Synthesis of New Cyclic Homoconjugated Oligodiacetylenes

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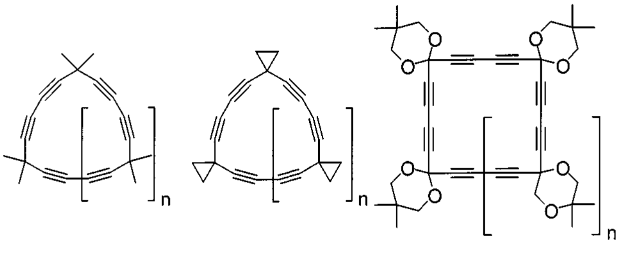
Keywords: Alkynes / Acetylenes / Conjugation / Pericyclynes

Cyclic homoconjugated oligodiacetylenes, consisting of butadiyne subunits interconnected with two different sp^3-linkers in alternation, were synthesized by coupling of different 1,4-pentadiyne synthons. The "exploded" [4]pericyclyne **7** was obtained in a "one-pot" random cyclodehydro-oligomerization reaction, by cross-coupling of two different 1,4-pentadiyne units. Larger ring structures such as the C_{30} macrocyclic [6]pericyclyne **22** and the unsymmetrically diyne-tetrayne expanded C_{24}-[4]pericyclyne **27** afforded a stepwise approach. Heterocoupling of two different 1,4-pentadiynes in a molecular ratio of 1:2 and 2:1 afforded the symmetrical pentadecahexaynes **12** and **20**, respectively. Cyclodehydrodimerization gave the symmetrically patterned cyclotriacontadodecayne **22**. A collective heterocoupling of two different 1,4-pentadiynes with TIPS-acetylene resulted in the formation of acyclic dodecapentayne **26**. Final cyclodimerization yielded the cyclotetracosadecayne **27**.

Introduction

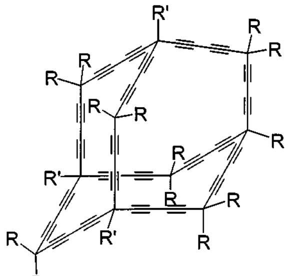
In 1990 Scott et al. prepared the first cyclic homoconjugated oligodiacetylenes **1**.[1] These macrocycles, which were termed expanded or "exploded" pericyclynes, consist of a cyclic arrangement of conjugated butadiyne units and saturated sp^3-fragments joined together in alternation. This first report stimulated other research groups to synthesize similar systems such as **2** and **3**, and to study the cyclic homoconjugation and electronic properties of this class of compounds[2−5] (Figure 1).



1 n = 1-4 **2** n = 3-9, 11 **3** n = 1-5

Figure 1. "Exploded" [*n*]pericyclynes synthesized by the groups of Scott (**1**),[1] de Meijere (**2**),[2] and Bunz (**3**)[3]

Whereas the compounds **1−3** possess butadiyne subunits interconnected by structurally identical sp^3-links, the compounds that were the goal of this project were cyclic homoconjugated oligobutadiynes with two different sp^3-links arranged in alternation. The possibility of distinguishing between the vicinal sp^3-connectors of the butadiynes makes these molecules potential precursor systems for the synthesis of carbon-rich cage molecules such as the "superadamantane" structure **4**.[6a] In **4**, each of the single bonds of the adamantane scaffold is replaced by a butadiyne unit.



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Results and Discussion

"One-Pot" Synthesis of an "Exploded" [4]Pericyclyne 7

As a first example of an oligoacetylene macrocycle we synthesized the cycloeicosaoctayne **7**. A simple approach to this new class of "exploded" pericyclynes is a "one-pot" random cyclodehydro-oligomerization reaction by cross-coupling of two different pentadiynes,[3,6] in order to form a macrocycle such as **7** (Scheme 1) under Cadiot−Chodkiewicz conditions.[7] For this purpose, 1,5-dibromo-3,3-dimethyl-1,4-pentadiyne (**6**),[8] obtained by NBS bromination of the corresponding TMS-protected pentadiyne, and 1,5-bistrimethylsilyl-1,4-pentadiyne **5**[3] were dissolved in pyridine and coupled by use of copper(I) iodide. The TMS protecting groups were cleaved in situ by very slow addition of a KF/18-crown-6/THF solution to keep the concentration of free acetylene functions low, in order to suppress homocoupling. After aqueous workup, extraction, and column chromatography, a white solid was obtained, and was precipitated from chloroform to furnish the four-membered macrocycle **7** in 1.2% yield, as small white needles (Scheme 1).

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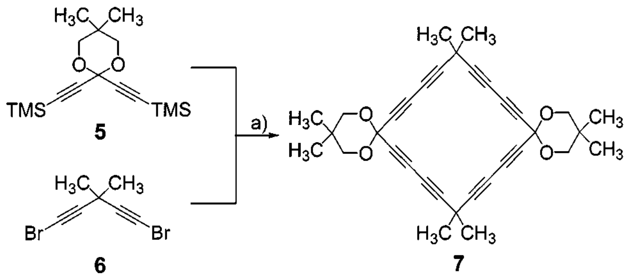
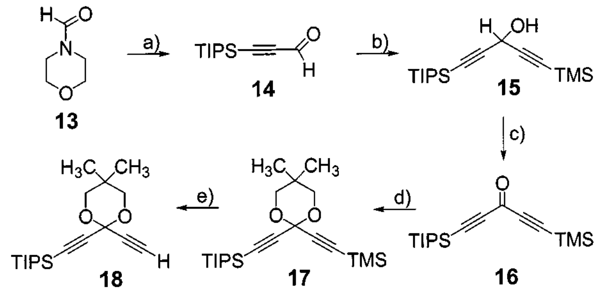


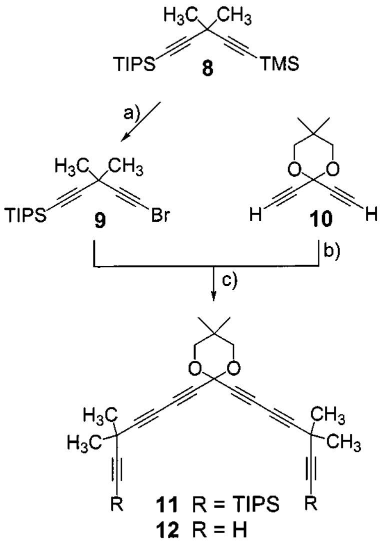
Scheme 1. One-pot synthesis of the "exploded" [4]pericyclyne **7**: a) CuI, pyridine; KF, 18-crown-6, THF



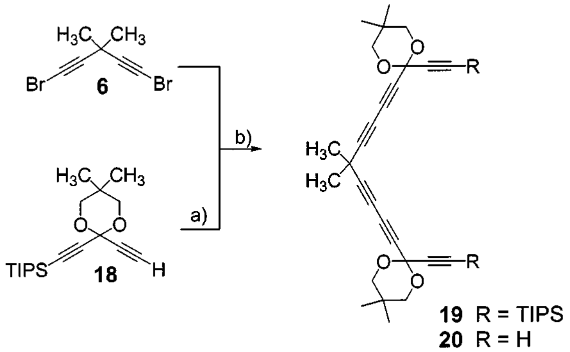
Scheme 3. a) LiC≡CTIPS; b) TMSC≡CMgBr; c) $K_2Cr_2O_7$, H_2SO_4; d) 2,2-dimethylpropane-1,3-diol, *p*TosOH; e) K_2CO_3, MeOH

