromatography (20% CH_2Cl_2 in pentane, R_f=0.22) yielded **17c** (50 mg, 0.033 mmol, 39%) as a yellow solid. M.p. 88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.22 (s, 36H, Si(CH_3)$_3$), 0.97 (ps-t, ^3J=7.4 Hz, 24H, $NCH_2CH_2CH_2CH_3$), 1.37 (ps-sextet, J=7.4 Hz, 16H, $NCH_2CH_2CH_2CH_3$), 1.55–1.62 (m, 16H, $NCH_2CH_2CH_2CH_3$), 3.07–3.13 (m, 4H, 1-H, 2-H, 9-H, 10-H), 3.29 (t, J=7.5 Hz, 16H, $NCH_2CH_2CH_2CH_3$), 3.62–3.70 (m, 4H, 1-, 2-, 9-, 10-H), 6.59 (dd, $^3J_{5',6'}$=8.8, $^4J_{5',3'}$=2.6 Hz, 4H, 5′-H), 6.75 (d, $^4J_{3',5'}$=2.6 Hz, 4H, 3′-H), 7.15 (s, 4H, 5-, 8-, 12-, 15-H), 7.42 (d, $^3J_{6',5'}$=8.8 Hz, 4H, 6′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.1 (q, Si(CH_3)$_3$), 14.0 (q, $NCH_2CH_2CH_2CH_3$), 20.3 (t, $NCH_2CH_2CH_2CH_3$), 29.4 (t, $NCH_2CH_2CH_2CH_3$), 32.8 (t, C-1, C-2, C-9, C-10), 50.6 (t, $NCH_2CH_2CH_2CH_3$), 91.1 (s, C-8′), 93.9 (s, C-7′), 96.6 (s, C-10′), 105.0 (s, C-9′), 112.2 (d, C-5′), 113.1 (s, C-1′), 115.1 (d, C-3′), 125.3 (s, C-4, -7, -13, -16), 125.9 (s, C-2′), 133.6 (d, C-6′), 134.4 (d, C-5, -8, -12, -15), 141.4 (s, C-3, -6, -11, -14), 147.3 (s, C-4′); IR (ATR): $\tilde{\nu}$=2956 (m), 2929 (m), 2868 (m), 2193 (w), 2151 (w), 1593 (vs), 1535 (m), 1506 (s), 1463 (w), 1363 (m), 1294 (w), 1246 (m), 1224 (m), 1180 (m), 1096 (s), 939 (w), 906 (w), 836 (vs), 804 (s), 755 (m), 722 cm^{-1} (m); UV (CH_2Cl_2): λ_{max} (lg ε)=246 (4.99), 262 (4.92), 358 (4.74), 422 nm (5.00); MS (EI): *m*/*z* (%): 1500 (18), 1501 (25), 1502 (20), 1503 (13), 1504 (7) [M^+], 1427 (6), 1428 (7), 1429 (5), 1277 (8), 1278 (8), 1279 (6), 73 (100).

PC/bis-DBA 10c: Polyyne **17c** (38 mg, 0.025 mmol) was subjected to general procedure D (35 mg, 0.25 mmol K_2CO_3; 200 mg, 1 mmol $Cu(OAc)_2{\cdot}H_2O$; 50 mL CH_3OH; 50 mL CH_3CN; 10 mL CH_2Cl_2). Purification by preparative thick layer chromatography (20% CH_2Cl_2 in pentane, R_f=0.6) yielded **10c** (20 mg, 0.017 mmol, 66%) as a yellow solid. M.p. ≈185 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.98 (ps-t, ^3J=7.4 Hz, 24H, $NCH_2CH_2CH_2CH_3$), 1.36 (ps-sextet, J=7.4 Hz, 16H, $NCH_2CH_2CH_2CH_3$), 1.54–1.70 (m, 16H, $NCH_2CH_2CH_2CH_3$), 3.05–3.16 (m, 4H, 1-, 2-, 9-, 10-H), 3.27–3.30 (m, 16H, $NCH_2CH_2CH_2CH_3$), 3.43–3.48 (m, 4H, 1-, 2-, 9-, 10-H), 6.61 (dd, $^3J_{5',6'}$=8.8 Hz, $^4J_{5',3'}$ not resolved, 4H, 5′-H), 6.72 (d, $^4J_{3',5'}$ not resolved, 4H, 3′-H), 7.14 (s, 4H, 5-, 8-, 12-, 15-H), 7.35 (d, $^3J_{6',5'}$=8.8 Hz, 4H, 6′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.0 (q, $NCH_2CH_2CH_2CH_3$), 20.3 (t, $NCH_2CH_2CH_2CH_3$), 29.4 (t, $NCH_2CH_2CH_2CH_3$), 33.1 (t, C-1, -2, -9, -10), 50.8 (t, $NCH_2CH_2CH_2CH_3$), 77.2 (s, C-10′), 82.7 (s, C-9′), 91.1 (s, C-8′), 93.6 (s, C-7′), 112.5 (d, C-5′), 113.3 (s, C-3′), 115.0 (d, C-1′), 124.4 (s, C-4, -7, -13, -16), 125.1 (s, C-2′), 133.4 (d, C-5, -8, -12, -15), 133.6 (d, C-6′), 142.5 (s, C-3, -6, -11, -14), 147.4 (s, C-4′); IR (ATR): $\tilde{\nu}$=2955 (m), 2928 (m), 2871 (m), 2187 (w), 1593

(vs), 1533 (m), 1504 (s), 1462 (m), 1366 (m), 1252 (w), 1217 (m), 1182 (w), 1110 (w), 1093 (m), 906 (w), 843 (w), 806 (m), 713 cm^{-1} (w); UV (CH_2Cl_2): λ_{max} (lg ε) = 232 (4.93), 292 (4.76), 330 (4.97), 346 (5.00), 366 (4.82), 452 nm (4.80); MS (MALDI-TOF): *m/z*: 1209.6, 1208.7, 1209.6, 1210.7, 1211.7, 1212.7, 1213.7.

