Completely Spirocyclopropanated Macrocyclic Oligodiacetylenes: The Family of "Exploding" [*n*]Rotanes**

Armin de Meijere,* Sergei Kozhushkov, Thomas Haumann, Roland Boese, Carsten Puls, Mark J. Cooney, and Lawrence T. Scott*

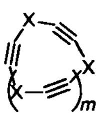
Dedicated to Professor Hansjörg Sinn on the occasion of his 65th birthday

Abstract: A general approach to the family of completely spirocyclopropanated macrocyclic polydiacetylenes, that is, cyclic dehydrooligomers of 1,1-diethynylcyclopropane **4**, is reported. The characterized examples of these "exploding" [*n*]rotanes are for $n = 5, 6, 7, 8, 9, 10$, and 12. X-ray crystal structure analyses for the hydrocarbons with $n = 5, 6, 7$, and 8 disclose a strong electronic interaction between the cyclopropane and the acetylene units leading to a significant shortening of the distal and lengthening of the proximal cyclopropane bonds. While the five-sided compound **18** can occur as a planar or envelope-shaped molecule, depending on the solvent from which crystals are grown, the six- (**19**), seven- (**20**), and eight-sided (**21**) molecules all have chair conformations. While the butadiyne units in **18** and **19** are bent slightly outwards, those in the seven- and eight-sided molecules **20** and **21**, respectively, are bent distinctly inward. All these compounds are extremely high-energy molecules: when struck with a spatula or a pestle, they go off with a puff to yield black soot.

Keywords
alkynes · coupling reactions · cyclopropanes · macrocycles · oligoalkadiynes

Introduction

Ever since the classical work of Sondheimer et al.,[1] macrocyclic oligoalkynes such as **1**[2–5] and oligoalkadiynes such as **2**[6–9] have intrigued organic chemists and are of continuing interest. The preparations and properties of some of these compounds (1: X = CMe_2 (so-called "pericyclynes"),[2–4] *t*BuP,[5a] and 2,3-thiophenediyl;[5b] 2: X = CMe_2,[6] 1,1′-dicyclopropanediyl,[7] *o*-phenylene,[8] diethynyl-substituted ethene-1,2-diyl,[9a] and diethynyl-substituted methylene[9b]) as well as novel potential building blocks for related structures[10–13] have been reported.



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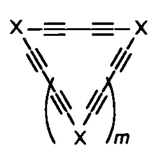

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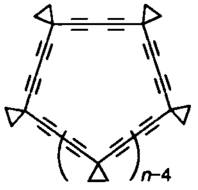

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Remarkably strong electronic interactions among the cyclically homoconjugated ethynyl and butadiynyl units have been evidenced in per-*gem*-dimethyl-substituted pericyclynes[3,4] and oligoalkadiynes.[6] Since the highest occupied molecular orbitals (HOMOs) of a cyclopropane ring[14] are much closer in energy to the π-MOs of an acetylene unit than are the σ-MOs of a *gem*-dimethylcarbon group, we were led to conceive the perspirocyclopropanated pericyclynes[7,15] and perspirocyclopropanated macrocyclic oligoalkadiynes of type **3**, which ought to show considerably stronger homoconjugative effects. This expectation is based on the fact that the splitting between the π-MOs parallel to the plane of the ring in 1,1-diethynylcyclopropane **4** is much larger (1.4 eV) than in 3,3-dimethylpenta-1,4-diyne (0.6 eV).[16] Stimulated by this concept, we set out to develop general methodology for the synthesis of macrocycles of type **3** consisting of 1,1-diethynylcyclopropane subunits.

Results and Discussions

The attempted one-step "shotgun" approach to **3** (Scheme 1) involving the oxidative coupling of **4**[17] in the $CuCl/Cu(OAc)_2$/pyridine system[18] led to a mixture of the open-chain dehydrooligomers **5**–**7**, consisting of two to four 1,1-diethynylcyclo-

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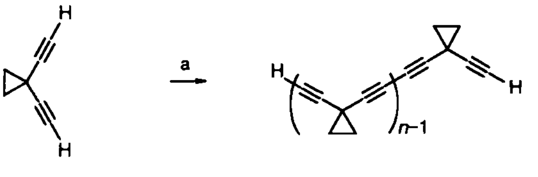


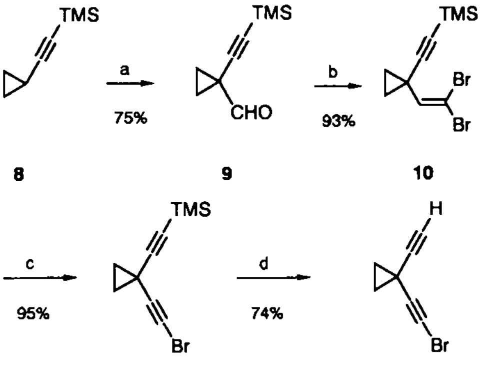
4

5, $n = 2$ (18%)
6, $n = 3$ (13%)
7, $n = 4$ (10%)

Scheme 1. a: 12 equiv CuCl, 16 equiv $Cu(OAc)_2$, pyridine, 20 °C, 7 d (inverse addition over a period of 3 d).

propane units, in low yields (higher oligomers may also have been formed, but were not isolated or characterized).

As has been demonstrated earlier,[6] permethyl-substituted macrocyclic oligodiacetylenes (e.g. **2**, $m = 1-4$) can be prepared most efficiently by a stepwise assembly of an appropriate acyclic precursor and subsequent cyclization by oxidative acetylene coupling. In keeping with this strategy, we first developed an efficient and versatile new route to **4**, some of its derivatives, and its dehydrooligomers of type **5**–**7** starting from (trimethylsilylethynyl)cyclopropane **8**[19] (Scheme 2). This approach is far more versatile than that starting with the synthesis of the parent 1,1-diethynylcyclopropane **4**.[17]

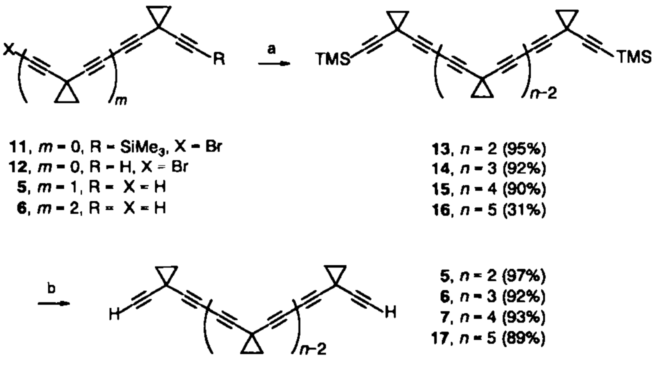


8 **9** **10** **11** **12**

Scheme 2. a: 1) *n*BuLi, Et_2O, 20 °C, 14 h; 2) DMF, 0 °C. b: Zn, Ph_3P, CBr_4, CH_2Cl_2, 20 °C, 30 h. c: *t*BuOK, THF, −78 °C, 5 h. d: 3 equiv $KF\cdot 2H_2O$, DMF, 20 °C, 3 h.

Deprotonation of **8** with *n*-butyllithium in ether and subsequent quenching with dimethylformamide (DMF) readily led to the aldehyde **9** (75%). This key functionalization sequence takes advantage of the enhanced acidity of cyclopropyl protons in a propargylic position reported by Köbrich et al.[20] Wittig-type olefination of **9** with a mixture of carbon tetrabromide, triphenylphosphane, and zinc in dichloromethane[21] gave **10** in 93% yield. Subsequent dehydrobromination of **10** with potassium *tert*-butoxide in THF yielded **11** in 95% yield, which was cleanly protiodesilylated with potassium fluoride in DMF to give the bromo-substituted 1,1-diethynylcyclopropane **12** in 74% yield.

Starting from the building blocks **11** and **12** and using only two standard repetitive operations—Cadiot-Chodkiewicz coupling[22] via intermediate copper derivatives and protiodesilylation with potassium fluoride—we were able to construct, step by step where necessary, any open-chain dehydrooligomer of **4** with a variety of chain lengths (Scheme 3).