The EI mass spectrum of the "exploded" [4]pericyclyne **7** shows the molecular ion peak M^+ at $m/z = 504$, corresponding to $C_{34}H_{32}O_4$. The ^{13}C NMR spectrum of **7** has the expected ten signals for this macrocycle. The sp-C atoms of the butadiyne units resonate at $\delta = 64.76, 70.09, 74.59$ and 86.17. In the ^1H NMR spectrum of **7**, the two singlets of the different methyl groups appear at $\delta = 0.94$ [diox(CH_3)$_2$] and $\delta = 1.48$ [C(CH_3)$_2$], respectively. The methylene protons of the dioxane ring produce a signal at $\delta = 3.64$. In the IR spectrum, two −C≡C− valence stretching modes are found at 2262 and 2169 cm^{-1}. The UV/Vis spectrum of **7** is characterized by typical absorption bands at 227, 237, 251, and 267 nm, also found in the pericyclynes **1−3** with identical sp^3-links.[1,2,3]

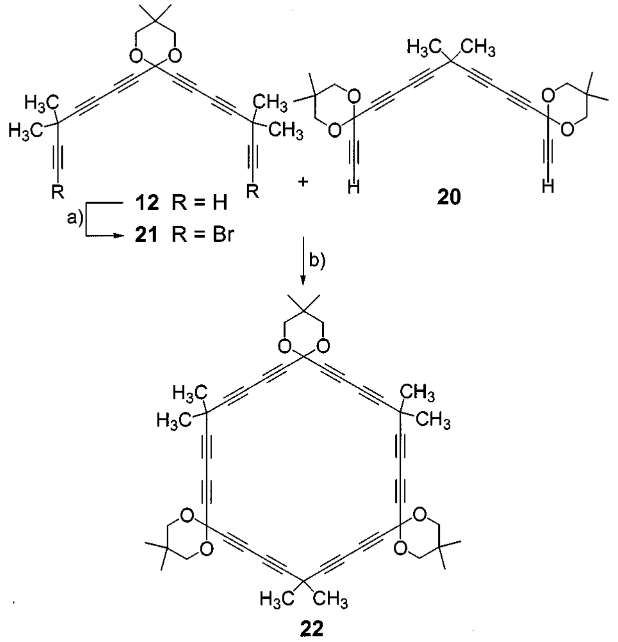
Synthesis of an "Exploded" [6]Pericyclyne 22



Scheme 2. Syntheses of the macrocycle precursor **12**: a) $AgNO_3$, NBS; b) *n*BuLi, THF; CuCl; c) pyridine



Scheme 4. a) *n*BuLi, THF; CuCl; b) pyridine



Scheme 5. Synthesis of **22** from the two diametrically constructed building blocks **20** and **21**: a) NBS, $AgNO_3$; b) *n*BuLi, THF; CuCl, pyridine

The one-pot approach was not successful for the synthesis of the corresponding "exploded" [6]pericyclyne **22**, containing a C_{30} macrocycle. We therefore elaborated a stepwise synthesis (Scheme 2−5). The final step was the cyclodehydro-dimerization of the two diametrically constructed 1,4,6,9,11,14-pentadecahexaynes **12** and **20** (Scheme 5). The bis-TIPS-protected building block **11** was obtained by heterocoupling of 1-bromo-3,3-dimethyl-5-triisopropylsilyl-1,4-pentadiyne (**9**), derived from the unsymmetrically TIPS/TMS-protected pentadiyne precursor **8**, with 2,2-diethynyldioxane **10** under high dilution conditions. Compound **8** was obtained by alkylation of the magnesium acetylide of TIPS-acetylene with 3-chloro-3-methyl-1-trimethylsilyl-1-butyne.[1a,9] After cleavage of the protecting groups of **8** with TBAF in THF and purification by column chromatography, the pentadecahexayne **12**, representing one half of the macrocycle, was obtained in 92% yield as a colorless oil (Scheme 2). The synthesis of the second building block **20**, representing the other half of the C_{30}-macrocycle, was achieved by a twofold heterocoupling of the 1,5-dibromopentadiyne **6** with two equivalents of mono-TIPS-protected dioxane-pentadiyne **18** (Scheme 4). For the lithiation of **18**, lithium TIPS-acetylene was acylated with 4-formylmorpholine **13** to give TIPS-propiolic aldehyde **14** (Scheme 3). Grignard coupling with trimethylsilylethyne afforded the TIPS/TMS-protected pentadiynol **15**, which was subsequently oxidized to the unsymmetrically disilylated diethynylketone **16**. Ketalization with 2,2-dimethylpropanediol in boiling benzene afforded **17** in $> 90\%$ yield. Specific deprotection of the TMS group resulted in the formation of **18** as a clear oil (61% yield) (Scheme 3). The final double cross-coupling of the precursors **6** and **18** was performed under the conditions described above (Scheme 4). The doubly TIPS-protected pentadecahexayne **19** was obtained in 58% yield as a colorless oil. Deprotection and chromatographic purification afforded the hexayne building block **20** as a light brown resin (Scheme 4).

All the compounds were completely characterized by ^{1}H NMR, ^{13}C NMR, DEPT NMR, FTIR, and UV/Vis spectroscopy and mass spectrometry. The chemical shifts of the 1,4,6,9,11,14-pentadecahexaynes **11** and **12** are shown in Table 1. Two doublets ($J = 11.8$ Hz) for the methylene protons, at $\delta = 3.57$ and $\delta = 3.85$, appear in the ^{1}H NMR spectrum of **18**, indicating the loss of the C_{2v} symmetry. The acetylenic sp-proton resonates at $\delta = 2.62$. The FT-IR spectrum of **20** shows, in addition to the two C≡C bands at 2262 and 2159 cm^{-1}, a band for the ≡C−H vibrations at 3285 cm^{-1}. A characteristic feature of these compounds is the presence of two ^{13}C signals, at $\delta = 22.14$ and $\delta = 22.37$, for the two different dioxane methyl groups. The ^{13}C chemical shifts of the remaining C atoms in **20** are listed in Table 1. The ^{1}H NMR spectrum has a singlet for the terminal acetylene protons found at $\delta = 2.23$. For the methylene protons of the dioxane ring, two doublets ($J = 11.5$ Hz) appear at $\delta = 3.63$ and $\delta = 3.72$. The protons of the dioxane methyl groups appear as two singlets at $\delta = 0.91$ and $\delta = 1.01$.

For the final cyclization of the two pentadecahexayne building blocks **12** and **20**, modified Cadiot−Chodkiewicz coupling conditions were applied (Scheme 5). Compound **12** was brominated to give the corresponding 1,15-dibromopentadecahexayne **21**, and then coupled with the bis-cuprate of the second component **20** under high dilution conditions. Subsequent column chromatography provided the six-membered target macrocycle **22** as a white solid (21% yield), which readily decomposed.

Cyclotriacontadodecayne **22** has nearly the same ^{1}H NMR spectrum [three singlets at $\delta = 0.95$ (diox CH_3), $\delta = 1.52$ (CCH_3), and $\delta = 3.66$ (OCH_2)] and ^{13}C NMR spectrum (Table 1), as the smaller C_{20} ring homologue **7**. The IR spectrum of **22** has two bands for the -C≡C- stretching modes at 2262 and 2159 nm. The UV/Vis spectrum, with bands at 234.0, 248.5, and 264.0 nm, looks almost the same as those of **7** and the acyclic precursors **12** and **20**. The different pentayne synthons **5**, **6**, **8−10**, **15−17**, and **18**, as well as the higher homologues **11**, **12**, **19**, **20**, and **21**, may be valuable building blocks for synthetic routes to a number of pericyclynes with different arrangement of sp^3-linkers. This is demonstrated with the following macrocycle synthesis.