1,2,4,5-Tetrakis(4′-*tert*-butyl-2′-[trimethylsilyl]ethynyl-phenylethynyl)benzene (19): KOH (500 mg, 9.0 mmol) was added to a solution of 1,2,4,5-Tetrakis[(trimethylsilyl)ethynyl]benzene[10] (**18**, 464 mg, 1.0 mmol) in Et_2O (10 mL) and CH_3OH (17 mL). The mixture was stirred overnight, acidified with 1 N HCl and extracted with Et_2O. The organic phase was dried with Na_2SO_4. The solution of 1,2,4,5-tetraethynylbenzene was concentrated to ca. 10 mL and subjected to general procedure B (178 mg; 5 mmol **13b**; 90 mg, 0.08 mmol [$Pd(PPh_3)_4$]; 15 mg, 0.08 mmol CuI; 50 mL THF; 60 mL *i*Pr_2NH). After stirring at 50 °C for 2 d, the solvents were evaporated and the residue purified by column chromatography on silica gel (10 % CH_2Cl_2 in pentane) to give **19** (427 mg, 0.39 mmol, 39 %) as a light yellow solid. M.p. 250 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.21 (s, 36 H, Si(CH_3)$_3$), 1.32 (s, 36 H, (CH_3)$_3$), 7.30 (dd, $^3J_{5',6'}$ = 8.3, $^4J_{5',3'}$ = 2.0 Hz, 4 H, 5′-H), 7.48 (d, $^3J_{6',5'}$ = 8.3 Hz, 4 H, 6′-H), 7.52 (d, $^4J_{3',5'}$ = 2.0 Hz, 4 H, 3′-H), 7.80 (s, 2 H, 3-H, 6-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 0.0 (q, Si(CH_3)$_3$), 31.1 (q, C(CH_3)$_3$), 34.8 (s, C(CH_3)$_3$), 90.6 (s, C-8′), 94.1 (s, C-7′), 98.2 (s, C-10′), 103.9 (s, C-9′), 123.1 (s, C-1′), 125.3 (s, C-1, -2, -4, -5), 125.4 (s, C-2′), 125.6 (d, C-5′), 129.2 (d, C-3′), 132.0 (d, C-6′), 135.6 (d, C-3, -6), 151.5 (s, C-4′); IR (ATR): $\tilde{\nu}$ = 2962 (m), 2903 (w), 2870 (w), 2156 (w), 1507 (m), 1464 (w), 1394 (w), 1363 (w), 1248 (m), 1203 (w), 1124 (w), 1087 (w), 930 (m), 895 (w), 834 (vs), 758 cm^{-1} (s); UV (CH_2Cl_2): λ_{max} (lg ε) = 228 (4.99), 232 (4.99), 237 (4.99), 268 (4.94), 333 (4.98), 364 (4.91), 385 nm (4.69); MS (EI): *m/z* (%): 1086 (38), 1087 (40), 1088 (25), 1089 (11), 1090 (6) [M^+], 1012 (16), 1013 (36), 1014 (42), 1015 (28), 1016 (12), 73 (100).

1,2,4,5-Tetrakis(4′-*tert*-butyl-2′-ethynyl-phenylethynyl)benzene: TMS protected polyyne **19** (136 mg, 0.13 mmol) in CH_2Cl_2 (4 mL) and CH_3OH (4 mL) was subjected to general procedure C (180 mg, 1.3 mmol K_2CO_3). The solvents were removed in vacuo and the residue dried in high vacuum to yield a pale yellow solid (96 mg, 0.12 mmol, 96 %). M.p. 91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.32 (s, 36 H, (CH_3)$_3$), 7.36 (dd, $^3J_{5',6'}$ = 8.3, $^4J_{5',3'}$ = 1.9 Hz, 4 H, 5′-H), 7.54 (d, $^3J_{6',5'}$ = 8.3 Hz, 4 H, 6′-H), 7.57 (d, $^4J_{3',5'}$ = 1.9 Hz, 4 H, 3′-H), 7.83 (s, 2 H, 3-H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 31.0 (q), 34.8 (s), 80.9 (d), 82.5 (s), 90.8 (s), 93.8 (s), 123.1 (s), 124.3 (s), 125.1 (s), 125.9 (d), 129.6 (d), 132.2 (d), 136.1 (d), 151.8 (s); IR (ATR): $\tilde{\nu}$ = 3286 (m), 2960 (m), 2903 (m), 2867 (m), 2112 (w), 1504 (m), 1463 (m), 1394 (m), 1362 (m), 1263 (m), 1189 (m), 1125 (m), 896 (m), 830 (s), 739 cm^{-1} (w); UV (CH_2Cl_2): λ_{max} (lg ε) = 231 (4.91), 261 (4.75), 331 (4.96), 364 nm (4.68); MS (ESI): *m/z* (%): 821 (100), 822 (65), 823 (22) [M^++Na].

