Structural Parameters and Electronic Interactions in Substituted 1,1-Diethynylcyclopropanes − An Experimental Study

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Dedicated to Professor Dieter Hoppe on the occasion of his 60th birthday

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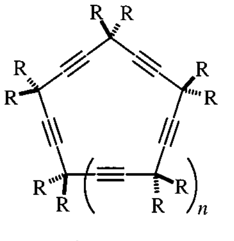
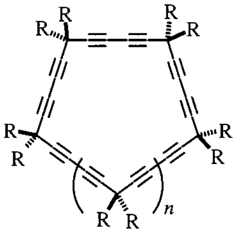
1,1-Bis(trimethylsilylethynyl)cyclopropane (**4**) and dimethyl 3,3′-(1,1-cyclopropanediyl)bis(2-propynoate) (**5**) have been prepared by silylation of the known 1-(bromoethynyl)-1-(trimethylsilylethynyl)cyclopropane (**7**) and by double carboxylation of 1,1-diethynylcyclopropane (**3**) followed by esterification, in 91 and 74% overall yields, respectively. 7,7-Diethynyldispiro[2.0.2.1]heptane (**6**) has been synthesized from ethyl dispiro[2.0.2.1]heptane-7-carboxylate (**9**) by a ten-step sequence in 41% overall yield. Upon UV irradiation, the diacetylene **4** underwent ethylene extrusion, and the resulting bis(trimethylsilylethynyl)carbene dimerized with electron reorganization to give 1,4,8-tris(trimethylsilyl)-3-(trimethylsilylethynyl)oct-3-ene-1,5,7-triyne (**20**) (24% yield). X-ray crystal structure analyses of **4**, **5**, and **6** revealed strong electronic interactions between the acetylene fragments and the cyclopropane rings, but no homoconjugative effects between two ethynyl fragments on the same cyclopropane ring of either compounds **4** and **5**, as the bond lengths in the C≡C–C–C≡C fragments were exactly the same in both molecules and very close to those in unsubstituted 1,1-diethynylcyclopropane (**3**). A gas-phase electron-diffraction structure analysis of **4** revealed triple bonds significantly longer [1.240(1) Å] than those found by crystal structure analysis [1.205(2) Å]. The observed shortening of the triple bonds in the dispiro[2.0.2.1]heptane derivative **6** [1.187(3) Å] relative to those in **4** and **5** [1.205(2) Å], as well as the slight increase in the angle α between the geminal ethynyl groups, are probably due to the different hybridization in the central ring of **6**.

Introduction

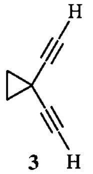
The effect of a cyclopropyl group as a powerful electron-donating substituent on electron-deficient centers is well documented.[1] The question of its ability to transmit electronic effects has also been probed with various model compounds[2] including the perspirocyclopropanated pericyclines (**1b**)[3] and the so-called expanded [*n*]rotanes (**2b**),[4] in comparison with the "pericyclines" (**1a**)[5,6] and "expanded pericyclines" (**2a**).[7,8]



1a R = Me
1b R,R = CH_2–CH_2



2a R = Me
2b R,R = CH_2–CH_2



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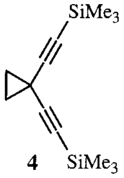

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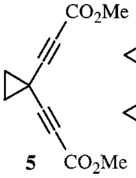

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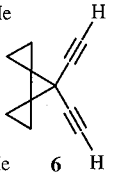

6

The numerous arguments, for and against homoconjugation and homoaromaticity in these cycles have been reviewed.[8] One of the most serious arguments against is found in the similarities in the energetic properties of **1b** ($n = 1$) (calculated at the B3LYP/D95d//B3LYP/6-31G* level of theory)[3b] and **2b** ($n = 2$) (calculated at the AM1 level of