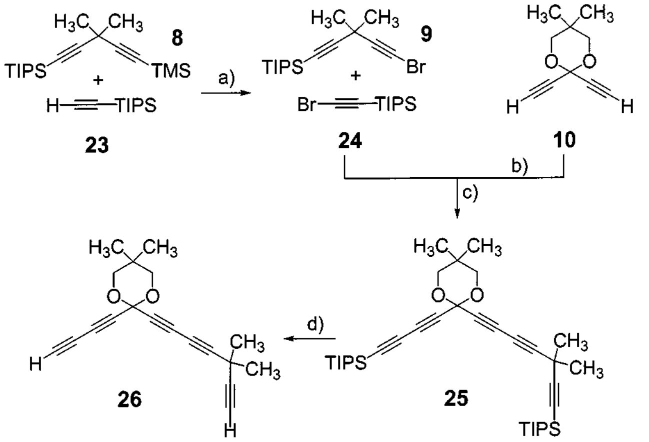
Synthesis of an Unsymmetrically Diyne-Tetrayne Expanded [4]Pericyclyne 27

By use of some of the acetylenic synthons (**8**, **9**, and **10**) described in the sections above, the synthesis of a pericyclyne with an unsymmetrically expanded diyne-tetrayne framework was also achieved. When a 1:1-mixture of TIPS-acetylene **23** and unsymmetrically protected 1-TIPS-5-TMS-3,3-dimethylpentadiyne **8** was treated with equivalent amounts of NBS and $AgNO_3$, the two TIPS-protected bromides **9** and **24** were obtained (Scheme 6). Without isolation, the THF solution was added to the previously prepared bis-cuprate of diethynyldioxane **10** in pyridine. The product mixture was purified by column chromatography and the bis-TIPS-protected unsymmetrical dodecapentayne **25** was obtained in 14% yield as a colorless oil.

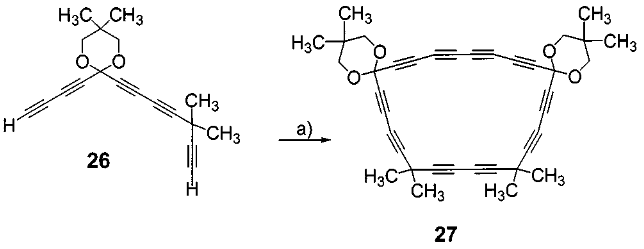
Table 1. ^{13}C NMR chemical shifts (δ values) of the acyclic precursors **11**, **12**, **19**, **20**, **21**, and the "exploded" [4]- and [6]pericyclynes **7** and **22** (100 MHz, CDCl3, 25 °C)

No.	CH_3 [a]	$C(CH_3)_2$	$C(CH_3)_2$ [a]	CH_3	C≡C	OCH_2	$(\equiv C)_2CO_2$	≡CTIPS	≡CH	≡CBr
11	22.33	27.26	29.88	30.86	63.17, 69.53, 71.40, 80.83, 85.73	72.90	87.29	106.51		
12	22.19	26.21	29.77	30.30	63.54, 69.13, 71.72, 84.93, 85.64	73.00	87.16		68.76	
19	22.31, 22.49	27.02	29.57	30.00	64.49, 67.21, 75.45, 82.84, 86.70	72.61	88.19	103.09		
20	22.14, 22.37	27.01	30.03	29.79	64.30, 68.98, 72.25, 78.24, 83.14,	72.71	86.70		73.18	
21	22.28	27.67	29.88	30.23	63.77, 69.18, 71.94, 81.29, 84.60	72.91	87.25			40.97
7	22.25	27.51	29.85	28.75	64.76, 70.09, 74.59, 77.64	73.31	86.17			
22	22.25	27.05	29.99	29.83	64.38, 69.02, 72.09, 83.32	72.98	87.21			

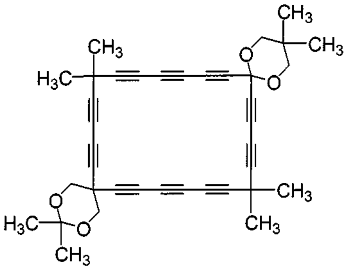
[a] Attached to the dioxane ring.



Scheme 6. Statistical synthesis of the unsymmetrical pentayne precursor **26**: a) $AgNO_3$, NBS; b) *n*BuLi, THF; CuCl; c) pyridine; d) Bu_4NF, THF



Scheme 7. Oxidative homo-coupling of precursor **26** to give the tetratriacontadecayne **27**: a) $Cu(OAc)_2{\cdot}H_2O$, MeCN



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Treatment with TBAF/THF gave the deprotected **26** (61% yield) as a clear, viscous oil, which readily darkened in the presence of light (Scheme 6).

The EI-mass spectrum of **25** shows the molecular ion peak M^+ at $m/z = 590$. The ^1H NMR spectrum has the two well-known doublets ($J = 11.2$ Hz) at $\delta = 3.66$ and $\delta = 3.72$ for the dioxane methylene protons. Consequently, the signal for the dioxane methyl groups splits into two lines at $\delta = 0.95$ and $\delta = 1.00$. In the ^{13}C NMR spectrum, the expected eleven signals for the quaternary C atoms are found (Table 2). The IR spectrum of **25** shows three intense C≡C-bands at 2263, 2172, and 2107 cm^{-1}, whereas in the spectrum of **26**, the three bands at wavenumbers 2264, 2159, and 2066 cm^{-1} have much lower intensities. A new, intense band appears at 3294 cm^{-1}, caused by the ≡C−H termini. The ^1H NMR spectrum of **26** has two singlet signals for the terminal acetylenic protons, at $\delta = 2.23$ and $\delta = 2.29$, while the ^{13}C NMR spectrum displays the two corresponding ≡*C*H signals at $\delta = 68.82$ and $\delta = 70.68$ (Table 2).

The final ring-closing step was the oxidative homo-coupling of dodecapentayne **26** with copper(II) acetate monohydrate in acetonitrile,[10] under modified Hay/Eglinton conditions (Scheme 7).[11,12] After aqueous workup and column chromatography, the tetratriacontadecayne **27** was obtained as a white solid. However, a conceivable formation of the constitutional isomer **28**, which might be expected from a different orientation of the coupling components, also had to be taken into account.

The EI mass spectrum of **27** showed a molecular ion peak at 552 *m*/*z*, corresponding to both of the expected macrocycles. In the FT-IR spectrum, four distinct bands at 2261, 2215, 2165, and 2116 nm can be assigned to -C≡C- alkyne units. No assignment of the obtained dimeric products to one of the two conceivable structures **27** or **28** can be expected from its NMR spectrum. Ten ^{13}C-resonance lines for the sp C atoms could be expected for both compounds, because of their symmetry: C_{2h} for **27** and C_{2v} for **28**. There were ten signals in the ^{13}C NMR spectrum, ranging from $\delta = 62$ to $\delta = 85$, plus the signal of the quaternary C(2) atoms of the dioxane rings at $\delta = 87.93$ (Table 2). The ^1H NMR spectra of **27** and **28** should also be very similar. In fact, the dimer spectrum had doublets ($J = 11.5$ Hz) at $\delta = 3.63$ and $\delta = 3.67$ for the methylene protons, similar to the monomer precursors **25** and **26**. The signal of the dioxane ring methyl protons was split into two resonances at $\delta = 0.93$ and $\delta = 0.96$. The signal for the methyl groups bound directly to the macrocycle was found as a singlet at $\delta = 1.50$.

Table 2. ^{13}C NMR chemical shifts (δ-values) of the pentaynes **25** and **26** and the resulting dimeric coupling product **27**

No.	*C*H3 [a]	*C*(CH3)2	*C*(CH3)2 [a]	*C*H3	C≡*C*, (≡*C*)2*C*O2	O*C*H2	≡*C*H
25	22.26, 22.39	27.29	29.90	30.87	63.19, 69.48, 69.77, 71.23, 77.60, 80.93, 85.84, 87.29, 87.95, 88.05, 109.54	72.95	
26	22.19, 22.28	26.27	29.83	30.34	63.48, 69.53, 71.39, 85.19, 85.66, 87.05, 66.62, 68.72, 69.80,		68.82, 70.68
27	22.21, 22.28	27.51	29.88	28.95	62.07, 64.74, 65.89, 66.17, 70.24, 70.44, 73.40 (2×), 83.50, 85.04, 87.93	73.31	

[a] Attached to the dioxane ring.