***tert*-Butyl-bis[14]annulene (11)**: A solution of [Pd(dppe)Cl_2] (6 mg, 0.01 mmol), CuI (3 mg, 0.015 mmol) and I_2 (13 mg, 0.05 mmol) in THF (100 mL) and *i*Pr_2NH (100 mL) was heated to 60 °C. To this solution was added a solution of 1,2,4,5-tetrakis(4′-*tert*-butyl-2′-ethynylphenylethynyl)-benzene (80 mg, 0.1 mmol) in THF (50 mL) with a syringe pump over 1 d. Heating was continued for 1 d, the solvents were evaporated and the residue filtered through a pad of silica gel (50 % CH_2Cl_2 in pentane). Treatment of a CH_2Cl_2 solution with pentane (5 equiv) gave **11** (60 mg, 0.075 mmol, 75 %) as a yellow solid. M.p. ≈260 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.37 (s, 36 H, (CH_3)$_3$), 7.55 (dd, $^3J_{5',6'}$ = 8.3, $^4J_{5',3'}$ = 1.9 Hz, 4 H, 5′-H), 7.63 (d, $^4J_{3',5'}$ = 1.9 Hz, 4 H, 3′-H), 7.92 (d, $^3J_{6',5'}$ = 8.3 Hz, 4 H, 6′-H), 8.45 (s, 2 H, 3-, 6-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.1 (q, C(CH_3)$_3$), 35.0 (s, C(CH_3)$_3$), 79.8 (s, C-10′), 86.0 (s, C-9′), 92.3 (s, C-8′), 95.1 (s, C-7′), 122.6 (s, C-1, -2, -4, -5), 122.7 (s, C-2′), 126.4 (s, d, d, C-1′, -3′, -5′), 133.0 (d, C-6′), 143.1 (d, C-3, -6), 151.9 (s, C-4′); IR (ATR): $\tilde{\nu}$ = 2961 (vs), 2904 (m), 2868 (m), 2114 (w), 2176 (w), 1596 (m), 1506 (vs), 1485 (vs), 1468 (s), 1427 (m), 1395 (m), 1364 (s), 1256 (s), 1200 (m), 1128 (m), 1100 (m), 1024 (m), 925 (vs), 890 (vs), 737 cm^{-1} (m); UV (CH_2Cl_2): λ_{max} (lg ε) = 230 (5.09), 297 (5.06), 342 (5.32), 356 (5.29), 371 (5.01), 389 (4.99), 400 (4.76), 419 nm (4.22); MS (ESI, Ag^+): *m/z* (%): 901 (82), 902 (53), 903 (100), 904 (57), 905 (8) [M^++Ag].

1,4-Bis(4′-*tert*-butyl-2′-[trimethylsilyl]ethynylphenylethynyl)benzene (21b): 1,4-Diethynylbenzene[11] (**20**, 126 mg, 1.0 mmol) in THF (2 mL) was coupled with 4-*tert*-butyl-2-[(trimethylsilyl)ethynyl]iodo-benzene (**13b**, 843 mg, 2.5 mmol) in THF (5 mL) and *i*Pr_2NH (7 mL) as described in general procedure B (46 mg, 0.04 mmol [$Pd(PPh_3)_4$]; 7 mg, 0.04 mmol CuI). Column chromatography on silica gel (5 % dichloromethane in pentane, R_f = 0.07) gave **21b** (329 mg, 0.56 mmol, 56 %) as a colorless solid. M.p. 190 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.21 (s, 18 H, Si(CH_3)$_3$), 1.24 (s, 18 H, C(CH_3)$_3$), 7.25 (dd, $^3J_{5',6'}$ = 8.2, $^4J_{5',3'}$ = 2.0 Hz, 2 H, 5′-H), 7.36 (d, $^3J_{6',5'}$ = 8.2 Hz, 2 H, 6′-H), 7.45 (d, $^4J_{3',5'}$ = 2.0 Hz, 2 H, 3′-H), 7.45 (s, 4 H, 2-, 3-, 5-, 6-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.1 (q, Si(CH_3)$_3$), 31.0 (q, C(CH_3)$_3$), 34.8 (s, C(CH_3)$_3$), 90.3 (s, C-7′), 92.5 (s, C-8′), 97.9 (s, C-10′), 104.0 (s, C-9′), 123.0 (s, C-1′), 123.3 (s, C-1, -4), 125.3 (s, C-2′), 125.7 (d, C-5′), 129.3 (d, C-3′), 131.4 (d, C-6′), 131.5 (d, C-2, -3, -5, -6), 151.5 (s, C-4′); IR (ATR): $\tilde{\nu}$ = 2956 (m), 2900 (w), 2867 (w), 2158 (m), 1512 (m), 1479 (w), 1462 (w), 1396 (m), 1363 (w), 1243 (m), 1204 (w), 1087 (w), 927 (m), 897 (w), 835 (vs), 756 cm^{-1} (s); UV (CH_2Cl_2): λ_{max} (lg ε) = 255 (4.49), 263 (4.63), 291 (4.16), 342 (4.63), 364 nm (4.47); MS (EI): *m/z* (%): 582 (100), 583 (54), 584 (19) [M^+], 567 (18), 276 (19), 221 (15), 145 (25), 73 (26); elemental analysis calcd (%) for $C_{40}H_{46}Si_2$ (582.95): C 82.41, H 7.95, Si 9.64; found C 82.13, H 8.09.