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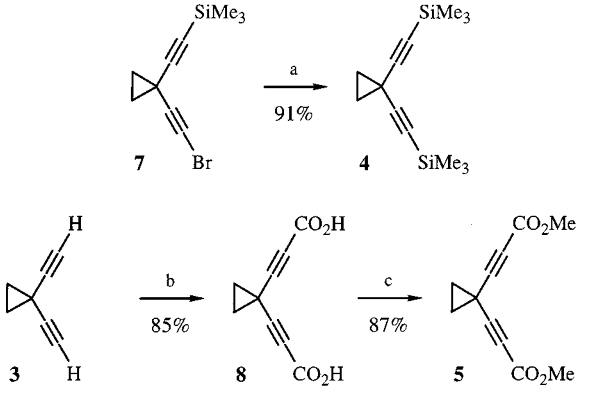
theory)[4b] to those of the parent 1,1-diethynylcyclopropane (**3**).[9,10] Observed structural features provide a second argument against homoconjugation, as all the bond lengths observed for the macrocyclic expanded [*n*]rotanes **2b** ($n = 1-4$)[4] are virtually the same as in their parent subunit (cf. ref.[11]).

In this contribution, we report the preparation and structural study of 1,1-diethynylcyclopropanes – namely 1,1-bis(trimethylsilylethynyl)cyclopropane (**4**) and dimethyl 3,3′-(1,1-cyclopropanediyl)bis(2-propynoate) (**5**) – with electron-donating and electron-withdrawing substituents attached to the triple bonds for the purpose of elucidating the potential influence of the substituents on their geometries, by comparison with the structures of the parent hydrocarbon **3** and its cyclic dehydrooligomers **2b**. To study the influence of additional strain and rehybridization on the structure of the 1,1-diethynylcyclopropane fragment, a hydrocarbon with two *gem*-ethynyl substituents on the central ring of the [3]triangulane[12] skeleton – 7,7-diethynyldispiro[2.0.2.1]heptane (**6**) – has also been synthesized and subjected to an X-ray structural investigation.

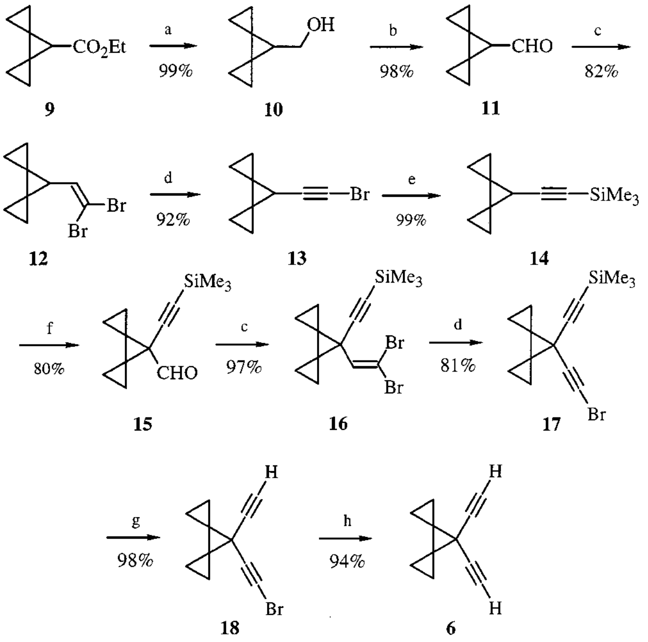
Results and Discussion

1,1-Bis(trimethylsilylethynyl)cyclopropane (**4**) was prepared in 91% yield from the known 1-(bromoethynyl)-1-(trimethylsilylethynyl)cyclopropane (**7**)[4] by simple lithiation followed by quenching with trimethylsilyl chloride (Scheme 1). The diester **5** was prepared in 74% overall yield from 1,1-diethynylcyclopropane (**3**) by double deprotonation with *n*-butyllithium, carboxylation of the intermediate dilithiodiacetylene with carbon dioxide, and esterification with methanol according to the Kabada procedure.[13]

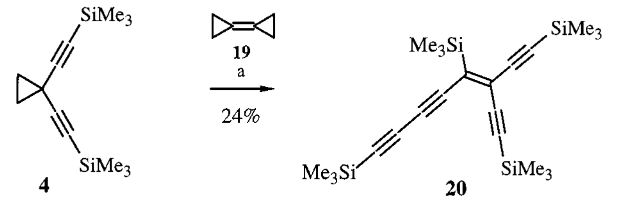


Scheme 1. Preparation of 1,1-diethynylcyclopropanes **4** and **5**: a) *n*BuLi, THF, −60 °C, 30 min, then Me_3SiCl, −78 → 20 °C; b) MeLi, THF, 0 °C, 1.5 h, then CO_2, −78 → 20 °C; c) $BF_3{\cdot}Et_2O$, MeOH, 65 °C, 2 h