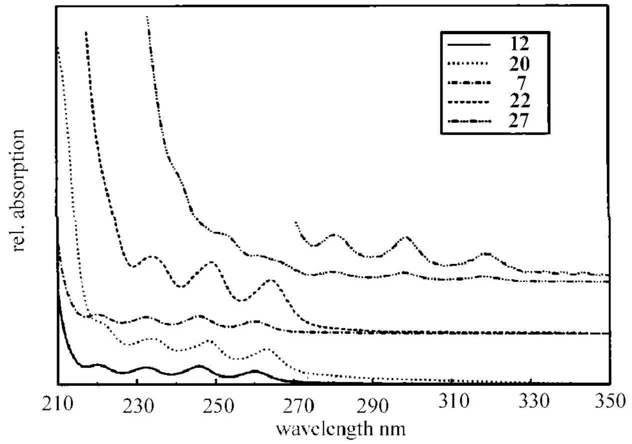

Figure 2. UV/Vis spectra of **12, 20, 7, 22,** and **27** (cyclohexane)

Finally, the UV/Vis spectrum of the new macrocycle was the only remaining possible means to distinguish between the two possible structures **27** or **28** and to assign the ring-closure product to one of them. This was achieved by a comparison of the spectrum of the new macrocycle with those of other polyyne building blocks presented in this study (Figure 2) and of related compounds described in the literature. The UV/Vis spectra of the C_{20}-macrocycle **7** and the C_{30}-macrocycle **22** showed no apparent difference in the position of the absorption maxima, compared with the acyclic precursors **12** and **20**. In the spectrum of the new dimer, however, in addition to maxima at 241, 252, and 260 nm belonging to the butadiyne units, three new absorption maxima were observed at 280, 298, and 318 nm. Consequently, this new series of absorption maxima showed a bathochromic shift of about 50 nm. Since there were as yet no comparable triyne or tetrayne expanded pericyclyne spectra in the literature, the spectra of a number of linear oligoyne systems that we had synthesized shortly before were examined.[13] This previous study had shown that the elongation of a conjugated α,ω-dicyanooligoyne by one triple bond effects a long wave shift of the absorption maxima by 20−27 nm.[13] Similar findings have been reported by D. Walton, for silyl-endcapped oligoynes, and by M. Whiting for oligoynes.[14,15] Both groups observed a shift in the absorption maxima of 20−25 nm for one triple bond chain elongation within an oligoyne series. As a result, a bathochromic shift of 50 nm corresponds to an extension by two triple bonds, going from a diyne to a tetrayne system. From all these spectroscopic results, the isolated C_{24}-macrocycle could be assigned as structure **27**.

Conclusion

The synthetic route reported here to the expanded and alternately functionalized pericyclynes and to their acyclic building blocks could be a general synthetic basis for the preparation of new oligodiacetylenic macrocyclic compounds. The required hydrolytic cleavage of ring dioxane ketal functions as potential bridgeheads has been successfully carried out by Kuwatani, for example, with diyne systems.[16] The synthesis principle presented here also opens routes to new three-dimensional oligoyne structures such as the "superadamantane" **4**,[6a] which we plan to prepare by way of pericyclyne intermediates.

Experimental Section

General Remarks: ^1H and ^{13}C NMR: Jeol Alpha 500, Bruker AMX 400, Jeol JNM EX 400, Jeol JNM GX 400. − MS: Varian MAT 311 A (EI), Micromass Zabspec (EI and FAB). − IR: Bruker FT-IR Vector 22. − UV/Vis: Shimadzu UV 3202 PC. − Elementary analysis: CE instruments EA 1110 CHNS; TLC: Riedel-de Haën, 60 F 254. − Materials and solvents were obtained from commercial suppliers and were dried and purified by following literature techniques.[17] 2,2-Diethynyl-5,5-dimethyl-1,3-dioxane (**10**) and the TMS-protected 5,5-dimethyl-2,2-bis[2-(trimethylsilyl)ethynyl]-1,3-dioxane (**5**) were prepared according to the procedure reported by Bunz.[3] The synthesis of 3-chloro-3-methyl-1-trimethylsilyl-1-butyne was performed according to the literature.[1a,18,19] Products were isolated, whenever possible, by flash column chromatography (silica gel 60, particle size 0.04−0.063 nm, Merck) and completely characterized by ^1H and ^{13}C NMR spectroscopy, EI and FAB mass spectrometry, FT-IR, and UV/Vis spectroscopy.

1,5-Dibromo-3,3-dimethyl-1,4-pentadiyne (6): *N*-Bromosuccinimide [NBS] (17.46 g, 99 mmol) and $AgNO_3$ (3.36 g, 0.02 mmol) were added at 0 °C to a stirred solution of 3,3-dimethyl-1,5-trimethylsilyl-1,4-pentadiyne[6,20,21] (7.73 g, 33 mmol) in acetone (150 mL). Stirring in the absence of light was continued at room temp. for 12 h. The reaction mixture was poured into ice-water and extracted with hexane, and the yellow precipitate was filtered off. The hexane solutions were washed with water, dried over magnesium sulfate, and concentrated in vacuo to give an orange, strongly irritant oil (6.93 g, 28 mmol, 84% yield), which was used without purification. [***Caution:*** Although we have never encountered difficulties with this type of bromo compound, bromoalkynes are sometimes explosive and precautions should be taken when handling this compound!]. − ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.48$ (s, 6 H, CH_3). − ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 28.24$ [$C(CH_3)_2$], 30.54 (CH_3), 40.04 ($\equiv C$Br), 82.34 ($-C\equiv$). − IR (film): $\tilde{\nu} = 2984$, 2933, 2853, 2224, 2067, 1719, 1639, 1558, 1450, 1363, 1247, 1066, 845 cm^{-1}. − MS (EI): *m/z* = 250 [M^+], 234, 169, 90. − $C_7H_6Br_2$ (249.9): calcd. C 33.64, H 2.42; found C 33.99, H 2.50.

3,3,11,11,19,19,26,26-Octamethyl-1,5,17,21-tetraoxadispiro[5.9.5.9]triaconta-7,9,12,14,22,24,27,29-octayne (7): A solution of 18-crown-6 (159 mg, 0.65 mmol) and KF (376 mg, 6.48 mmol) in dry THF (20 mL) was slowly added by syringe pump, under nitrogen protection and over 6 h, to 5,5-dimethyl-2,2-bis[2-(trimethylsilyl)ethynyl]-1,3-dioxane (**5**) (500 mg, 1.62 mmol), copper(I) iodide (309 mg, 1.62 mmol), and 1,5-dibromo-3,3-dimethyl-1,4-pentadiyne (**6**) in oxygen-free pyridine (125 mL). After 12 h stirring at room temp., the pyridine solution was concentrated under reduced pressure and an ice-cold 10% aqueous HCl solution was added. The mixture was extracted with $CHCl_3$, washed with 10% aqueous HCl and a saturated solution of $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure to give a black oil. The oil was filtered through a silica plug and a yellowish filtrate was obtained. After concentration, **7** was precipitated at −40 °C from chloroform as colorless needles (10 mg, 1.2% yield). − ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.94$ (s, 12 H, diox. CH_3), 1.48 (s, 12 H, CH_3), 3.64 (s, 8 H, CH_2). − ^{13}C NMR spectrum given in Table 1. − IR (KBr): $\tilde{\nu}$ = 2965.1, 2933.4, 2869.6, 2261.6, 2168.6, 1600.5, 1465.8, 1182.5, 1133.9, 1085.9, 1006.7, 983.7 cm^{-1}. − MS (EI): *m/z* =504 [M$^+$], 274. − UV/Vis (dichloromethane): λ_{max} = 227.0, 237.0, 251.5, 267.0 nm. − $C_{34}H_{32}O_4$ (504.6): calcd. C 80.93, H 6.39; found C 80.52, H 5.92.