1,4-Bis(4′-*tert*-butyl-2′-ethynylphenylethynyl)benzene (22b): TMS protected polyyne **21b** (145 mg,0.25 mmol) in CH_2Cl_2 (7.5 mL) and CH_3OH (7.5 mL) was subjected to general procedure C (276 mg, 2 mmol K_2CO_3). The solvents were removed in vacuo and the residue dried in high vacuum to yield **22b** (101 mg, 0.23 mmol, 92 %) as a colorless solid. M.p. 168 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 18 H, C(CH_3)$_3$), 3.35 (s, 2 H, C≡C-*H*), 7.36 (dd, $^3J_{5',6'}$ = 8.3, $^4J_{5',3'}$ = 2.0 Hz, 2 H, 5′-H), 7.47 (d, $^3J_{6',5'}$ = 8.3 Hz, 2 H, 6′-H), 7.52 (s, 4 H, 2-, 3-, 5-, 6-H), 7.56 (d, $^4J_{3',5'}$ = 2.0 Hz, 2 H, 3′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.0 (q, CCH_3), 34.8 (s, $C$$CH_3$), 80.5 (d, C-10), 82.7 (s, C-9), 89.9 (s, C-7), 92.6 (s, C-8), 123.2 (s, C-1′ or C-1, -4), 123.3 (s, C-1, -4 or C-1′), 124.3 (s, C-2′), 126.0 (d, C-5′), 129.7 (d, C-3′), 131.6 (C-6′), 131.6 (d, C-2, -3, -5, -6), 151.6 (s, C-4′); IR (ATR): $\tilde{\nu}$ = 3274 (s), 3061 (w), 3039 (w), 2955 (m), 2899 (m), 2861 (m), 2111 (w), 2109 (w), 1908 (w), 1783 (w), 1507 (m), 1472 (m), 1397 (m), 1361 (m), 1261 (m), 1188 (m), 1123 (w), 1098 (w), 897 (s), 828 (s), 741 cm^{-1} (m); UV (CH_2Cl_2): λ_{max} (lg ε) = 286 (4.47), 318 (4.06), 330 (4.52), 338 (4.61), 338 (4.7), 360 nm (4.52); MS (EI): *m/z* (%): 440 (7), 439 (34), 438 (100) [M^+], 425 (4), 424 (18), 423 (52); elemental analysis calcd (%) for $C_{34}H_{30}$ (438.61): C 93.11, H 6.89; found C 93.05, H 6.91.

***tert*-Butyl-annulene 12b**: Polyyne **22b** (329 mg, 0.75 mmol) in pyridine/Et_2O (90 mL/30 mL) was dimerized as described in general procedure E (900 mg, 4.5 mmol $Cu(OAc)_2 \cdot H_2O$; 190 mL pyridine; 65 mL Et_2O). Column chromatography on silica gel (20 % dichloromethane in pentane) gave **12b** (25 mg, 0.03 mmol, 8 %) as a colorless solid. M.p. 170 °C (decomp). Single crystals suitable for X-ray structure analysis were obtained by slow diffusion of methanol into a dichloromethane solution of **12b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 36 H, C(CH_3)$_3$), 7.28 (s, 8 H, 2-, 3-, 5-, 6-, 8-, 9-, 11-, 12-H), 7.38 (dd, $^3J_{5',6'}$ = 8.3, $^4J_{5',3'}$ = 1.9 Hz, 4 H, 5′-H), 7.44 (d, $^3J_{6',5'}$ = 8.3 Hz, 4 H, 6′-H), 7.59 (d, $^4J_{3',5'}$ = 1.9 Hz, 4 H, 3′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.0 (q, CCH_3), 34.8 (s, $C$$CH_3$), 77.5 (s, C-10′), 81.6 (s, C-9′), 89.3 (s, C-7′), 93.9 (s, C-8′), 122.6 (s, C-1, -4, -7, -10), 124.6 (s, C-2′), 124.6 (s, C-1′), 126.4 (d, C-5′), 129.3 (d, C-3′), 131.1 (d, C-6′), 131.5 (d, C-2, -3, -5, -6, -8, -9, -11, -12), 151.5 (s, C-4′); IR (ATR): $\tilde{\nu}$ = 2957 (m), 2926 (m), 2901 (m), 2866 (m), 2215 (w), 1909 (w), 1594 (w), 1512 (m), 1460 (m), 1393 (m), 1363 (m), 1254 (m), 2101 (m), 1126 (m), 1099 (m), 1018 (m), 891 (m), 828 (vs), 736 cm^{-1} (m); UV (CH_2Cl_2): λ_{max} (lg ε) = 304 (5.05), 330 (4.96), 360 nm (4.73); MS (MALDI-TOF): *m/z*: 872.3, 873.3, 874.3 [M^+].