7,7-Diethynyl[3]triangulane (**6**) was prepared in 41% overall yield by a tedious, ten-step sequence, exploiting a set of synthetic transformations designed for a route to expanded [*n*]rotanes **2b**[4] (Scheme 2). The starting ethyl dispiro[2.0.2.1]heptane-7-carboxylate (**9**)[14] was obtained by rhodium-catalyzed addition of ethyl diazoacetate to bicyclopropylidene (**19**).[15] A much simpler approach to the diyne **6** would have been by direct addition of bis(trimethylsilylethynyl)methylene to bicyclopropylidene (**19**) (cf. refs.[16,17]). Although bicyclopropylidene (**19**) proved to be efficiently cyclopropanated with functionally substituted carbenes,[18] no cycloadduct of **19** was detected in the attempted cyclopropanation under conditions analogous to those reported for the generation of diethynylmethylenes.[16,17] The bis(trimethylsilylethynyl)carbene generated by photochemically initiated C_1 extrusion[19] from **4** also did not undergo cycloaddition to **19**, but dimerized with electron reorganization to give the tetrayne **20**[16] in 24% yield (Scheme 3). The structure of **20** was confirmed by X-ray crystal structure analysis (Figure 1).



Scheme 2. Preparation of 7,7-diethynyldispiro[2.0.2.1]heptane (**6**): a) $LiAlH_4$, Et_2O, 34 °C, 2 h; b) pyridinium chlorochromate (PCC), CH_2Cl_2, 20 °C, 3 h; c) CBr_4, Ph_3P, Zn, CH_2Cl_2, 20 °C, 72 h; d) *t*BuOK, THF, −78 °C, 5 h; e) *n*BuLi, THF, −60 °C, 30 min, then Me_3SiCl, −78 → 20 °C; f) *n*BuLi, Et_2O, 20 °C, 24 h, then DMF, 0 °C; g) $KF{\cdot}2H_2O$, DMF, 20 °C, 3 h; h) MeLi, Et_2O, 0 °C, 1 h, then H_2O, −10 °C



Scheme 3. Photochemical behavior of 1,1-bis(trimethylsilyl)cyclopropane (**4**): a) *n*-hexane, UV irradiation, 0 °C, 5 h

The structural and data collection parameters for all four *gem*-diethynylcyclopropanes **4**−**6** and **20**, as well as those of the parent ethynylcyclopropane (**21**) obtained by X-ray

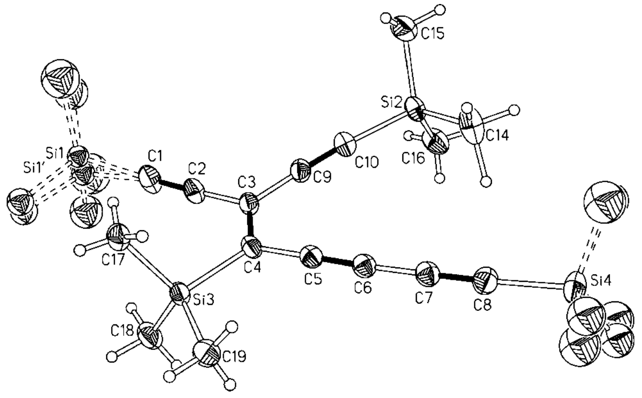


Figure 1. Molecular structure of the tetraacetylene **20** in the crystal; displacement ellipsoids are shown at 50% probability level

crystal structure analysis (RSA), are listed in Table 1 (**4**−**6**, **21**) and 2 (**4**−**6**, **20**, **21**) (see Exp. Sect.). For comparison, the corresponding parameters for the parent hydrocarbon **3** and its cyclic dehydrooligomers **2b** ($n = 1-4$) are also presented in Table 1. The bond lengths and angles in the bis(trimethylsilyl) derivative **4** were also determined by gas electron diffraction (GED) (Table 1). Graphical representations of the molecular structures of compounds **4**−**6** and **21** are given in Figure 2.