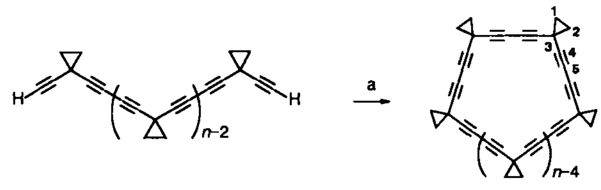
11, $m = 0$, R = $SiMe_3$, X = Br
12, $m = 0$, R = H, X = Br
5, $m = 1$, R = X = H
6, $m = 2$, R = X = H

13, $n = 2$ (95%)
14, $n = 3$ (92%)
15, $n = 4$ (90%)
16, $n = 5$ (31%)

5, $n = 2$ (97%)
6, $n = 3$ (92%)
7, $n = 4$ (93%)
17, $n = 5$ (89%)

Scheme 3. a: 1) 1–2 equiv MeLi, Et_2O, 0 °C, 0.5 h; 2) 1–2 equiv CuCl, THF, 0 °C, 2 h; 3) 1–2 equiv **11**, pyridine, 20 °C, 4 h. b: 3 equiv $KF\cdot 2H_2O$, DMF, 20 °C, 3 h.

When solutions in pyridine of the acyclic precursors **5**–**7**, **17**, or mixtures of two of these products were added over a period of three days to a slurry of cuprous chloride and cupric acetate in pyridine[18] and the reaction mixture was stirred at ambient temperature for an additional four days, the cyclic dehydrooligomers of **4** could be isolated in relatively good yields by column chromatography and/or recrystallization (Scheme 4). A 1:1 mixture of the short-chain starting materials **5** and **6** gave rise to the cyclic dehydropenta-, dehydrohexa-, dehydrohepta-, dehydroocta-, and dehydrononamers **18**, **19**, **20**, **21**, and **22**, respectively, which result from the coupling of all the simple possible combinations of $n \times [3] + m \times [2]$; acyclic compounds **7** (5%) and **17** (3%) were also isolated as by-products. Similar results were obtained with a mixture of **6** and **7**. A direct ring closure of the acyclic dehydrotetramer **7** did not occur, but compound **7**, after dimerization to an acyclic dehydrooctamer, cyclized reasonably well (46% yield) to the "expanded" [8]rotane **21**.[23a] The acyclic dehydropentamer **17** cyclized rather efficiently (70% yield) to give the "expanded" [5]rotane **18**. By-products, most probably the higher cyclic dehydrooligomers **23** ($n = 10$) and **24** ($n = 12$), were obtained in negligible quantities.[23b] The oxidative dimerization of the monosilylated acyclic dehydrotetramer **25** led to the cyclic dehydrooctamer **21** in even better yield (55%) than the analogous reaction with the desilylated precursor **7** (46%). This demon-



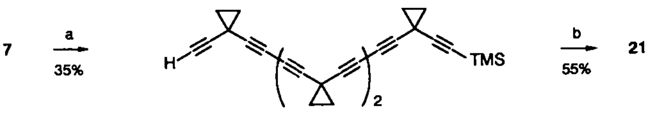
5, $n = 2$
6, $n = 3$
7, $n = 4$
17, $n = 5$

18, $n = 5$
19, $n = 6$
20, $n = 7$
21, $n = 8$
22, $n = 9$
23, $n = 10$
24, $n = 12$

Acyclic precursors ([*n*])	Product distribution				
5 + **6** ([2] + [3])	**18**([5]): 35%	**19**([6]): 20%	**20**([7]): 13%	**21**([8]): 3%	**22**([9]): trace
6 ([3])	**19**([6]): 39%	**22**([9]): 8%			
6 + **7** ([3] + [4])	**19**([6]): 28%	**20**([7]): 44%	**21**([8]): 14%	**22**([9]): trace	
7 ([4])	**21**([8]): 46%	**24**([12]): 1%			
17 ([5])	**18**([5]): 70%	**23**([10]): 0.2%			

Scheme 4. a: 12 equiv CuCl, 16 equiv $Cu(OAc)_2$, pyridine, 20 °C, 7 d (inverse addition over a period of 3 d).

strates that desilylation does occur under the applied conditions and that at least a trimethylsilyl residue does not provide sufficient protection if long-chain acyclic dehydrooligomers are to be synthesized (Scheme 5).



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Scheme 5. a: 1) 1 equiv EtMgBr, THF, 0 °C, 0.5 h; 2) 1.1 equiv Me_3SiCl, 0–20 °C, 0.5 h. b: 12 equiv CuCl, 16 equiv $Cu(OAc)_2$, pyridine, 20 °C, 3 d (inverse addition over a period of 3 h).

All cyclic compounds **18**–**24** were characterized by their diagnostically simple ^1H and ^{13}C NMR spectra (see Table 1). Surprisingly, the ^{13}C chemical shifts of the cyclic compounds differ only slightly from those of the acyclic dimers and the simple subunit 1,4-dicyclopropylbutadiyne.[7] Some regularities can be observed, however. On going from **18** to **24** (i.e., with an increase of the central ring size), a small but steady downfield shift is noticeable in the ^1H NMR spectra. The same effect holds for the methylene carbon signals in the ^{13}C NMR spectra, whereas all the other carbon signals experience upfield shifts with growing ring size. The latter effect is clearly detectable for the lower members and negligible for the higher members of this family.

Table 1. NMR chemical shifts of "exploding" [*n*]rotanes ($n = 5, 6, 7, 8, 9, 10$, and 12): $CDCl_3$, $\delta(CHCl_3) = 7.26$ and $\delta(CDCl_3) = 77.0$. Numbering of atoms as in Scheme 4.

	18	**19**	**20**	**21**	**22**	**23**	**24**
$\delta(^1H)$	1.252	1.285	1.297	1.304	1.305	1.312	1.308
							→
δ(C-5)	62.882	62.515	62.409	62.396	62.415	62.388	62.343
	←						
δ(C-4)	78.038	77.765	77.787	77.807	77.733	77.785	77.737
	←						
δ(C-3)	3.925	3.906	3.873	3.860	3.871	3.871	3.835
	←						
δ(C-1,2)	20.375	21.018	21.285	21.333	21.299	21.317	21.322
							→

Attempts to determine the molecular masses of **18**–**24** by mass spectrometry with routine ionization methods (EI, CI, DCI, FD) failed, as the compounds apparently decomposed irregularly in the inlet system of the mass spectrometer. The molecular masses of compounds **18**–**21**, but not of **22**–**24**, were successfully determined by the MALDI-TOF-MS[24] method with a 9-nitroanthracene matrix and found to be 440.2 (**18**: calcd for $C_{35}H_{20}$ 440.5), 527.3 (**19**: calcd for $C_{42}H_{24}$ 528.6), 616.2 (**20**: calcd for $C_{49}H_{28}$ 616.7), and 704.7 g mol^{-1} (**21**: calcd for $C_{56}H_{32}$ 704.8).[25] The molecular masses of compounds **19**, **21**, and **22** were also determined by vapor pressure osmometry in dichloromethane solution to be 529, 700, and 783 g mol^{-1} (**22**: calcd for $C_{63}H_{36}$ 792.9 g mol^{-1}), respectively. Thus, the compounds **18**, **19**, **20**, **21**, and **22** were identified as the cyclic dehydropentamer, dehydrohexamer, dehydroheptamer, dehydrooctamer, and dehydrononamer of 1,1-diethynylcyclopropane **4**, respectively.

While attempts to grow good quality crystals of the higher "expanded" [*n*]rotanes failed, X-ray crystal structure analyses were successfully performed for the "expanded" [5]rotane **18** (crystals from CH_2Cl_2 and CCl_4), [6]rotane **19** (crystals from $CHCl_3$), [7]rotane **20**, and [8]rotane **21** (crystals from Et_2O) (Fig. 1–3, for bond lengths and angles see Table 2).