1,4-Bis(4′-*N*,*N*-dibutylamino-2′-[trimethylsilyl]ethynylphenylethynyl)benzene (21c): 1,4-Diethynylbenzene (**20**, 189 mg, 1.5 mmol) in THF (1.5 mL) was coupled with *N*,*N*-dibutyl-4-iodo-3-[(trimethylsilyl)-ethynyl]aniline (**13c**, 1.513 g, 3.75 mmol) as described in general procedure B (69 mg, 0.06 mmol [$Pd(PPh_3)_4$]; 11 mg, 0.06 mmol CuI; 4 mL THF; 5.5 mL *i*Pr_2NH). Column chromatography on silica gel (20 % CH_2Cl_2 pentane, R_f = 0.1) gave **21c** (428 mg, 0.59 mmol, 39 %) as a yellow solid. M.p. 140–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.29 (s, 18 H, Si-(CH_3)$_3$), 0.94 (ps-t, ^3J = 7.4 Hz, 12 H, $NCH_2CH_2CH_2CH_3$), 1.32 (ps-sextet, ^3J = 7.4 Hz, 8 H, $NCH_2CH_2CH_2CH_3$), 1.52 (ps-q, ^3J = 7.5 Hz, 8 H, $NCH_2CH_2CH_2CH_3$), 3.22 (ps-t, ^3J = 7.6 Hz, 8 H, $NCH_2CH_2CH_2CH_3$), 6.52

(dd, $^3J_{5',6'}=8.9$, $^4J_{5',3'}=2.7$ Hz, 2H, 5′-H), 6.71 (d, $^4J_{3',5'}=2.7$ Hz, 2H, 3′-H), 7.31 (d, $^3J_{6',5'}=8.9$ Hz, 2H, 6′-H), 7.47 (s, 4H, 2-, 3-, 5-, 6-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=0.1$ (q, Si(CH_3)$_3$), 13.9 (q, $NCH_2CH_2CH_2CH_3$), 20.2 (t, $NCH_2CH_2CH_2CH_3$), 29.3 (t, $NCH_2CH_2CH_2CH_3$), 50.4 (t, $NCH_2CH_2CH_2CH_3$), 90.8 (s, C-8′), 91.3 (s, C-7′), 96.6 (s, C-10′), 104.7 (s, C-9′), 111.8 (s, C-1′), 111.9 (d, C-5′), 114.6 (d, C-3′), 123.2 (s, C-1, C-4), 126.4 (s, C-2′), 130.9 (d, C-2, -3, -5, -6), 132.7 (d, C-6′), 147.5 (s, C-4′); IR (ATR): $\tilde{\nu}=2956$ (m), 2929 (m), 2894 (m), 2872 (m), 2857 (m), 2204 (m), 2152 (m), 1593 (vs), 1534 (m), 1515 (s), 1493 (m), 1463 (m), 1427 (m), 1399 (m), 1386 (m), 1295 (m), 1247 (m), 1221 (m), 1182 (m), 1097 (s), 940 (w), 905 (w), 833 (vs), 803 (s), 753 cm^{-1} (m); UV (CH_2Cl_2): λ_{max} (lg ε)=258 (4.56), 266 (4.57), 300 (4.05), 360 (4.48), 402 nm (4.67); MS (EI): m/z (%): 724 (100), 725 (24) [M^+], 681 (20), 639 (16), 319 (14), 277 (15), 73 (10) [$SiMe_3^+$]; elemental analysis calcd (%) for $C_{48}H_{64}N_2Si_2$ (725.22): C 79.50, H 8.90, N 3.86, Si 7.74; found C 79.17, H 9.13, N 3.86.