According to the X-ray crystal structure analyses (Figure 2), the angles in the acetylenic bonds in **4** are bent by 1.7(1)° (C−C≡C) and 2.5(1)° (C≡C−Si), with both trimethylsilyl substituents lying out of the C7,C6,C1,C4,C5 plane by 0.139 and 0.056 Å, respectively. The methoxycarbonyl substituents in **5** are rotated out of coplanarity by 23.6°. In the GED structure analysis of **4**, however, no such deviations of the C−C≡C and C≡C−Si fragments from linearity and planarity were detectable. The rotational angles around the ≡C−Si bonds also could not be determined reliably by the GED method.

The best indicators for strong interactions between the π-orbitals of the triple bonds and the Walsh orbitals of the cyclopropane unit are the bond lengths[20] in the three-membered rings of compounds **4** and **5** in comparison with those in the parent hydrocarbon **3** and its cyclic dehydrooligomers **2b**. In **4** and **5**, as in other cyclopropane derivatives,[20] these interactions result in a shortening of the distal bonds and a lengthening of the proximal ones (Table 1). However, the geometries of the cyclopropane rings in **4** and **5** are very close to those in the parent hydrocarbon **3**, its cyclic dehydrooligomers **2b** (accounting for standard deviations), and even in 1,1-dicyanocyclopropane.[21] For ethynylcyclopropane (**21**), MP2/6-31G(d) calculations found the structural parameters $a = 1.222$, $b = 1.441$, $c = 1.515$, $d = 1.497$ Å, with $\alpha = 115.3°$. These are close to those determined by GED[22] but exceed the structural parameters determined for **21** in the crystal (Table 1) by 0.034 Å for the triple bond and by 0.012−0.02 Å for the other bonds. No marked fine effects resulting from the nature of the substituents attached to the triple bonds could be detected; while the distal bond in **4** is insignificantly (0.003 Å) shorter than that in **3** and that in **5** is insignificantly (0.004 Å) longer, the proximal bonds are slightly longer in both **4** (by 0.003 Å) and **5** (0.014 Å).

There was also no indication of any significant homoconjugation between the two C≡C bonds in the crystal structures of **4** and **5**, with the geometries of the C≡C−C−C≡C fragments being exactly identical in both molecules and very close to that in 1,1-diethynylcyclopropane (**3**). It is questionable whether crystal structural parameters are sensitive enough towards such fine effects as homoconjugation, because packing effects may well overrule them, at least in the case of 1,1-diethynylcyclopropanes and their cyclic dehydrooligomers. For example, on going from ethynylcyclopropane to 1,1-diethynylcyclopropane (**3**), the incorporation of the second ethynyl group does induce a shift of the first ionization event in the photoelectron spectrum from 10.09 to 9.26 eV,[9b] which indicates a significant electronic interaction between the two ethynyl fragments, but essentially does not affect the structural parameters of these molecules. The slightly longer triple bond in **4** (1.238 Å) observed in the gas-phase electron-diffraction (GED) structure analysis, compared to that in **3** (1.197 Å) in the crystal may be due to a systematic difference, as the GED determinations for 1-methyl-2-(trimethylsilyl)acetylene [1.231(4) Å][23a,23b] and 1-chloro-2-trimethylsilylacetylene [1.238(6) Å][23c] also showed longer C≡C bond lengths.

The X-ray crystal structure analysis of 7,7-diethynyldispiro[2.0.2.1]heptane (**6**) revealed that the triangulane moiety of this molecule can be described essentially in terms of a

Table 1. Experimentally determined (X-ray) bond lengths and angles for 1,1-diethynylcyclopropanes **4**−**6** in comparison with those for **3**,[10] **2b** ($n = 1-4$),[4b] and ethynylcyclopropane (**21**)