The crystals of **18**(C_s), **20**, and **21** all contain one molecule of solvent per molecule of macrocycle; those of **19** contain two molecules of chloroform per molecule of **19**. Except for **18** in crystals obtained from CH_2Cl_2 (Fig. 1 top), none of the "expanded" [*n*]rotanes are planar. Therefore, a maximum overlap does not occur between the Walsh orbitals of the spirocyclopropane units and the π orbitals of the adjacent ethynyl groups. In crystals from CCl_4 compound **18** has an envelope conforma-

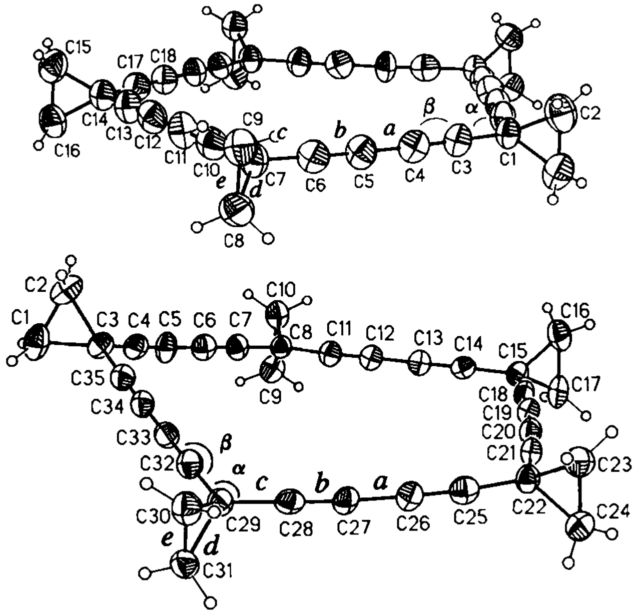


Fig. 1. Crystal structures of **18**. Top: crystals from CH_2Cl_2. Bottom: crystals from CCl_4. The numbering of atoms is not the same as the systematic numbering according to IUPAC nomenclature.

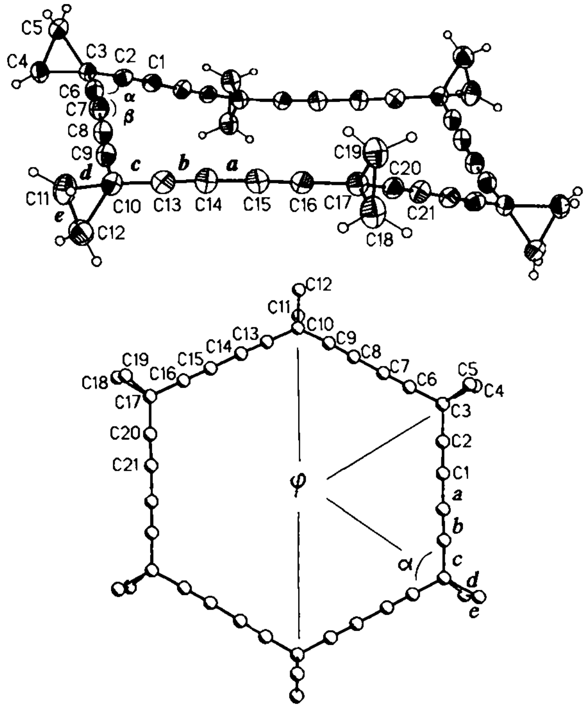


Fig. 2. Crystal structure of **19**. The numbering of atoms is not the same as the systematic numbering according to IUPAC nomenclature.

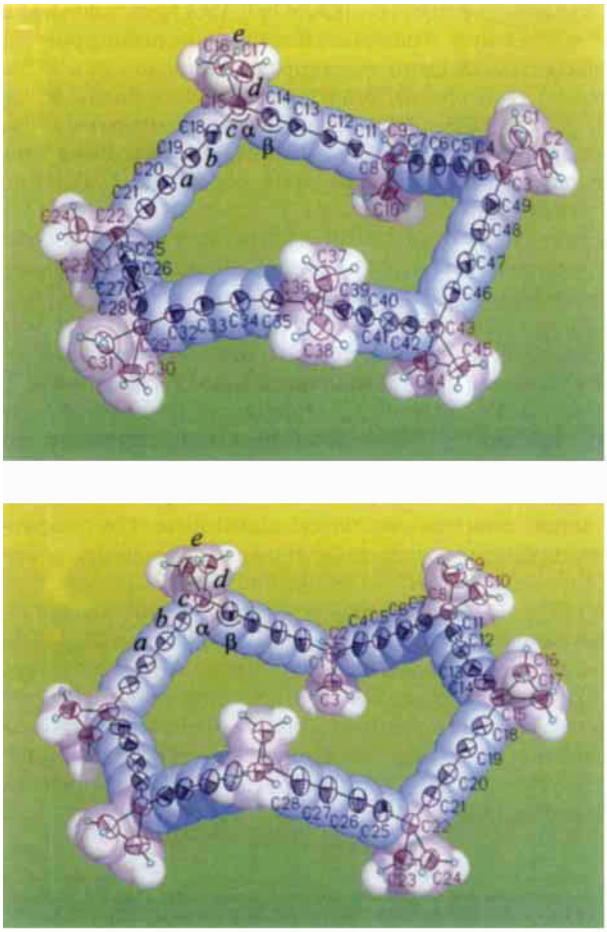


Fig. 3. Crystal structures of **20** (top) and **21** (bottom). The numbering of atoms is not the same as the systematic numbering according to IUPAC nomenclature.

tion with torsional angles of C29-C3-C8-C15 = – 25.0°, C3-C8-C15-C22 = 17.0°, C8-C15-C22-C29 = – 2.1°, C15-C22-C29-C3 = – 13.9°, and C8-C3-C29-C22 = 25.2°. The ring is, however, less puckered than in [5]rotane (corresponding angles: – 39.6, 27.2, 4.6, 36.7, and – 19.8°[26]) and cyclopentane (– 40.3, 25.0, 0, 40.3, and – 25.0°).[27] This effect is caused by the fact that the exocyclic bond angle between two substituents on the same carbon of a cyclopropane ring is usually larger than the tetrahedral angle of 109.47°. However, the puckering can apparently be easily overcome by crystal packing forces, as is demonstrated by the planar 25-membered ring in the crystals obtained from CH_2Cl_2 (Fig. 1 top). Similarly, the chair of the 30-membered ring of compound **19** with an average torsional angle of $\phi = 41.4(4)°$ is less puckered than cyclohexane (ϕ = 55.1°)[28] and [6]rotane (ϕ = 54.6°).[29]

Table 2. Averaged structural parameters (standard deviations in parentheses) for compounds **18–21** (see Figs. 1–3).

	18	**18**	**19**	**20**	**21**
Symmetry [a]	D_{5h}	C_s	D_{3d}	C_s	C_{2h}
a [Å]	1.377(10)	1.377(5)	1.379(4)	1.373(4)	1.383(9)
b [Å]	1.191(7)	1.196(3)	1.190(3)	1.195(3)	1.191(6)
c [Å]	1.439(10)	1.450(4)	1.443(2)	1.445(3)	1.452(6)
d [Å]	1.520(9)	1.528(4)	1.526(3)	1.527(3)	1.530(7)
e [Å]	1.465(6)	1.475(6)	1.467(3)	1.471(6)	1.476(12)
α [°]	114.3(5)	114.7(4)	115.5(4)	115.5(4)	116.2(6)
β [°]	178.3(6)	177.3(7)	178.8(2)	176.6(5)	175.6(11)
β_{min} [°]	176.9(10) C7-C10-C11	174.1(6) C6-C7-C8	177.0(3) C6-C7-C8	172.9(4) C34-C35-C36	173.9(8) C12-C13-C14

[a] Apparent mean symmetry of the respective molecules in the crystals.