1,4-Bis(4′-*N*,*N*-dibutylamino-2′-ethynyl-phenylethynyl)benzene (22c): TMS-protected polyyne **21c** (181 mg, 0.25 mmol) was subjected to general procedure C (276 mg, 2 mmol K_2CO_3; 7.5 mL CH_2Cl_2; 7.5 mL CH_3OH). The solvents were removed in vacuo and the residue was dried in high vacuum to yield **21c** (132 mg, 0.23 mmol, 91%) as a yellow solid. M.p. 128°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.94$ (ps-t, $J=7.3$ Hz, 12H, $NCH_2CH_2CH_2CH_3$), 1.33 (sextet, $J=7.5$ Hz, 8H, $NCH_2CH_2CH_2CH_3$), 1.50–1.57 (m, 8H, $NCH_2CH_2CH_2CH_3$), 3.24 (t, $J=7.6$ Hz, 8H, $NCH_2CH_2CH_2CH_3$), 3.28 (s, 2H, 10-H), 6.55 (dd, $^3J_{5',6'}=8.9$, $^4J_{5',3'}=2.7$ Hz, 4H, 5′-H), 6.74 (d, $^4J_{3',5'}=2.7$ Hz, 4H, 3′-H), 7.32 (d, $^3J_{6',5'}=8.9$ Hz, 4H, 6′-H), 7.45 (s, 4H, 2-, 3-, 5-, 6-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.9$ (q, $NCH_2CH_2CH_2CH_3$), 20.2 (t, $NCH_2CH_2CH_2CH_3$), 29.3 (t, $NCH_2CH_2CH_2CH_3$), 50.6 (t, $NCH_2CH_2CH_2CH_3$), 79.5 (d, C-10′), 83.3 (s, C-9′), 90.9 (s, C-7′, C-8′), 111.9 (s, C-1′), 112.2 (d, C-5′), 115.0 (d, C-3), 132.2 (s, C-4, C-5), 125.4 (s, C-2′), 131.1 (d, C-2, -3, -5, -6), 132.9 (d, C-6′), 147.6 (s, C-4′); IR (ATR): $\tilde{\nu}=3292$ (m), 2957 (m), 2928 (m), 2873 (m), 2859 (m), 2201 (m), 2107 (w), 1593 (vs), 1534 (m), 1516 (s), 1463 (m), 1425 (w), 1399 (m), 1369 (s), 1292 (m), 1257 (m), 1221 (m), 1179 (m), 1091 (s), 1015 (w), 941 (w), 880 (w), 836 (vs), 807 (vs), 746 cm^{-1} (w); UV (CH_2Cl_2): λ_{max} (lg ε)=241 (4.58), 249 (4.56), 298 (4.17), 359 (4.58), 397 (4.8), 406 nm (4.78); MS (EI): m/z (%): 580 (100), 581 (45) [M^+], 539 (12), 537 (36), 495 (23), 395 (17), 247 (17), 226 (14), 205 (19), 198 (12), 86 (27); elemental analysis calcd (%) for $C_{42}H_{48}N_2$ (580.85): C 86.85, H 8.33, N 4.82; found C 86.45, H 8.37, N 4.57.

Tetrakis-*N*,*N*-dibutylaminoannulene 12c: Polyyne **22c** (153, 0.26 mmol) in pyridine/Et_2O (38 mL/12 mL) was dimerized as described in general procedure E (312 mg, 1.56 mmol $Cu(OAc)_2\cdot H_2O$; 95 mL pyridine; 30 mL Et_2O). Preparative thick layer chromatography on ALOX (20% Et_2O in pentane $R_f=0.33$) gave **12c** (23 mg, 0.02 mmol, 15%) as a yellow solid (m.p. 248–250°C). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.94$ (ps-t, $J=7.3$ Hz, 12H, $NCH_2CH_2CH_2CH_3$), 1.33 (sextet, $J=7.5$ Hz, 8H, $NCH_2CH_2CH_2CH_3$), 1.50–1.57 (m, 8H, $NCH_2CH_2CH_2CH_3$), 3.24 (t, $J=7.6$ Hz, 8H, $NCH_2CH_2CH_2CH_3$), 6.52 (dd, $^3J_{5',6'}=8.9$, $^4J_{5',3'}=2.7$ Hz, 4H, 5′-H), 6.70 (d, $^4J_{3',5'}=2.7$ Hz, 4H, 3′-H), 7.15 (s, 4H, 2-, 3-, 5-, 6-, 8-, 9-, 11-, 12-H), 7.24 (d, $^3J_{6',5'}=8.9$ Hz, 4H, 6′-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$ (q, $NCH_2CH_2CH_2CH_3$), 20.3 (t, $NCH_2CH_2CH_2CH_3$), 29.4 (t, $NCH_2CH_2CH_2CH_3$), 50.8 (t, $NCH_2CH_2CH_2CH_3$), 76.8 (s, C-10′), 81.9 (s, C-9′), 89.9 (s, C-7′), 92.2 (s, C-8′), 113.7 (s, C-1′), 112.5 (d, C-5′), 114.5 (d, C-3′), 122.6 (s, C-1, C-4, C-7, C-10), 125.7 (s, C-2′), 131.0 (d, C-2, -3, -5, -6, -8, -9, -11, -12), 132.4 (d, C-6′), 147.4 (s, C-4′); IR (ATR): $\tilde{\nu}=$ 3078 (m), 3044 (s), 2853 (m), 2208 (w), 1718 (m), 1591 (vs), 1535 (m), 1515 (s), 1493 (m), 1458 (m), 1397 (w), 1364 (s), 1279 (m), 1254 (m), 1216 (s), 1183 (w), 1124 (m), 1092 (s), 1016 (w), 926 (w), 832 (m), 804 (m), 725 cm^{-1} (m); UV (CH_2Cl_2): λ_{max} (lg ε)=234 (4.75), 304 (4.67), 324 (4.73), 344 (4.75), 368 (4.74), 420 nm (4.54); MS (MALDI-TOF): m/z: 1156.7, 1157.7, 1158.7, 1159.7 [M^+].