3,3-Dimethyl-1-triisopropylsilyl-5-trimethylsilyl-1,4-pentadiyne (8): Under nitrogen protection, TIPS-acetylene **23** (2.93 g, 17.4 mmol) in dry THF (10 mL) was added dropwise to a solution of ethylmagnesium bromide, prepared from magnesium (418 mg, 17.2 mmol) and ethyl bromide (1.80 g, 17.4 mmol) in 50 mL THF. The mixture was heated to reflux until the evolution of gas stopped. After this had cooled to room temp., 3-chloro-3-methyl-1-trimethylsilyl-1-butyne (2.70 g, 15.5 mmol) in THF (10 mL) was added dropwise and the mixture was subsequently heated to 70 °C and stirred at this temperature for 12 h. After cooling to room temp., the reaction mixture was poured onto ice-cold 10% aqueous H_2SO_4 and extracted with diethyl ether. The combined ether phases were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography on SiO_2, using pentane as eluent, gave **8** (3.01 g, 60% yield) as a clear oil. − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.12 (s, 9 H, $SiCH_3$), 1.04 (m, 21 H, SiC_3H_7), 1.47 (s, 6 H, CCH_3). − ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 0.01 ($SiCH_3$), 11.26 (SiCH), 18.59 ($CHCH_3$), 27.40 (CCH_3), 31.24 (CCH_3), 79.26, 82.94 ($C{\equiv}CSi$), 110.06 ($C{\equiv}C$TMS), 112.19 ($C{\equiv}C$TIPS). − IR (film): $\tilde{\nu}$ = 2944.2, 2867.1, 2166.2, 1464.4, 1250.6, 1228.8, 843.4, 676.7 cm^{-1}. − MS (EI): *m/z* = 320 [M$^+$], 305, 277, 235, 207, 165. − $C_{19}H_{36}Si_2$ (320.7): calcd. C 71.16, H 11.32; found C 70.78, H 11.02.

1-Bromo-3,3-dimethyl-5-triisopropylsilyl-1,4-pentadiyne (9): Equivalent quantities of $AgNO_3$ (160 mg, 9.35 mmol) and NBS were added in small portions at 0 °C to a stirred solution of **8** in 50 mL acetone. The reaction was monitored by TLC [Al_2O_3, pentane]. The mixture was subsequently treated with ice-water and the precipitate was filtered off. The filtrate was extracted with pentane and the combined organic phases were dried over $MgSO_4$. Concentration under reduced pressure afforded a yellow oil (1 g, 98% yield), which was used without further purification. − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ =1.03 (m, 21 H, SiC_3H_7), 1.49 (s, 6 H, CH_3). − ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.15 ($SiCHCH_3$), 18.54 ($SiCHCH_3$), 27.85 (CCH_3), 31.12 (CCH_3), 39.02 (${\equiv}C$Br), 79.83, 83.27 ($CC{\equiv}$), 111.00 (${\equiv}C$TIPS). − IR (film): $\tilde{\nu}$ = 2943.7, 2866.4, 2725.2, 2167.3, 2120.9, 1715.8, 1641.6, 1463.7, 1236.9, 996.5, 883.2, 797.2, 677.4 cm^{-1}.

2,2-Bis(5′,5′-dimethyl-7′-triisopropylsilyl-1,3,6-heptatriynyl)-5,5-dimethyl-1,3-dioxane (11): *n*-Butyllithium (1.9 mL, 3 mmol of a 1.6 M solution in hexane) was added at 0 °C under nitrogen to a solution of 2,2-diethynyl-5,5-dimethyl-1,3-dioxane (**10**) (250 mg, 1.5 mmol) in dry THF (50 mL). After stirring for 30 min at room temp., the mixture was cooled again to 0 °C and CuCl (0.3 g, 3 mmol) was added. The yellow suspension formed was diluted with oxygen-free pyridine (200 mL) to obtain a clear solution. Next, bromoalkyne **9** (1 g, 3 mmol) in THF (20 mL) was slowly added (syringe pump, ≈ 0.175 mL/min) over 2 h. The resulting dark solution was stirred for 48 h at room temp. and then poured slowly into ice-cold 10% aqueous HCl. The reaction mixture was extracted several times with ether and the combined organic phases were washed with 10% aqueous HCl until no pyridine could be smelled. After the organic phases had been dried over $MgSO_4$, the solvent was evaporated under reduced pressure and a brown oil was obtained. Further purification by chromatography [SiO_2, cyclohexane/CH_2Cl_2, 9:1] afforded a colorless resin (288 mg, 29% yield). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.97 (s, 6 H, diox. CCH_3), 1.03 (m, 42 H, SiC_3H_7), 1.52 (s, 12 H, CCH_3), 3.68 (s, 4 H, OCH_2). − ^{13}C NMR in Table 1. − IR (film): $\tilde{\nu}$ = 2942.9, 2865.8, 2725.1, 2264.6, 2173.4, 1464.0, 1396.1, 1383.2, 1363.9, 1321.8, 1225.8, 1204.8, 1181.9, 1137.5, 1087.2, 980.9, 927.9, 882.9, 727.5, 701.1, 676.6, 618.3 cm^{-1}. − MS (EI): *m/z* = 656 [M$^+$], 641, 626, 613, 590, 545, 385. − UV/Vis (cyclohexane): λ_{max} (ε) = 232.5 (2300), 248 (2100), 263 (1600) nm. − $C_{42}H_{64}Si_2O_2$ (625.2): calcd. C 76.76, H 9.82; found C 76.51, H 9.51.

2,2-Bis(5′,5′-dimethyl-1′,3′,6′-heptatriynyl)-5,5-dimethyl-1,3-dioxane (12): The TIPS-protected hexayne **11** (280 mg, 0.43 mmol) was dissolved in THF (20 mL) containing a few drops of water, and a TBAF-THF solution (1 M, 0.85 mL, 0.85 mmol) in THF (5 mL) was added dropwise. After 1 h, the reaction was quenched by addition of water. The mixture was extracted with CH_2Cl_2 and the organic phases were washed with water and dried over $MgSO_4$. Concentration under reduced pressure gave a brown oil, which was filtered through a SiO_2 plug with hexane/dichloromethane (7:3) to afford a clear oil (134.2 mg, 90% yield). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.96 (s, 6 H, diox. CCH_3), 1.53 (s, 12 H, CCH_3), 2.23 (s, 2 H, $C{\equiv}CH$), 3.67 (OCH_2). − ^{13}C NMR in Table 1. − IR (film): $\tilde{\nu}$ = 3037.3, 2942.6, 2866.8, 2265.8, 2158.8, 1466.9, 1322.0, 1183.6, 1086.5, 981.6, 928.1, 883.1, 805.7, 646.5 cm^{-1}. − MS (EI): *m/z* = 344 [M$^+$], 259, 230, 213. − UV/Vis (cyclohexane): λ_{max} (ε) = 220.5 (2300), 234.0 (1700), 248 (1600), 262.5 (1300) nm. − $C_{24}H_{24}O_2$ (344.5): calcd. C 83.69 H 7.02; found C 83.11 H 7.02.