The cyclic oligodiacetylenes **20** and **21** adopt chair-like conformations with the following torsional angles: C43-C3-C8-C15 = 69.0°, C3-C8-C15-C22 = – 90.8°, C8-C15-C22-C29 = 81.2°, C15-C22-C29-C36 = – 13.9°, C22-C29-C36-C43 = – 45.8°, C29-C36-C43-C3 = 99.4°, and C8-C3-C43-C36 = – 97.0° for **20** and C1-C8-C15-C22 = – 20.8°, C8-C15-C22-C1 = – 69.5°, C15-C22-C1-C8 = 101.4°, and C22-C1-C8-C15 = – 82.7° for **21**. This means that the "expanded" seven-membered ring in **20** is puckered almost to the same extent as or perhaps even more severely than cycloheptane (corresponding angles: 66.0, – 89.5, 70.7, 0, – 70.7, 89.5, and – 66.0°).[30] A chair-like conformation for cyclooctane analogous to that in the "expanded" [8]rotane **21** was not found experimentally.[31] Apparently, the exocyclic bond angles on the spirocyclopropane moieties in the whole series of "expanded" [*n*]rotanes **18–21** are maintained as closely as possible to the value observed between the two exocyclic C–C bonds in 1,1-diethynylcyclopropane **4** (115.1°).[32] This forces the macrocycles **18** and **19** to be less puckered than the five-membered rings in cyclopentane (106.1°)[27] and [5]rotane (105.3°)[26] or the six-membered rings in cyclohexane (111.4°)[28] and [6]rotane (111.5°).[29] The corresponding angle in **20** is comparable to the mean values in cycloheptane (115.3 and 113.5°).[30] Only in the "expanded" [8]rotane **21** is this bond angle 116.2° and thus slightly larger than in 1,1-diethynylcyclopropane.[32] This is probably a result of an energetic compromise between further inward bending of the 1,3-butadiyne units and angle deformation on the three-membered ring, although the C-C-C angle in cyclooctane (mean value) is practically the same as in **21** (116.4°).[31]

The three-membered rings thus provoke a significant bending of the triple bonds (Table 2, averaged values). The minimum value for β of 172.9(4)° was found for the "expanded" [7]rotane **20**. Surprisingly, the bending of the acetylene units is practically the same in the quasi-planar conformation of **18** (torsional angles: C7a-C1-C7-C14 = – 1.4°, C1-C7-C14-C14a = 3.7°, C7-C14-C14a-C7a = – 4.7°, C7-C1-C7a-C14a = – 1.4°, and C14-C14a-C7-C1 = 3.7°) as in the envelope conformation of **18** and **19** (cf., the bond angle of 114.3(5)° in the spirocyclopropane unit of **18** to that of 108° calculated for the D_{5h} symmetry in cyclopentane[27]). In one respect both **20** and **21** are unique: the 1,3-butadiyne units in these macrocycles are bent inwards. This feature has not previously been observed for any macrocyclic oligodiacetylene, while outward bending is quite common.[7–9a] The small local differences in the structural parameters can be attributed to crystal packing effects and the influence of solvent molecules. Thus, an abnormally short contact (1.83 Å) between the two hydrogen atoms adjacent to C3 in **21** and the methylene group of an incorporated diethyl ether was determined.

The ethynyl groups on the cyclopropane rings in **18–21** are apparently electron withdrawing, as the proximal and the distal bonds in the three-membered rings are found to be significantly different (Table 2). The observed lengthening of the proximal and shortening of the distal bonds is also found for 1,1-diethynylcyclopropane **4** [1.526(1) vs. 1.483(1) Å][32] and is consistent with the known effect of electron-withdrawing substituents on cyclopropane[33] put forward by MO theory.[34] Such a bond differentiation is not observed in [5]- and [6]rotane[26, 29] and is opposite to that in [3]rotane, in which the proximal bonds are shortened and the distal bonds are lengthened.[35] In a 1,1-diethynylcyclopropane, both dominant interactions—the electron donation from the in-plane filled π-MOs of the acetylene units into the cyclopropane LUMO and the electron donation out of the cyclopropane HOMO into the out-of-plane vacant MOs of the acetylene units—lead to an increased bonding in the distal and a decreased bonding in the proximal ring bonds.[15] The electron donating action of the spirocyclopropane groups on the other hand does not affect the C≡C triple-bond lengths.

The UV spectra for the macrocyclic compounds **18**–**22** and **24** all look alike and quite similar to those for the basic chromophore 1,4-dicyclopropylbutadiyne and the acyclic dehydrotrimer **6** in the long-wavelength region, with bathochromic shifts of about 2 nm for the absorption maxima. The intense main absorptions in the region 200–220 nm ($\varepsilon = 128000$–450000), however, are strikingly different. A distinct bathochromic shift is observed on going from 1,4-dicyclopropylbutadiyne through **18**–**22** to **24**; more interestingly, this absorption splits into two bands for macrocycles **18**–**22** and **24**, but with different magnitudes (Fig. 4). This effect must be related to the expected increase in homoconjugative interaction between ethynyl units in the "expanded" [*n*]rotanes, as corresponding effects are not observed in the UV spectra of the analogous permethylated macrocycles of types **1** and **2**.[2, 3, 6]

Another striking feature common to all "expanded" [*n*]rotanes **18**–**21** is their shock sensitivity: when struck too hard with a spatula, a pestle, or a falling ball, they ignite and yield a cloud of black soot. Attempts to determine the melting point of the macrocycle **18** led to the complete destruction of a Büchi instrument. This unusual behavior of the whole family, which led to the term "exploding" [*n*]rotanes, can be attributed to the additional strain introduced by the three-membered rings; the analogous permethylated macrocyclic oligodiynes **2** exhibit no such sensitivities.[6]

In view of the strain energy incorporated in a carbocyclic three-membered ring (28.1 kcal mol^{-1} [36]), the completely spirocyclopropanated "exploding" [*n*]rotanes must be true high-energy molecules, as their acetylene units also have very unfavorable heats of formation (acetylene itself has a $\Delta H_f^\circ = +54.47$ kcal mol^{-1} [37]). According to AM1 calculations,[38] the six-sided "exploding" [6]rotane **19** has $\Delta H_f^\circ = +773.1$ kcal mol^{-1}. The heat of formation determined experimentally for 1,1-diethynylcyclopropane (**4**) is $\Delta H_f^\circ = 128.7$ kcal mol^{-1},[39] and $128.7 \times 6 = 772.2$ kcal mol^{-1} incidentally almost coincides with the calculated value. For comparison, the hydrocarbon cubane **26**, known for its high strain energy, has only a $\Delta H_f^\circ = 148.7$ kcal mol^{-1} [40a] (a value of 158.8 kcal mol^{-1} has also been reported[40b]), and even the extremely strained perspirocyclopropanated [3]rotane **27** and the elusive octacyclotriangulane **28**[41] with $\Delta H_f^\circ = 274.2$ and 247.5 kcal mol^{-1}, respectively, do not come close to **19**, even when the values are normalized according to the relative molecular masses of the compounds (see Table 3). The buckminsterfullerene **29** with $\Delta H_f^\circ = 846$ cal g^{-1} is a "low-energy" molecule compared to **19** (see Table 3).

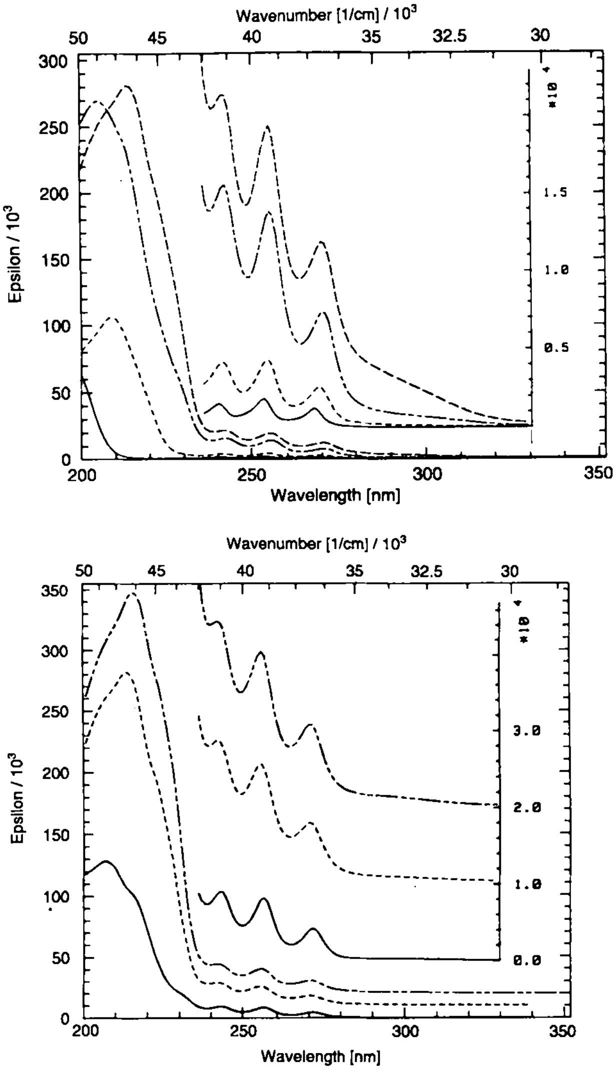
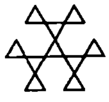
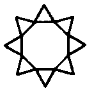
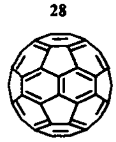


Fig. 4. UV spectra in *tert*-butyl methyl ether. Top: 1,4-dicyclopropylbutadiyne (——) in methanol, **6** (- - - -), **19** (— — –), and **22** (– – –). Bottom: **18** (——), **21** (- - - -), and **24** (— — –).