1,12-Diphenyldodeca-3,9-dien-1,5,7,11-tetrayne (32): $Cu(OAc)_2$ (1.96 g, 10.8 mmol), CuCl (1.07 g, 10.8 mmol), and K_2CO_3 (1.49 g, 10.8 mmol) were added to a solution of 1-phenyl-6-(trimethylsilyl)hexa-3-en-1,5-diyne[24] (80 mg, 0.36 mmol) in pyridine (18 mL) and CH_3OH (18 mL). The dark blue-green reaction mixture was stirred overnight at 50°C. The cooled slurry was diluted with Et_2O, washed with 10% HCl solution, dried ($MgSO_4$), and filtered. Chromatography on silica gel (10% CH_2Cl_2 in hexanes) provided **32** (50 mg, 92%) as a yellow solid. M.p. 77–80°C; ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=6.02$ (d, $J=10.5$, 2H), 6.25 (d, $J=10.5$, 2H), 7.29–7.37 (m, 6H), 7.47–7.50 (m, 4H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta=81.5$, 82.4, 87.4, 99.5, 118.3, 123.0, 123.7, 129.0, 129.5, 132.4; IR (neat): $\tilde{\nu}=3079$, 3141, 2968, 2925, 2852, 2200, 2174, 2121, 1597, 1576, 1554, 1488, 1442, 1389, 1069, 1032, 916, 755, 742 cm^{-1}; UV (CH_2Cl_2): λ_{max} (log ε)= 230 (4.40), 266 (4.21), 294 (4.31), 306 (4.35), 319 (4.31), 348 (4.35), 369 nm (4.34); MS (FAB): m/z: 302 (100) [M^+], 154 (78), 136 (88).

X-ray structure determinations: Numerical details are presented in Table 1.

Table 1. Details of X-ray structure analyses of **4** and **12b**.

Compound	**4**	**12b**
formula	$C_{24}H_{16}$	$C_{68}H_{56}$
M_r	304.37	873.13
habit	colorless tablet	pale brown prism
crystal size [mm]	0.2×0.2×0.13	0.45×0.3×0.3
crystal system	orthorhombic	monoclinic
space group	$Pna2_1$	$C2/c$
cell constants		
a [Å]	13.7087(16)	24.185(3)
b [Å]	9.4745(12)	14.024(2)
c [Å]	12.7205(16)	16.621(2)
α [°]	90	90
β [°]	90	111.143(5)
γ [°]	90	90
V [Å^3]	1652.2	5258.1
Z	4	4
ρ [Mg m^{-3}]	1.224	1.103
μ [mm^{-1}]	0.07	0.06
F(000)	640	1856
T [°C]	−140	−140
$2\theta_{max}$	60	60
no. reflections		
measured	18176	29739
independent	2524	7679
R_{int}	0.030	0.080
parameters	233	313
$wR(F^2$, all refl.)	0.092	0.151
$R(F, >4\sigma(F))$	0.033	0.051
S	1.06	1.02
max. $\Delta\rho$ [e Å^{-3}]	0.27	0.31

Data collection: Crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCDC). Measurements were performed with monochromated $Mo_{K\alpha}$ radiation.

Structure refinement: The structures were refined anisotropically against F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model.

Special features and exceptions: For compound **13**, which crystallizes in a non-centrosymmetric space group, Friedel opposite reflections were merged because of the lack of significant anomalous scattering. Its acetylenic hydrogens were refined freely but with C–H bond lengths restrained to be equal.

CCDC-603577 (**4**), -603576 (**12b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We are grateful to Dr. M. Nimtz, GBF Braunschweig, Germany, for recording the MALDI-TOF mass spectra. Financial support from the Fonds der Chemischen Industrie, and the Petroleum Research Fund, administered by the American Chemical Society is gratefully acknowledged. H. Hinrichs thanks the Förderverein der Freunde des Instituts für Organische Chemie an der Technischen Universität Braunschweig for a travel grant.

[1] a) J. Chen, M. A. Reed, S. M. Dirk, D. W. Prince, A. M. Realett, J. M. Tour, D. S. Grubisha, D. W. Bennet, *NATO Sci. Ser. II: Math. Phys. Chem.* **2003**, *96*, 59–195; b) B. Domerco, R. D. Hreha, Y.-D. Zhang, A. Haldi, S. Barlow, S. R. Marder, B. J. Kippelen, *J. Polym. Sci. Part B* **2003**, *41*, 2726–2732; c) Y. Shirota, *J. Mater. Chem.* **2000**, *10*, 1–25; d) S. A. Jenekhe, K. J. Wynne, *Photonic and Optoelectronic Polymers*, American Chemical Society, Washington, DC, **1995**; e) Special Issue: *Chem. Rev.* **1994**, *94*, 1–278; f) W. R. Lunström, I. Salaneck, B. Rånby, *Conjugated Polymers and Related Materials. The Interconnection of Chemical and Electronic Structure*, Oxford University Press, Oxford, **1993**; g) M. B. Nielsen, F. Diederich in *Modern Arene Chemistry* (Ed.: D. Astruc), Wiley-VCH, Weinheim, Germany, **2002**, pp. 196–216; h) J. Cornil, D. Beljonne, J.-P. Calbert, J.-L. Brédas, *Adv. Mater.* **2001**, *13*, 1053–1067.

[2] a) A. T. Balaban, M. Banciu, V. Ciorba, *Annulenes, Benzo-, Hetero-, Homo-Derivatives and Their Valence Isomers, Vol. 1–3*, CRC, Boca Raton, FL, **1987**; b) H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, Germany, **2000**; c) F. Diederich, P. J. Stang, R. R. Tykwinski, *Acetylene Chemistry: Chemistry, Biology and Material Science*, Wiley-VCH, Weinheim, Germany, **2005**; d) M. M. Haley, R. R. Tykwinski, *Carbon-Rich Compounds: From Molecules to Materials*, Wiley-VCH, Weinheim, Germany, **2006**.