3-Triisopropylsilyl-2-propynal (14): *n*-Butyllithium (7.13 mL, 17.8 mmol of a 2.5 M solution in hexane) was added at 0 °C under nitrogen protection to a solution of TIPS-acetylene (3.25 g, 17.8 mmol) in dry THF (25 mL). After this had stood for 2 h at room temp., *N*-formyl morpholine **13** (2.05 g, 17.8 mmol) in THF (10 mL) was added dropwise at 0 °C and the reaction mixture was stirred for another 12 h at room temp. It was then poured into ice-cold 10% aqueous HCl and extracted several times with diethyl ether. The combined organic phases were washed with water, dried over $MgSO_4$, and concentrated in vacuo. The resulting brown oil was purified by flash chromatography (SiO_2, pentane) (with unchanged TIPS-acetylene being recovered) to give a clear oil (1.93 g, 93% yield, calculated for consumed TIPS-acetylene). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.02 (m, 21 H, SiC_3H_7), 9.14 (s, 1 H, CHO). − ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 10.91 ($SiCHCH_3$), 17.62 ($SiCHCH_3$), 100.45, 104.40 ($C{\equiv}C$), 176.38 ($C{=}$O). − IR (film): $\tilde{\nu}$ = 3317.4, 2946.2, 2868.0, 2731.1, 2149.5, 1669.0, 1463.6, 1385.4, 1240.6, 1073.1, 998.8, 920.4, 883.9, 679.3, 586.2 cm^{-1}. − MS (EI): *m/z* = 210 [M$^+$], 167, 139, 125, 111, 97. − $C_{12}H_{22}OSi$ (210.4): calcd. C 68.50, H 10.54; found C 68.17, H 10.33.

5-Triisopropylsilyl-1-trimethylsilyl-1,4-pentadiyn-3-ol (15): TIPS-protected propargyl aldehyde **14** was added at 0 °C to a solution of the Grignard compound of TMS-acetylene [prepared from magnesium (0.34 g, 14 mmol), ethyl bromide (1.50 g, 14 mmol), and TMS-acetylene (1.28 g, 13 mmol)] in dry THF. After 12 h heating at reflux, the mixture was poured onto ice-cold 10% aqueous HCl and extracted several times with diethyl ether. The combined organic phases were washed with a saturated aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The solution was subsequently concentrated under reduced pressure to give a brown oil, which was purified by flash chromatography [SiO_2, pentane to pentane/ether, 9:1] to give a light brown oil (2.56 g, 66% yield). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.15 (s, 9 H, $SiCH_3$), 1.05 (m, 21 H, SiC_3H_7), 2.40 (b, 1 H, OH), 5.05 (s, 1 H, CHOH). − ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = −0.43 ($SiCH_3$), 11.12 ($SiCHCH_3$), 18.47 (SiCH*C*H$_3$), 52.90 (*C*HOH), 86.09, 89.19 (*C*≡CSi), 102.18, 104.06 (C≡*C*Si). − IR (film): $\tilde{\nu}$ = 3389.5, 2944.5, 2894.7, 2866.8, 2759.4, 2726.7, 2176.5, 1463.9, 1384.6, 1288.1, 1251.1, 1047.2, 920.4, 845.7, 761.1, 677.2 cm^{-1}. − MS (EI): *m*/*z* = 308 [M$^+$], 265, 221. − $C_{17}H_{32}OSi_2$ (308.6): calcd. C 66.16 H 10.45; found C 66.00 H 10.62.

5-Triisopropylsilyl-1-trimethylsilyl-1,4-pentadiyn-3-one (16): A solution of $K_2Cr_2O_7$ (0.83 g, 2.8 mmol) and H_2SO_4 (0.63 mL) in water (10 mL) was added dropwise at 0 °C to **15** (2.56 g, 8.3 mmol) in acetone (25 mL). The solution was stirred at room temp. and the reaction was monitored by TLC (pentane/ether, 9:1). The green reaction mixture was extracted with diethyl ether, the organic phases were washed with water and dried over $MgSO_4$, and the solvent was distilled off under reduced pressure to give a brown oil (1.28 g, 51% yield), which was used without further purification. − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.21 (s, 9 H, SiC*H*$_3$), 1.07 (m, 21 H, SiC$_3$*H*$_7$). − ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = −1.05 (SiCH$_3$), 10.97 (Si*C*HCH$_3$), 18.34 (SiCH*C*H$_3$), 97.9, 99.14, 102.78, 104.99 (*C*≡*C*), 159.89 (C=O). − IR (film): $\tilde{\nu}$ = 2946.3, 2894.4, 2868.1, 2728.9, 2158.2, 1638.0, 1463.7, 1385.8, 1253.1, 1160.3, 1072.2, 997.6, 881.3, 845.9, 761.9, 726.2, 680.5 cm^{-1}. − MS (EI): *m*/*z* = 306 [M$^+$], 291, 263.

5,5-Dimethyl-2-[(triisopropylsilyl)ethynyl]-2-[(trimethylsilyl)ethynyl]-1,3-dioxane (17): Ketone **16** (1.27 g, 4.16 mmol), 2,2-dimethylpropane-1,3-diol (2.17 g, 20.8 mmol), and *p*TosOH (0.79 g, 4.16 mmol) were refluxed for 20 h in benzene (150 mL) using a Dean−Stark trap (TLC monitoring with pentane/ether, 9.5:0.5). After cooling to room temp., the solution was washed twice with a 1:1 mixture of water and ethanol. Evaporation of the benzene afforded a light brown oil (1.59 g, 97% yield). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.17 (s, 9 H, SiC*H*$_3$), 0.83 (s, 6 H, CC*H*$_3$), 1.08 (m, 21 H, SiC$_3$*H*$_7$), 3.56 (d, *J* = 11.5 Hz, 2 H, OC*H*$_2$), 3.85 (d, *J* = 11.5 Hz, 2 H, OC*H*$_2$). − ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = −0.54 (Si*C*H$_3$), 11.16 (Si*C*HCH$_3$), 18.52 (SiCH*C*H$_3$), 22.25, 22.90 (C*C*H$_3$), 29.75 (*C*CH$_3$), 72.51 (O*C*H$_2$), 86.74 (*C*O$_2$), 87.72, 88.80 (*C*≡CSi), 100.04, 100.75 (C≡*C*Si). − IR (film): $\tilde{\nu}$ = 2958.1, 2866.9, 2757.9, 2726.9, 2168.2, 1465.5, 1239.3, 1181.0, 1083.4, 1041.5, 982.3, 929.8, 862.4, 795.6, 761.2, 678.1 cm^{-1}. − MS (EI): *m*/*z* = − 392 [M$^+$], 349, 310, 281, 267, 199. − $C_{22}H_{40}O_2Si_2$ (392.7): calcd. C 67.28, H 10.27; found C 66.91, H 10.32.