Table 3. Estimated heat of formation (ΔH_f°) and strain energy (SE) for "exploding" [6]rotane **19** compared with those for some highly strained model compounds.

Compound	ΔH_f° [kcal mol^{-1}]	M [g mol^{-1}]	ΔH_f° [cal g^{-1}]	SE[a] [kcal mol^{-1}]	Ref.
19	773.1[b]	528.6	1462.5	855.4	This work
	772.2[c]		1460.8	854.5	This work
4	128.7[d]	90.1	1428.4	144.2	[39]
 **26**	145.1–149.7[e]	104.1		154.7–166.9[e]	[40,42]
	148.7[d]		1428.4	157.0[f]	
	158.8[d]		1525.4	161.0[f]	
	151.2[b]		1452.4	168.5	
 **27**	274.2[g]	276.4	999.3	355.7	[41,43]
 **28**	247.5[g]	208.3	1188.0	290.9	[41]
	268.1[b]		1287.1		This work
 **29**	609.6[d]	720.6	846.0	627.6	[44]

[a] Calculated for a strain-free model using the increments of Schleyer et al. [36]. [b] Calculated according to the AM 1 method [38]. [c] Estimated as the sixfold value of ΔH_f° for compound **4** without appropriate additional corrections. [d] Based on experimentally determined heat of combustion. [e] Calculated by different theoretical methods [42]. [f] As calculated in the original publications [40] on the basis of experimental data. [g] Calculated using homodesmic reactions and the empirical rule of additivity [41].

Conclusion

The reported efficient synthesis for perspirocyclopropanated macrocyclic and acyclic homoconjugated oligodiacetylenes can be applied quite generally for these and other members of the family. It is expected that the use of appropriate methods will lead to more information about unusual properties and probably evidence about the electronic interaction in the macrocycles in the near future.[45] In any case, it has already been demonstrated that appropriate chemical transformations of such macrocyclic oligodiacetylenes, for example, thiocyclization with sodium sulfide in dimethylsulfoxide, can lead to interesting novel macroheterocyclic materials.[46]

Experimental Procedure

Materials: The procedures for the preparation of compounds **4** [17] and **8** [19] have been published previously. All operations were performed under nitrogen in flame-dried glassware. Commercially available CuCl and Zn were washed with 3% HCl, water, ethanol, and diethyl ether and activated by heating under reduced pressure (0.1 Torr, 100 °C, 12 h). Anhydrous $Cu(OAc)_2$ was prepared from the commercially available dihydrate by heating under reflux in acetic anhydride for 48 h. The salt was filtered under nitrogen, washed with anhydrous Et_2O, and dried under vacuum. Diethyl ether and THF were dried by distillation from sodium benzophenone ketyl, pyridine and DMF from calcium hydride, and CH_2Cl_2 from P_2O_5. ^1H NMR: Bruker AM 250 (250 MHz). ^{13}C NMR: Bruker AM 250 (62.9 MHz); multiplicities were determined by DEPT (distortionless enhancement by polarization transfer) measurements. Chemical shifts refer to $\delta_{TMS} = 0.00$ and are measured relative to the chemical shifts of residual $CHCl_3$ signals. UV: Cary 219. GC analyses: Siemens Sichromat 1–4. Melting points: Büchi 510 and Thomas Hoover capillary melting point apparatus; uncorrected. Elemental analyses: Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Universität Göttingen and Spang Microanalytical Laboratory, Eagle Harbour, Michigan. Column Chromatography: Baker silica gel, 600–200 mesh, and Merck silica gel, grade 60, 230–400 mesh.

Crystal structure determination: suitable crystals were grown by slow concentration of diluted solutions. The X-ray data (Table 4) were collected on an automated diffractometer Nicolet R 3m/v, graphite monochromator, Mo_{K_α} radiation, Wyckoff scan. The structures were solved by direct methods (SHELXTL-PLUS). The structural parameters (C anisotropic, H isotropic) were refined by full-matrix least-squares technique. Further details of the structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-401338 (D_{5h}-**18**), CSD-401339 (C_s-**18**), CSD-400451 (**19**), CSD-401323 (**20**), and CSD-401340 (**21**).

Table 4. Crystal and data collection parameters for compounds **18**–**21**.

	D_{5h}-**18**	C_s-**18**	**19**	**20**	**21**
Formula	$C_{35}H_{20}$	$C_{35}H_{20} \cdot CCl_4$	$C_{42}H_{24} \cdot 2CHCl_3$	$C_{49}H_{28} \cdot Et_2O$	$C_{56}H_{32} \cdot Et_2O$
M	440.5	594.4	767.4	690.9	779.0
Cryst. size [mm]	0.31 × 0.29 × 0.20	0.26 × 0.39 × 0.29	0.65 × 0.52 × 0.45	0.26 × 0.47 × 0.29	0.24 × 0.26 × 0.17
Cryst. color	colorless	colorless	colorless	colorless	colorless
Space group	$C2/c$	$P4_2/n$	$P2_1/n$	C/c	$P2_1/c$
a [Å]	16.765(4)	27.375(7)	6.053(2)	16.599(4)	15.531(4)
b [Å]	14.793(3)	27.375(7)	21.121(8)	24.806(7)	17.405(7)
c [Å]	15.860(3)	8.366(5)	15.161(4)	11.379(4)	10.988(4)
α [°]	90	90	90	90	90
β [°]	121.19(1)	90	92.34(2)	115.73(2)	105.91(2)
γ [°]	90	90	90	90	90
V [Å^3]	3364.5(11)	6269.7(50)	1936.6(9)	4220.6(22)	2856.4(10)
ρ_{calcd} [g cm^{-3}]	0.870	1.259	1.360	1.163	0.906
Z	4	8	2	4	2
T [K]	293	200	200	200	200
Refl. independent	2187	3998	3397	6304	3614
Refl. observed [$F_0 \geq 4\sigma(F)$]	1501	2462	2566	5111	2130
R	0.1143	0.0718	0.0471	0.0534	0.1038
R_w	0.1034	0.0804	0.0472	0.0570	0.1004
μ [mm^{-1}]	0.05	0.40	0.26	0.07	0.05
2θ [°]	3–45	3–45	3–50	3–50	3–45
No. refined parameters	159	381	229	489	271

Oxidative coupling of oligoacetylenes (general procedure GP 1): A solution of oligoacetylene (3.75 mmol) in anhydrous pyridine (50 mL) was added dropwise over 72 h to a slurry of CuCl (5.72 g, 57.77 mmol) and $Cu(OAc)_2$ (14.39 g, 79.22 mmol) in anhydrous, oxygen-free pyridine (1250 mL) at 25 °C. The reaction mixture was stirred for an additional 4 d, and then 1250 mL of concentrated HCl was added at −5 to −10 °C; during this addition the reaction mixture was cooled with a dry ice acetone bath. The aqueous layer was extracted with 4 × 250 mL of CH_2Cl_2, and the combined extracts were washed with 2 × 250 mL of ice cold 5% HCl, 250 mL of 5% $NaHCO_3$ solution, and 250 mL of water; they were then dried over $MgSO_4$ and concentrated under reduced pressure. The products were isolated by column chromatography or crystallization from an appropriate solvent (**CAUTION**: the isolated products should not be heated too high or scratched too hard with a spatula, as they may suddenly decompose to leave only black soot).