Compound	**4**	**4**[a]	**5**	**6**[b]	**3**	**2b** ($n = 1$)	**2b** ($n = 2$)	**2b** ($n = 3$)	**2b** ($n = 4$)	**21**
Symmetry	ca. C_s	C_s	ca. C_2	C_{2v}	C_{2v}	D_{5h}	D_{3d}	C_{2s}	C_{2h}	C_s
a [Å]	1.205(1)	1.238(1)	1.206(1)	1.187(3)	1.197(1)	1.191(7)	1.190(3)	1.195(3)	1.191(6)	1.188(1)
b [Å]	1.449(1)	1.444(2)	1.439(1)	1.449(3)	1.442(1)	1.439(10)	1.443(2)	1.445(3)	1.452(6)	1.429(1)
c [Å]	1.529(1)	1.543(3)	1.540(1)	1.530(4)	1.526(1)	1.520(9)	1.526(3)	1.527(3)	1.530(7)	1.503(1)
d [Å]	1.480(2)	1.482(6)	1.487(1)	1.446(4)	1.483(1)	1.465(6)	1.467(3)	1.471(6)	1.476(12)	1.477(1)
α [°]	116.0(1)	117.1(7)	114.9(1)	117.0(3)	115.1(1)	114.3(5)	115.4(4)	115.5(4)	116.2(6)	−
Ref.	this work	this work	this work	this work	[10]	[4b]	[4b]	[4b]	[4b]	this work

[a] r_a values; determined by the gas-phase electron-diffraction method. [b] The bond lengths in the outer spiro-annulated cyclopropane rings are 1.480(3) and 1.540(3) Å for the proximal and distal bonds, respectively.