2-Ethynyl-3,3-dimethyl-2-[(triisopropylsilyl)ethynyl]-1,3-dioxane (18): K_2CO_3 (8.0 g) was added to a solution of **17** (1.8 g, 4.59 mmol) in methanol (150 mL) and several drops of water. The reaction progress was monitored by TLC [pentane/ether, 9.5:0.5]. At the end of the reaction, water was added to dissolve the carbonate and the mixture was extracted with diethyl ether. The organic phases were washed with water and dried over $MgSO_4$. Evaporation of the solvent afforded a orange oil, which was purified by column chromatography (SiO_2, pentane/ether, 9:1) to give a clear oil (0.89 g, 61% yield). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.85 (s, 3 H, C*H*$_3$), 1.08 (m, 24 H, SiC$_3$*H*$_7$, CH$_3$), 2.62 (s, 1 H, C≡C*H*), 3.57 (d, 2 H, *J* = 11.8, C*H*$_2$), 3.85 (d, 2 H, *J* = 11.8, C*H*$_2$). − ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 11.06 (Si*C*HCH$_3$), 18.52 (SiCH*C*H$_3$), 22.20, 22.74 (C*C*H$_3$), 29.76 (*C*CH$_3$), 71.58 (C≡*C*H), 72.39 (*C*H$_2$), 79.46 (*C*≡CH), 86.50, 86.72 (*C*≡CSi, *C*O$_2$), 100.09 (C≡*C*Si). − IR (film): $\tilde{\nu}$ = 3309.9, 2957.8, 2867.0, 2727.0, 2135.1, 1466.6, 1237.2, 1179.9, 1083.3, 1041.4, 982.6, 930.3, 883.2, 678.3 cm^{-1}. − MS (EI): *m*/*z* = 320 [M$^+$], 277, 191. − $C_{19}H_{32}O_2Si$ (320.6): calcd. C 71.19, H 10.06; found C 70.82, H 10.23.

{2-[2-(9-{5,5-Dimethyl-2-[2-(triisopropylsilyl)ethynyl]-1,3-dioxane-2-yl}-5,5-dimethyl-1,3,6,8-nonatetraynyl)-5,5-dimethyl-1,3-dioxane-2-yl]ethynyl}triisopropylsilane (19): *n*-Butyllithium (1.11 mL, 2.8 mmol of a 2.5 M solution in hexane) in THF (10 mL) was added to a solution of **18** (890 mg, 2.8 mmol) in dry THF (20 mL) at 0 °C under nitrogen as protecting gas. After stirring for 30 min at room temp., the mixture was again cooled to 0 °C and CuCl (275 mg, 2.8 mmol) was added. Oxygen-free pyridine (250 mL) was added to the resulting orange suspension and a yellow solution was obtained. Next, dibromopentadiyne **6** in dry THF (20 mL) was added by syringe pump over 2 h at room temp. and stirring was continued for 3d. The mixture was then slowly poured onto ice-cold 10% aqueous HCl and extracted three times with diethyl ether. The combined organic phases were washed with 10% aqueous HCl and water, dried over $MgSO_4$, and concentrated under reduced pressure to give a dark brown oil. Further purification by flash chromatography [SiO_2, cyclohexane/CH_2Cl_2, 6:4] afforded a colorless resin (585 mg, 58% yield). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.91, 0.99 (s, 12 H, diox. CC*H*$_3$), 1.06 (m, 42 H, SiC$_3$*H*$_7$), 1.61 (s, 6 H, CC*H*$_3$), 3.60 (d, 4 H, OC*H*$_2$, *J* = 11.5), 3.76 (d, 4 H, OC*H*$_2$, *J* = 11.5). − ^{13}C NMR is presented in Table 1. − IR (film): $\tilde{\nu}$ = 2930.0, 2866.5, 2264.4, 2168.5, 1464.7, 1395.7, 1364.4, 1321.3, 1231.2, 1181.8, 1133.6, 1087.3, 1039.7, 980.0, 928.5, 883.2, 678.5 cm^{-1}. − MS (EI): *m*/*z* = 728 [M$^+$], 685, 599. − UV/Vis (cyclohexane): λ_{max} (ε) = 233.0 (1000), 246.5 (900), 261 (600) nm. − $C_{45}H_{68}O_4Si_2$ (729.2): calcd. C 74.12, H 9.40; found C 74.01, H 9.67.

2-Ethynyl-2-[9-(2-ethynyl-5,5-dimethyl-1,3-dioxan-2-yl)-5,5-dimethyl-1,3,6,8-nonatetraynyl]-5,5-dimethyl-1,3-dioxane (20): A TBAF-THF solution (1 M, 0.8 mL, 0.8 mmol) in THF (10 mL) was slowly added to a solution of **19** (585 mg, 0.8 mmol) in THF (50 mL) with a few drops of water. After 2 h stirring, the reaction was quenched with water and the solution was extracted with diethyl ether. The organic phases were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to afford a light brown resin (320 mg, 96% yield). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.91 (s, 6 H, diox. CC*H*$_3$), 1.01 (s, 6 H, diox. CC*H*$_3$), 1.53 (s, 1 H, CC*H*$_3$), 2.23 (s, 2 H, ≡C*H*), 3.63 (d, 4 H, OC*H*$_2$, *J* = 11.5), 3.72 (d, 4 H, OC*H*$_2$, *J* = 11.5). − ^{13}C NMR in Table 1. − IR (film): $\tilde{\nu}$ = 3284.5, 2986.9, 2961.2, 2933.0, 2868.2, 2265.1, 2134.1, 1469.7, 1397.0, 1366.8, 1320.3, 1230.5, 1179.2, 1133.8, 1089.2, 1065.7, 1028.5, 1005.7, 982.5, 929.5 cm^{-1}. − MS (EI): *m*/*z* = 416 [M$^+$], 330, 245. − UV/Vis (cyclohexane): λ_{max} (ε) = 220.0 (1500), 232.5 (1300), 246.0 (1400), 260.0 (1000) nm. − $C_{27}H_{28}O_4$ (416.5): calcd. C 77.86 H 6.78; found C 77.44 H 6.92.

2,2-Bis(7′-bromo-5′,5′-dimethyl-1′,3′,6′-heptatriynyl)-5,5-dimethyl-1,3-dioxane (21): NBS (252 mg, 1.44 mmol) and $AgNO_3$ (60 mg, 0.36 mmol) were added in small portions to a solution of **12** (245 mg, 0.71 mmol) in acetone (50 mL) at 0 °C. The progress of the reaction was monitored by TLC [SiO_2, pentane/CH_2Cl_2, 8:2]. The mixture was poured onto ice-water, the precipitate was filtered off, the mixture was extracted with pentane, and the extract was dried over $MgSO_4$. Evaporation of the solvent gave a yellow oil. Further purification by chromatography [SiO_2, cyclohexane/CH_2Cl_2, 7:3] afforded a colorless resin (330 mg, 93%). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.96 (s, 6 H, diox. CC*H*$_3$), 1.51 (s, 12 H, CC*H*$_3$), 3.67 (s, 4 H, OC*H*$_2$). − ^{13}C NMR given in Table 1. − IR (film): $\tilde{\nu}$ = 2983.9, 2961.1, 2934.1, 2867.7, 2263.9, 2218.3, 2160.5, 1468.7, 1396.4, 1364.0, 1321.6, 1302.9, 1226.8, 1182.6, 1138.5, 1086.5, 980.7, 734.1 cm^{-1}. − MS (FAB): *m*/*z* = 503 [M$^+$], 417. − UV/Vis (cyclohexane): λ_{max} (ε) = 222.0 (4000), 232.0 (2000), 248.5 (1600), 263.0 (1200) nm. − $C_{24}H_{22}O_2Br_2$ (502.3); calcd. C 57.39, H 4.42; found C 56.88, H 4.87.