Cadiot–Chodkiewicz coupling (general procedure GP 2): A solution of methyllithium in ether (6 mmol for **11** and 12 mmol for **5**, **6**, and **12**) was added at 0 °C over 30 min to a solution of oligoacetylenes **5** or **6** (12 mmol) or bromooligoacetylenes **11** or **12** (6 mmol) in anhydrous ether (25 mL). After the mixture was stirred for 30 min, the solvent was carefully removed under vacuum and replaced by anhydrous THF (40 mL) at −20 °C. CuCl (for **11**: 0.58 g, 5.86 mmol; for **5**, **6**, and **12**: 1.158 g, 11.7 mmol) was added to this solution at −20 °C, and the mixture was stirred for an additional 2 h at 0 °C (**CAUTION**: copper acetylides can be explosive when dry). The THF was then carefully removed under vacuum and replaced by anhydrous pyridine (50 mL). A solution of **11** (for **11**: 1.4 g, 5.8 mmol; for **5**, **6**, and **12**: 2.8 g, 11.6 mmol) in THF (20 mL) was added dropwise over a period of 2 h at 0 °C. After stirring for 2 h at 20 °C, the resulting mixture was poured into 100 mL of ice cold 15% HCl. The organic layer was washed with 50 mL of 5% $NaHCO_3$ solution and 50 mL of water, dried over $MgSO_4$, and concentrated under reduced pressure. The crude products were purified by column chromatography.

Desilylation of trimethylsilyl-protected oligoacetylenes (general procedure GP 3): To a solution of 3 equiv of $KF \cdot 2H_2O$ per trimethylsilyl group in DMF was added the respective trimethylsilyl-substituted acetylene, and the reaction mixture was stirred for 3 h at room temperature. The resulting mixture was poured into water and extracted three times with Et_2O. The combined organic layers were washed with 5% HCl, 5% $NaHCO_3$ solution, and H_2O, dried over $MgSO_4$, and concentrated under reduced pressure. The products were purified by column chromatography.

3:3,8:8-Bisethanodeca-1,4,6,9-tetrayne (5): The reaction mixture obtained from the desilylation of **13** (2.396 g, 7.43 mmol) with $KF \cdot 2H_2O$ (4.19 g, 44.5 mmol) in DMF (50 mL) according to GP 3 gave, after column chromatography (120 g of silica gel, 40 × 4 cm), 1.284 g (97%) of **5** ($R_f = 0.37$, pentane/diethyl ether 35/1): M.p. 34–35 °C (from hexane); ^1H NMR: $\delta = 1.27$ (s, 8H; CH_2), 1.98 (s, 2H; CH); ^{13}C NMR: $\delta = 20.63$ (CH_2), 83.73 (CH), 2.97, 61.81, 65.42, 78.35 (C); $C_{14}H_{10}$ (178.2): calcd C 94.34, H 5.66; found C 94.29, H 5.59.

3:3,8:8,13:13-Trisethanopentadeca-1,4,6,9,11,14-hexayne (6): The reaction mixture obtained from the desilylation of **14** (2.495 g, 6.07 mmol) with $KF \cdot 2H_2O$ (3.426 g, 36.40 mmol) in DMF (50 mL) according to GP 3 gave, after column chromatography (120 g of silica gel, 40 × 4 cm), 1.490 g (92%) of **6** ($R_f = 0.24$, pentane/diethyl ether 35/1): M.p. 101–102 °C (from MeOH); ^1H NMR: $\delta = 1.28$ (s, 8H; CH_2), 1.30 (s, 4H; CH_2), 1.98 (s, 2H; CH); ^{13}C NMR: $\delta = 20.67$, 21.32 (CH_2), 83.71 (CH), 3.00, 3.82, 61.76, 62.36, 65.43, 77.27, 78.69 (C); $C_{21}H_{14}$ (266.3): calcd C 94.70, H 5.30; found C 94.59, H 5.19.

3:3,8:8,13:13,18:18-Tetrakisethanoeicosa-1,4,6,9,11,14,16,19-octayne (7): The reaction mixture obtained from the desilylation of **15** (4.00 g, 8.02 mmol) with $KF \cdot 2H_2O$ (4.52 g, 48.0 mmol) in DMF (70 mL) according to GP 3 gave, after column chromatography (130 g of silica gel, 40 × 4 cm), 2.643 g (93%) of **7** ($R_f = 0.31$, pentane/diethyl ether 10/1): M.p. 143–144 °C (from hexane/CCl_4 10/1); ^1H NMR: $\delta = 1.29$ (s, 8H; CH_2), 1.31 (s, 8H; CH_2), 1.98 (s, 2H; CH); ^{13}C NMR: $\delta = 20.67$, 21.36 (CH_2), 83.69 (CH), 2.99, 3.82, 61.74, 62.25, 62.36, 65.43, 77.37, 77.73, 78.68 (C); $C_{28}H_{18}$ (354.4): calcd C 94.88, H 5.12; found C 94.47, H 4.98.

Oxidative coupling of 1,1-diethynylcyclopropane (4): From 1.00 g (11.1 mmol) of **4**, 13.27 g (0.134 mol) CuCl, and 48.32 g (0.266 mol) of $Cu(OAc)_2$ in pyridine (1 L) according to GP 1, 182 mg (18%) of **5**, 129 mg (13%) of **6**, and 98 mg (10%) of **7** were isolated after column chromatography (200 g of silica gel, 30 × 7 cm, pentane/diethyl ether 10/1).

1-Formyl-1-(trimethylsilylethynyl)cyclopropane (9): To a solution of **8** (30.00 g, 0.217 mol) in anhydrous ether (400 mL) was added a 2.4 M solution of *n*BuLi in hexane (90.5 mL, 0.22 mol). The reaction mixture was stirred for 14 h at room temperature, then cooled to 0 °C, and anhydrous DMF (40 mL) was added dropwise. This solution was allowed to warm to 20 °C and was then poured into 400 mL of ice cold water. The layers were separated, and the aqueous layer was extracted with 2 × 50 mL of ether. The combined organic layers were washed with 2 × 100 mL of H_2O and dried over $MgSO_4$. After evaporation of the solvent, the residue was fractionally distilled to give 27.17 g (75%) of **9**: B.p. 67–70 °C (27 Torr); ^1H NMR: $\delta = 0.16$ (s, 9H; $SiMe_3$), 1.48 (m, 2H; CH_2), 1.51 (m, 2H; CH_2), 9.44 (s, 1H; CHO); ^{13}C NMR: $\delta = -0.17$ (CH_3), 26.84 (CH_2), 198.03 (CH), 21.16, 85.34, 104.29 (C).

1-(2,2-Dibromoethenyl)-1-(trimethylsilylethynyl)cyclopropane (10): Zinc (19.61 g, 0.30 mol), triphenylphosphane (78.69 g, 0.30 mol), and carbon tetrabromide (99.49 g, 0.30 mol) were mixed in anhydrous CH_2Cl_2 (600 mL) at −20 °C and then stirred for 30 h at room temperature. Compound **9** (25.0 g, 0.15 mol) was added to the resulting mixture, and stirring was continued for an additional 2 h. The reaction mixture was then poured into 800 mL of pentane, and the insoluble material was removed by filtration. The insoluble fraction was worked up by two additional cycles of methylene chloride extraction and pentane precipitation to remove all of the olefinic product. Evaporation of the solvent gave 45.0 g (93%) of **10**: M.p. 46–47 °C (from MeOH); ^1H NMR: $\delta = 0.11$ (s, 9H; $SiMe_3$), 0.98–1.30 (m AA'BB', 4H; CH_2), 6.40 (s, 1H; CH); ^{13}C NMR: $\delta = 0.12$ (CH_3), 18.80 (CH_2), 137.14 (CH), 15.10, 81.36, 94.80, 107.23 (C); $C_{10}H_{14}Br_2Si$ (322.1): calcd C 37.28, H 4.38, Br 49.62; found C 37.37, H 4.46, Br 49.45.