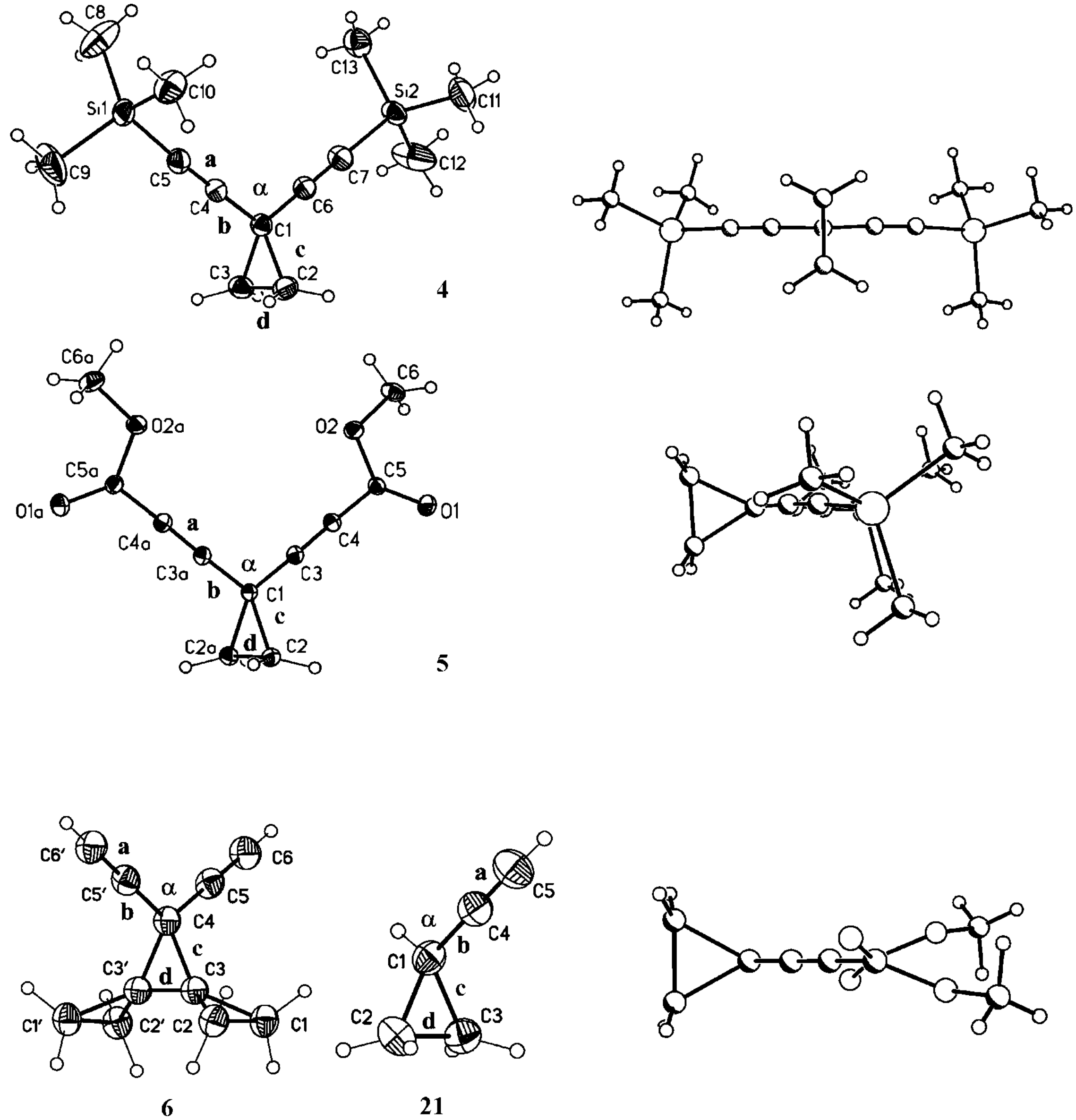


Figure 2. Molecular structures of compounds **4**−**6** and **21** in the crystals, presentations with thermal probability plots of 50% (left side), and deviations of molecules **4** and **5** from the ideal C_{2v} symmetry (right side)

superposition of 1,1-diethynylcyclopropane (**3**) and dispiro[2.0.2.1]heptane[24] as far as bond lengths are concerned. The length of bond d [1.446(4) Å] in the central ring of **6** can be derived quite accurately from the corresponding value in **3** (1.483 Å) by using the previously derived general bond increment scheme for triangulanes[24] [with an increment of −0.0234 Å for each spiro-attached three-membered ring, the estimated length is 1.483 − (2 × 0.0234) = 1.436 Å]. However, the exocyclic bond angle between the two ethynyl groups on the dispiroheptane moiety is larger than that in **3** (117.0° versus 115.1°), and the acetylenic bonds are slightly shorter (1.187 versus 1.197 Å). This is believed to result from the rehybridization of the carbon atoms in the central ring of the dispiroheptane moiety of **6**.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded at 250 (^{1}H) and 62.9 MHz [^{13}C, additional DEPT (Distortionless Enhancement by Polarization Transfer)] with a Bruker AM 250 instrument in $CDCl_3$ solution, $CHCl_3/CDCl_3$ as internal reference; δ in ppm, *J* in Hz. MS (EI): Finnigan MAT 95 spectrometer (70 eV). IR: Bruker IFS 66 (FT-IR) spectrophotometer, measured as KBr pellets, oils between KBr plates. M.p.: Büchi 510 capillary melting point apparatus, uncorrected values. TLC: Macherey−Nagel precoated sheets, 0.25 mm Sil G/UV_{254}. Column chromatography: Merck silica gel, grade 60, 230−400 mesh. Starting materials: Anhydrous diethyl ether and THF were obtained by distillation from sodium benzophenone ketyl, Me_3SiCl from magnesium, DMF from CaH_2, hexane and dichloromethane from P_4O_{10}. 1,1-Diethynylcyclopropane

(**3**),[9a] ethyl dispiro[2.0.2.1]heptane-7-carboxylate (**9**),[14] 1-(bromoethynyl)-1-(trimethylsilylethynyl)cyclopropane (**7**),[4b] and bicyclopropylidene (**19**)[25] were prepared according to published procedures. All other chemicals were used as commercially available (Merck, Acrõs, BASF, Bayer, Hoechst, Degussa AG, and Hüls AG). All reactions were performed under argon. Organic extracts were dried with $MgSO_4$.