3,3,11,11,19,19,26,26,34,34,41,41-Dodecamethyl-1,5,17,21,32,36-hexaoxatri-spiro[5.9.5.9.5.9]pentatetraconta-7,9,12,14,22,24,27,29,37,39,42-undecayne (22): Under nitrogen as protecting gas, *n*-butyllithium (0.64 mL, 1.6 mmol of a 2.5 M solution in hexane) in THF (10 mL) was added dropwise at 0 °C to **20** (320 mg, 0.77 mmol) in dry THF (10 mL). The mixture was stirred at room temp. for 30 min and then CuCl (152 mg, 1.54 mmol) was added at 0 °C. Oxygen-free pyridine (250 mL) was added to the resulting orange suspension and a yellow solution was obtained. A solution of dibromopentadecahexayne **21** in THF (20 mL) was then slowly added by syringe pump over 2 h. Stirring was continued over 3 days at room temp. The dark reaction mixture was poured slowly into ice-cold 10% aqueous HCl, extracted three times with diethyl ether, washed with 10% aqueous HCl and water, and dried over $MgSO_4$. Concentration under reduced pressure afforded a dark oil, which was purified by column chromatography (SiO_2, cyclohexane/CH_2Cl_2, 7:3 to 1:1). Compound **22** was isolated as a white solid (111 mg, 21% yield). − ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.95 (s, 18 H, diox. CCH_3), 1.52 (s, 18 H, CCH_3), 3.66 (s, 12 H, OCH_2). − ^{13}C NMR in Table 1. − IR (KBr): $\tilde{\nu}$ = 2959.4, 2935.3, 2866.7, 2261.5, 2158.7, 1468.5, 1396.4, 1364.8, 1320.9, 1182.6, 1135.9, 1086.4, 981.5 cm^{-1}. − MS (FAB): *m/z* = 757 [M^+]. − UV/Vis (cyclohexane): λ_{max} (ε) = 234.0 (5100), 249 (4800), 264.0 (3600) nm. − $C_{51}H_{48}O_6$ (756.9): calcd. C 80.93, H 6.39; found C 80.54, H 6.77.

2-[5′,5′-Dimethyl-7′-(triisopropylsilyl)-1,3,6-heptatriynyl]-2-[4′-(triisopropylsilyl)butadiynyl]-5,5-dimethyl-1,3-dioxane (25): *n*-Butyllithium (3.45 mL, 8.60 mmol of a 2.5 M solution in hexane) was added under a nitrogen atmosphere at 0 °C to a solution of diethynyldioxane **10** (750 mg, 4.45 mmol) in dry THF (20 mL). After this had stirred for 30 min at room temp., CuCl (853 mg, 8.6 mmol) was added at 0 °C. Oxygen-free pyridine (250 mL) was added to the resulting orange suspension and a yellow solution was obtained. Next, a 1:1 mixture of bromopentadiyne **9** (1.72 g, 4.3 mmol) and TIPS-protected bromoacetylene **24** (1.12 g, 4.3 mmol, produced from bromination of a 1:1 mixture of **8** and TIPS-acetylene **23** with NBS and $AgNO_3$) in THF (20 mL) was added dropwise by syringe pump over 2 h. After stirring for 3 days at room temp., the reaction was quenched with ice-cold 10% aqueous HCl and extracted with diethyl ether. The organic phases were washed with 10% aqueous HCl and water and dried over $MgSO_4$. Evaporation of the solvent provided a dark oil, which was purified by flash chromatography (SiO_2, cyclohexane/CH_2Cl_2, 9:1) to give a colorless resin (347 mg, 14% yield). − ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.95 (s, 3 H, diox. CCH_3), 1.00 (s, 3 H, diox. CCH_3) 1.03 (m, 42 H, SiC_3H_7), 1.06 (m, 42 H, SiC_3H_7), 1.52 (s, 12 H, CCH_3), 3.66 (d, *J* = 11.2 Hz, 2 H, OCH_2), 3.72 (d, *J* = 11.2 Hz, 2 H, OCH_2). − ^{13}C NMR given in Table 1. − IR (film): $\tilde{\nu}$ = 2943.7, 2892.2, 2866.1, 2756.9, 2725.9, 2263.2, 2172.6, 2107.2, 1459.9, 1395.8, 1365.0, 1319.0, 1227.5, 1205.8, 1138.6, 1082.8, 981.7, 949.8, 920.5, 882.8, 677.3 cm^{-1}. − MS (EI): *m/z* = 590 [M^+], 575, 560, 547, 524, 505. − UV/Vis (cyclohexane): λ_{max} (ε) = 244.5 (2100), 246 (2100), 258.5 (1600), 261.5 (1600), 273.5 (1100) nm. − $C_{37}H_{58}O_2Si_2$ (591.1): calcd. C 75.18, H 9.89; found C 74.79, H 9.99.

2-(Butadiynyl)-2-(5′,5′-dimethyl-1′,3′,6′-heptatriynyl)-5,5-dimethyl-1,3-dioxane (26): The TIPS-protected dodecapentayne **25** (347 mg, 0.59 mmol) was dissolved in THF (25 mL) with several drops of water and a TBAF-THF solution (1.18 mL, 1.18 mmol) in THF (5 mL) was slowly added. After stirring for 2 h at room temp., the reaction mixture was quenched with water and extracted with diethyl ether. The organic phases were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to give a brown oil. Purification by chromatography (SiO_2, pentane/CH_2Cl_2, 7:3) afforded a clear oil (100 mg, 61% yield), which decomposed on exposure to light. − ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.94 (s, 3 H, diox. CCH_3), 0.97 (s, 3 H, diox. CCH_3), 1.52 (s, 6 H, CCH_3), 2.23 (s, 1 H, $\equiv CH$), 2.29 (s, 1 H, $\equiv CH$), 3.63 (d, *J* = 11.4 Hz, 2 H, OCH_2), 3.68 (d, *J* = 11.4 Hz, 2 H, OCH_2). − ^{13}C NMR is given in Table 1. − IR (KBr): $\tilde{\nu}$ = 3293.5, 2984.1, 2962.9, 2936.3, 2869.4, 2264.3, 2158.6, 2065.8, 1470.1, 1397.1, 1364.9, 1248.7, 1226.2, 1203.6, 1126.2, 1074.5, 981.7, 928.9, 643.6 cm^{-1}. − MS (EI): *m/z* = 278 [M^+], 193, 163. − $C_{19}H_{18}O_2$ (278.4): calcd. C 81.99 H 6.52; found C 81.57 H 6.78.

3,3,18,18,25,25,30,30-Octamethyl-1,5,16,20-tetraoxadispiro-[5.8.5.14]-tetratriaconta-7,9,11,13,21,23,26,28,31,33-decayne (27): The dodecapentayne **26** (100 mg, 0.26 mmol) in CH_2Cl_2/CH_3CN (40 mL) was added by syringe pump over 24 h to a solution of $Cu(OAc)_2$ monohydrate (720 mg, 3.6 mmol) in CH_3CN. After this had stirred for a further 24 h at room temp., the solvent was evaporated to dryness under reduced pressure and the brown residue was extracted with diethyl ether. The organic phases were then washed with 10% aqueous HCl and water and dried over $MgSO_4$. Concentration under reduced pressure gave a brown oil, which was purified by chromatography [SiO_2, cyclohexane/CH_2Cl_2, 7: 3 to 6:4) to afford a white solid (17 mg, 17% yield). − ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.93, 0.96 (s, 12 H, diox. CCH_3), 1.50 (s, 12 H, CCH_3), 3.63 (d, 4 H, OCH_2, *J* = 11.5 Hz), 3.67 (d, 4 H, OCH_2, *J* = 11.5 Hz). − ^{13}C NMR in Table 1. − IR (KBr): $\tilde{\nu}$ = 2964.0, 2930.9, 2869.5, 2261.0, 2215.1, 2165.3, 2115.6, 1465.1, 1343.7, 1261.8, 1122.9, 1094.2, 1069.1, 1010.3, 982.6, 802.6 cm^{-1}. − MS (EI): *m/z* = 552 [M^+], 503, 429. − UV/Vis (cyclohexane): λ_{max} (ε) = 241.0 (10100), 252.0 (4600), 260.0 (2600), 280.0 (1100), 297.5 (1000), 318.0 (700) nm. − $C_{38}H_{32}O_4$ (552.7): calcd. C 82.58, H 5.84; found C 82.33, H 5.98.

Acknowledgments

This work was supported by the Fonds der Chemischen Industrie.

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Received May 10, 2001
[O01234]