1-(Bromoethynyl)-1-(trimethylsilylethynyl)cyclopropane (11): To a solution of **10** (45.0 g, 0.139 mol) in anhydrous THF (1800 mL) was added in portions sublimed potassium *tert*-butoxide (31.4 g, 0.28 mol) at −78 °C over a period of 2 h. The resulting reaction mixture was stirred for an additional 5 h at −78 °C and then poured into 2 L of H_2O. The aqueous layer was extracted with 3 × 750 mL of pentane. The combined extracts were washed with 1 L of 5% HCl, 1 L of 5% $NaHCO_3$ solution, and 3 × 1 L of water and dried over $MgSO_4$. After evaporation of the solvent, the residue (31.9 g, 95%) can be used without further purification. **11**: M.p. 36–38 °C (from MeOH); ^1H NMR: $\delta = 0.13$ (s, 9H; $SiMe_3$), 1.24 (s, 4H; CH_2); ^{13}C NMR: $\delta = 0.01$ (CH_3), 20.51 (CH_2), 4.55, 35.99, 80.60, 81.08, 105.99 (C); $C_{10}H_{13}BrSi$ (241.2): calcd C 49.80, H 5.43; found C 49.91, H 5.40.

1-(Bromoethynyl)-1-ethynylcyclopropane (12): The reaction mixture obtained from the desilylation of **11** (5.00 g, 20.73 mmol) according to GP3 (DMF: 50 mL; $KF \cdot 2H_2O$: 5.8 g, 62 mmol) gave after distillation 2.58 g (74%) of **12**: B.p. 35–40 °C (1 Torr); ^1H NMR: $\delta = 1.27$ (s, 4H; CH_2), 2.00 (s, 1H; CH); ^{13}C NMR: $\delta = 19.59$ (CH_2), 84.02 (CH), 3.29, 36.31, 65.13, 80.04 (C); C_7H_5Br (169.0): calcd C 49.74, H 2.98; found C 49.51, H 3.13.

1,10-Bis(trimethylsilyl)-3:3,8:8-bisethanodeca-1,4,6,9-tetrayne (13): The reaction mixture obtained from the coupling of **11** (2.89 g, 11.98 mmol) with 2.79 g (11.57 mmol) of **11** according to GP2 gave, after column chromatography (140 g of silica gel, 40 × 4 cm), 3.55 g (95%) of **13** ($R_f = 0.38$, pentane/diethyl ether 20/1): M.p. 87–88 °C (from MeOH); ^1H NMR: $\delta = 0.12$ (s, 18H; $SiMe_3$), 1.28 (s, 8H; CH_2); ^{13}C NMR: $\delta = -0.07$ (CH_3), 21.29 (CH_2), 4.00, 61.69, 78.61, 81.55, 105.36 (C); $C_{20}H_{26}Si_2$ (322.6): calcd C 74.46, H 8.13; found C 74.58, H 8.09.

1,15-Bis(trimethylsilyl)-3:3,8:8,13:13-trisethanopentadeca-1,4,6,9,11,14-hexayne (14): The reaction mixture obtained from the coupling of **12** (2.00 g, 11.83 mmol) and **11** (5.60 g, 23.22 mmol) according to GP2 gave, after column chromatography (150 g of silica gel, 40 × 4 cm), 4.47 g (92%) of **14** ($R_f = 0.42$, pentane/diethyl ether 35/1): M.p. 112–114 °C (from MeOH); ^1H NMR: $\delta = 0.12$ (s, 18H; $SiMe_3$), 1.27 (s, 8H; CH_2), 1.29 (s, 4H; CH_2); ^{13}C NMR: $\delta = 0.05$ (CH_3), 21.33 (CH_2), 3.86, 4.03, 61.47, 62.54, 77.22, 77.42, 79.15, 105.30 (C); $C_{27}H_{30}Si_2$ (410.7): calcd C 78.96, H 7.36; found C 79.02, H 7.41.

1,20-Bis(trimethylsilyl)-3:3,8:8,13:13,18:18-tetrakisethanoeicosa-1,4,6,9,11,14,16,19-octayne (15): The reaction mixture obtained from the coupling of **5** (1.78 g, 10.0 mmol) and **11** (4.66 g, 19.3 mmol) according to GP2 gave, after column chromatography (140 g of silica gel, 40 × 4 cm), 4.33 g (90%) of **15** ($R_f = 0.35$, pentane/diethyl ether 30/1): M.p. 144–145 °C (decomp.) (from MeOH); ^1H NMR: $\delta = 0.12$ (s, 18H; $SiMe_3$), 1.28 (s, 8H; CH_2), 1.30 (s, 8H; CH_2); ^{13}C NMR: $\delta = -0.09$ (CH_3), 21.32 (CH_2), 3.81, 3.99, 61.43, 62.23, 62.55, 77.15, 77.76, 79.11, 81.64, 105.23 (C); $C_{34}H_{34}Si_2$ (498.8): calcd C 81.87, H 6.87; found C 81.76, H 6.88.

1,25-Bis(trimethylsilyl)-3:3,8:8,13:13,18:18,23:23-pentakisethanopentacosa-1,4,6,9,11,14,16,19,21,24-decayne (16): The reaction mixture obtained from the coupling of **6** (2.663 g, 10.0 mmol) and **11** (4.66 g, 19.3 mmol) according to GP2 (the addition of MeLi was performed at −15 °C) gave, after column chromatography (130 g of silica gel, 40 × 4 cm), 1.767 g (31%) of **16** ($R_f = 0.34$, pentane/CH_2Cl_2 4/1): M.p. 164–166 °C (decomp.) (from hexane/CCl_4 10/1); ^1H NMR: $\delta = 0.12$ (s, 18H; $SiMe_3$), 1.27 (s, 8H; CH_2), 1.30 (s, 12H; CH_2); ^{13}C NMR: $\delta = -0.08$ (CH_3), 21.34 (CH_2), 3.83, 4.01, 61.42, 62.22, 62.28, 62.55, 77.16, 77.66, 77.80, 79.14, 81.66, 105.24 (C); $C_{41}H_{38}Si_2$ (586.9): calcd C 83.90, H 6.53; found C 83.80, H 6.72.

3:3,8:8,13:13,18:18,23:23-Pentakisethanopentacosa-1,4,6,9,11,14,16,19,21,24-decayne (17): The reaction mixture obtained from the desilylation of **16** (1.549 g, 2.64 mmol) with $KF \cdot 2H_2O$ (1.46 g, 15.5 mmol) in DMF (80 mL) according to GP3 gave, after column chromatography (120 g of silica gel, 40 × 4 cm), 1.039 g (89%) of **17** ($R_f = 0.36$, pentane/CH_2Cl_2 3/1): decomp. > 146 °C (from hexane/CCl_4 10/1); ^1H NMR: $\delta = 1.28$ (s, 8H; CH_2), 1.31 (s, 12H; CH_2), 1.98 (s, 2H; CH); ^{13}C NMR: $\delta = 20.67$, 21.36 (CH_2), 83.68 (CH), 2.88, 3.81, 61.73, 62.25, 62.27, 62.35, 65.44, 77.36, 77.67, 77.73, 78.67 (C). Attempted analytical combustion led to an explosion.

1-Trimethylsilyl-3:3,8:8,13:13,18:18-tetrakisethanoeicosa-1,4,6,9,11,14,16,19-octayne (25): A solution of **7** (877 mg, 2.47 mmol) in THF (50 mL) was treated with 1 equiv of EtMgBr (0.91 mL of 2.7 M solution in Et_2O) at 0 °C. After 30 min, chlorotrimethylsilane (0.30 g, 0.35 mL, 2.76 mmol) was added. After being stirred at 20 °C for 30 min, the mixture was quenched with water, washed with 5% $NaHCO_3$ solution (20 mL) and H_2O (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography over silica gel (100 g of silica gel, 50 × 3 cm, pentane/diethyl ether 10/1) gave **7** (223 mg, 25%, $R_f = 0.26$), **15** (432 mg, 35%, $R_f = 0.51$), and **25** (371 mg, 35%, $R_f = 0.38$): decomp. > 140 °C; ^1H NMR: $\delta = 0.11$ (s, 9H; $SiMe_3$), 1.24 (s, 4H; CH_2), 1.25 (s, 4H; CH_2), 1.28 (s, 8H; CH_2), 1.96 (s, 1H; CH); ^{13}C NMR: $\delta = -0.09$ (CH_3), 20.65, 21.31 (CH_2), 83.67 (CH), 2.98, 3.81, 3.99, 59.46, 61.45, 61.76, 62.26, 62.38, 62.58, 65.43, 76.75, 77.16, 77.37, 77.80, 78.69, 79.15, 81.65, 105.27 (C); $C_{31}H_{26}Si$ (426.6): calcd C 87.27, H 6.14; found C 87.11, H 6.25.