[3] L. Bondarenko, I. Dix, H. Hinrichs, H. Hopf, *Synthesis* **2004**, 2751–2759.

[4] M.-K. Leung, M. B. Viswanath, P.-T. Chou, S.-C. Pu, H.-C. Lin, B.-Y. Jin, *J. Org. Chem.* **2005**, *70*, 5360–5368.

[5] S. K. Collins, G. P. A. Yap, A. G. Fallis, *Org. Lett.* **2000**, *2*, 3189–3192.

[6] R. H. Mitchell, *Chem. Rev.* **2001**, *101*, 1301–1315.

[7] J. M. Kehoe, J. H. Kiley, J. J. English, C. A. Johnson, R. C. Petersen, M. M. Haley, *Org. Lett.* **2000**, *2*, 969–972.

[8] M. M. Haley, M. L. Bell, S. C. Brand, D. B. Kimball, J. J. Pak, W. B. Wan, *Tetrahedron Lett.* **1997**, *38*, 7483–7486.

[9] a) J. A. Marsden, J. J. Miller, M. M. Haley, *Angew. Chem.* **2004**, *116*, 1726–1729; *Angew. Chem. Int. Ed.* **2004**, *43*, 1694–1697; b) J. A. Marsden, J. J. Miller, L. D. Shirtcliff, M. M. Haley, *J. Am. Chem. Soc.* **2005**, *127*, 2464–2476; c) C. A. Johnson, E. Rather, F. Han, T. J. R. Weakley, M. M. Haley, *Organometallics* **2005**, *24*, 1161–1172.

[10] B. C. Berris, G. H. Hovakeemian, Y.-H. Lai, H. Mestdagh, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1985**, *107*, 5670–5687.

[11] J. A. Tour, A. M. Rawlett, M. Kozaki, Y. Yao, R. C. Jagessar, S. M. Dirk, D. W. M. Price, M. A. Reed, C.-W. Zhou, J. Chen, W. Wang, I. Campbell, *Chem. Eur. J.* **2001**, *7*, 5118–5134.

[12] a) M. Laskoski, J. Roidl, H. L. Ricks, J. G. M. Morton, M. D. Smith, U. H. F. Bunz, *J. Organomet. Chem.* **2003**, *673*, 13–24; b) M. Laskoski, M. D. Smith, J. G. M. Morton, U. H. F. Bunz, *J. Org. Chem.* **2001**, *66*, 5174–5181; c) M. Laskoski, G. Roidl, M. D. Smith, U. H. F. Bunz, *Angew. Chem.* **2001**, *113*, 1508–1511; *Angew. Chem. Int. Ed.* **2001**, *40*, 1460–1463; d) M. Laskoski, W. Steffen, M. D. Smith, U. H. F. Bunz, *Chem. Commun.* **2001**, 691–692.

[13] W. B. Wan, M. M. Haley, *J. Org. Chem.* **2001**, *66*, 3893–3901.

[14] J. Zhang, D. J. Pesak, J. L. Ludwick, J. S. Moore, *J. Am. Chem. Soc.* **1994**, *116*, 4227–4239.

[15] J. J. Pak, T. J. R. Weakley, M. M. Haley, *J. Am. Chem. Soc.* **1999**, *121*, 8182–8192.

[16] S. Kajigaeshi, T. Kakinami, H. Yamasaki, S. Fujisaki, T. Okamoto, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 600–602.

[17] D. Chemin, G. Linstrumelle, *Tetrahedron* **1994**, *50*, 5335–5344.

[18] H. Hinrich, A. K. Fischer, P. G. Jones, H. Hopf, M. M. Haley, *Org. Lett.* **2005**, *7*, 3793–3795.

[19] a) R. Herges, D. Geuenich, *J. Phys. Chem. A* **2001**, *105*, 3214–3220; b) D. Geuenich, K. Hess, F. Koehler, R. Herges, *Chem. Rev.* **2005**, *105*, 3758–3722.

[20] K. P. Baldwin, A. J. Matzger, D. A. Scheiman, C. A. Tessier, K. P. C. Vollhardt, W. J. Youngs, *Synlett* **1995**, 1215–1218.

[21] H. S. Rzepa, *Org. Lett.* **2005**, *7*, 4637–4639.

[22] a) D. Ajami, O. Oeckler, A. Simon, R. Herges, *Nature* **2003**, *426*, 819–821; b) H. S. Rzepa, *Chem. Rev.* **2005**, *105*, 3697–3715; c) D. Ajami, K. Hess, F. Köhler, C. Näther, O. Oeckler, A. Simon, C. Yamamoto, R. Herges, *Chem. Eur. J.* **2006**, *12*, 5434–5445; d) E. Heilbronner, *Tetrahedron Lett.* **1964**, 1923–1928.

[23] A. J. Boydston, L. Bondarenko, I. Dix, T. J. R. Weakley, H. Hopf, M. M. Haley, *Angew. Chem.* **2001**, *113*, 3074–3077; *Angew. Chem. Int. Ed.* **2001**, *40*, 2986–2989.

[24] J. Uenishi, R. Kawahama, O. Yonemitsu, J. Tsuji, *J. Org. Chem.* **1996**, *61*, 5716–5717.

Received: April 7, 2006
Published online: August 7, 2006