Oxidative cyclizations of 5–7 and 17:

1. The reaction mixture obtained from **5** (0.445 g, 2.50 mmol), **6** (0.665 g, 2.50 mmol), CuCl (5.70 g, 57.6 mmol), and $Cu(OAc)_2$ (14.37 g, 79.1 mmol) in pyridine (1.0 L) according to GP1 was adsorbed on 10 g of silica gel from CH_2Cl_2 (50 mL) and chromatographed over silica gel (200 g, 30 × 7 cm, pentane/diethyl ether 2/1) to give 22 mg (5%) of **7** ($R_f = 0.47$), 35 mg (3%) of **17** ($R_f = 0.42$), 387 mg (35%) of **18** ($R_f = 0.33$), 134 mg (20%) of **19** ($R_f = 0.25$), 100 mg (13%) of **20** ($R_f = 0.18$), 26 mg (3%) of **21** ($R_f = 0.14$), and 4 mg (0.6%) of **22** ($R_f = 0.09$).
2. The reaction mixture obtained from **6** (1.00 g, 3.76 mmol), CuCl (5.72 g, 57.8 mmol), and $Cu(OAc)_2$ (14.39 g, 79.2 mmol) in pyridine (1250 mL) according to GP1 was recrystallized from $CHCl_3$ to give 282 mg of **19**. The mother liquor was adsorbed on 10 g of silica gel from CH_2Cl_2 (40 mL) and chromatographed over silica gel (200 g, 30 × 7 cm, pentane/diethyl ether 2/1) to give **18** (49 mg), **19** (103 mg, overall yield 39%), and **22** (78 mg, 8%).
3. The reaction mixture obtained from **6** (0.205 g, 0.770 mmol), **7** (0.274 g, 0.773 mmol), CuCl (1.76 g, 17.8 mmol), and $Cu(OAc)_2$ (4.44 g, 24.4 mmol) in pyridine (300 mL) according to GP1 was adsorbed on 8 g of silica gel from CH_2Cl_2 (30 mL) and chromatographed over silica gel (150 g, 30 × 5 cm, pentane/diethyl ether 2/1) to give **18** (11 mg), **19** (57 mg, 28%), **20** (210 mg, 44%), **21** (39 mg, 14%), and **22** (5 mg, 2%).
4. The reaction mixture obtained from **7** (1.00 g, 2.82 mmol), CuCl (5.70 g, 57.6 mmol), and $Cu(OAc)_2$ (14.37 g, 79.1 mmol) in pyridine (1.0 L) according to GP1 was recrystallized from CCl_4 to give 304 mg of **21**. The mother liquor was adsorbed on 20 g of silica gel from CH_2Cl_2 (60 mL) and chromatographed over silica gel (200 g, 30 × 7 cm, pentane/diethyl ether 1/1) to give **18** (14 mg, $R_f = 0.47$), **19** (5 mg, $R_f = 0.37$), **21** (152 mg, overall yield 46%, $R_f = 0.30$), and **24** (10 mg, 1%).
5. The reaction mixture obtained from **17** (1.05 g, 2.37 mmol), CuCl (5.00 g, 50.5 mmol), and $Cu(OAc)_2$ (14.0 g, 77.1 mmol) in pyridine (1.0 L) according to GP1 was recrystallized from CCl_4 to give 629 mg of **18**. The mother liquor was adsorbed on 20 g of silica gel from CH_2Cl_2 (50 mL) and chromatographed over silica gel (200 g, 30 × 7 cm, pentane/diethyl ether 1/1) to give 99 mg of **18** [total yield of **18** was 728 mg (70%)], **19** (16 mg), and **23** (2 mg, 0.2%, $R_f = 0.21$).
6. The crude product from the reaction mixture obtained from **25** (0.441 g, 1.03 mmol), CuCl (1.20 g, 12.1 mmol), and $Cu(OAc)_2$ (3.10 g, 17.1 mmol) in pyridine (100 mL) according to GP1 (addition was complete in 1 h) was recrystallized from CCl_4 to give **21** (201 mg, 55%).

Pentaspiro[2.4.2.4.2.4.2.4.2.4]pentatriaconta-4,6,11,13,18,20,25,27,32,34-decayne (18): decomp. > 90 °C; expl. ≥ 150 °C; ^1H NMR: $\delta = 1.25$ (s); ^{13}C NMR: $\delta = 20.38$ (CH_2), 3.93, 62.90, 78.08 (C); MS (MALDI-TOF): m/z (%): 463.2 (100) [$M^+ + Na$], 413.1 (68) [$M^+ - C_2H_3$].

Hexaspiro[2.4.2.4.2.4.2.4.2.4.2.4]dotetraconta-4,6,11,13,18,20,25,27,32,34,39,41-dodecayne (19): decomp. > 130 °C; ^1H NMR: $\delta = 1.28$ (s); ^{13}C NMR: $\delta = 21.02$ (CH_2), 3.91, 62.52, 77.77 (C); MS (MALDI-TOF): m/z (%): 527.3 (100) [$M^+ - 1$], 500.38 (50) [$M^+ - C_2H_4$]; determination of mol. mass by vapor pressure osmometry: $C_{42}H_{24}$ (528.6): found 529.

Heptaspiro[2.4.2.4.2.4.2.4.2.4.2.4.2.4]nonatetraconta-4,6,11,13,18,20,25,27,32,34,39,41,46,48-tetradecayne (20): decomp. > 100 °C; ^1H NMR: $\delta = 1.30$ (s); ^{13}C NMR: $\delta = 21.29$ (CH_2), 3.87, 62.41, 77.79 (C); MS (MALDI-TOF): m/z (%): 639.2 (100) [$M^+ + Na$].

Octaspiro[2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4]hexapentaconta-4,6,11,13,18,20,25,27,32,34,39,41,46,48,53,55-hexadecayne (21): decomp. > 115 °C; ^1H NMR: $\delta = 1.30$ (s); ^{13}C NMR: $\delta = 21.30$ (CH_2), 3.86, 62.40, 77.81 (C); MS (MALDI-TOF): m/z (%): 727.7 (100) [$M^+ + Na$]; determination of mol. mass by vapor pressure osmometry: $C_{42}H_{24}$ (704.9): found 700.

Nonaspiro[2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4]trihexaconta-4,6,11,13,18,20,25,27,32,34,39,41,46,48,53,55,60,62-octadecayne (22): decomp. > 100 °C; ^1H NMR: $\delta = 1.31$ (s); ^{13}C NMR: $\delta = 21.30$ (CH_2), 3.87, 62.41, 77.73 (C); determination of mol. mass by vapor pressure osmometry: $C_{63}H_{36}$ (793.0): found 783.

Decaspiro[2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4]heptaconta-4,6,11,13,18,20,25,27,32,34,39,41,46,48,53,55,60,62,67,69-eicosayne (23): decomp. > 100 °C; ^{1}H NMR: $\delta = 1.31$ (s); ^{13}C NMR: $\delta = 21.32$ (CH_2), 3.87, 62.39, 77.79 (C).

Dodecaspiro[2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4]tetraoctaconta-4,6,11,13,18,20,25,27,32,34,39,41,46,48,53,55,60,62,67,69,74,76,81,83-tetracosayne (24): decomp. > 100 °C; ^{1}H NMR: $\delta = 1.31$ (s); ^{13}C NMR: $\delta = 21.32$ (CH_2), 3.84, 62.34, 77.74 (C).

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[24] MALDI-TOF-MS: matrix-assisted laser desorption time-of-flight mass spectrometry.

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