1,1-Bis(trimethylsilylethynyl)cyclopropane (4): A solution of 1-(bromoethynyl)-1-(trimethylsilylethynyl)cyclopropane (**7**)[4b] (2.412 g, 10 mmol) in anhydrous THF (30 mL) was treated at −60 °C with *n*BuLi (10 mmol, 5.26 mL of a 1.90 M solution in hexane). After further stirring for 30 min at this temp., the solution was cooled to −78 °C and Me_3SiCl (1.195 g, 1.40 mL, 11 mmol) was added in one portion. The resulting mixture was allowed to warm to ambient temperature, poured into ice-cold water (100 mL), and extracted with Et_2O (3×20 mL). The combined organic solutions were washed with brine (50 mL), dried, and concentrated under reduced pressure. Column chromatography of the residue (50 g of silica gel, 30×3 cm column, hexane/Et_2O, 40:1, $R_f = 0.38$) followed by recrystallization from wet MeOH and then sublimation at 50 °C/0.2 Torr gave **4** (2.14 g, 91%) as a colorless solid, m.p. 44−46 °C. ^{1}H NMR: $\delta = 0.11$ (s, 18 H, 6 CH_3), 1.22 (s, 4 H, 2 CH_2). ^{13}C NMR: $\delta = 0.0$ (6 CH_3), 21.3 (2 CH_2), 80.6, 108.9 (2 C), 4.3 (C). IR: $\tilde{\nu} = 2966$ cm^{-1}, 2900, 2167, 1252, 840.

[1-(Carboxyethynyl)cyclopropyl)]propynoic Acid (8): A solution of MeLi (115.2 mmol, 73.85 mL of a 1.56 M solution in Et_2O) was added dropwise at 0 °C over 1 h to a solution of 1,1-diethynylcyclopropane (**3**)[9a] (5.19 g, 6.13 mL, 57.6 mmol) in anhydrous THF (100 mL). After further stirring for 30 min at this temp., the solution was cooled to −78 °C, and an excess of CO_2 powder was added in one portion. The resulting mixture was allowed to warm to ambient temperature, poured into ice-cold water (200 mL), and extracted with Et_2O (2×50 mL). With cooling with ice, the aqueous phase was acidified to pH ≈ 1 with conc. HCl and extracted with Et_2O (5×50 mL). The combined organic solutions were washed with brine (50 mL), dried, and concentrated under reduced pressure to give **8** (8.73 g, 85%) as a colorless solid, which was used without further purification. The analytical sample was obtained by recrystallization from hexane/EtOH, 1:1, and had m.p. 215 °C (decomp.). ^{1}H NMR: $\delta = 1.43$ (s, 4 H, 2 CH_2), 9.15 (s, 2 H, 2 OH). ^{13}C NMR: $\delta = 21.7$ (2 CH_2), 70.4, 86.3, 154.1 (2 C), 2.2 (C). IR: $\tilde{\nu} = 3029$ cm^{-1}, 2602, 2230, 1676, 1412, 1283, 1236. $C_9H_6O_4$ (178.14): calcd. C 60.68, H 3.39; found C 60.91, H 3.65.

Methyl 3-{1-[2-(Methoxycarbonyl)ethynyl]cyclopropyl}propynoate (5): $BF_3{\cdot}Et_2O$ (6.63 mL) was added dropwise at 0 °C to a solution of the diacid **8** (5.89 g, 33.05 mmol) in anhydrous MeOH (150 mL), and the resulting solution was heated under reflux for 2 h. After cooling to ambient temperature, the mixture was poured into ice-cold aqueous Na_2CO_3 solution (5%, 400 mL) and extracted with Et_2O (4×50 mL). The combined organic solutions were washed with 5% $NaHCO_3$ (100 mL) and brine (50 mL), dried, and concentrated under reduced pressure. The residue was recrystallized from *tert*-butyl methyl ether to give **5** (5.95 g, 87%) as a colorless solid, m.p. 123−125 °C. ^{1}H NMR: $\delta = 1.59$ (s, 4 H, 2 CH_2), 3.86 (s, 6 H, 2 CH_3). ^{13}C NMR: $\delta = 52.8$ (2 CH_3), 22.1 (2 CH_2), 68.9, 87.2, 153.5 (2 C), 2.6 (C). IR: $\tilde{\nu} = 3105$ cm^{-1}, 3012, 2963, 2231, 1710, 1428, 1279, 1219.

(Dispiro[2.0.2.1]hept-7-yl)methanol (10): A solution of ethyl dispiro[2.0.2.1]heptane-7-carboxylate (**9**)[14] (8.61 g, 51.80 mmol) in anhydrous diethyl ether (30 mL) was added dropwise to a suspension of $LiAlH_4$ (1.38 g, 36.36 mmol) in Et_2O (100 mL) at such a rate as to maintain a gentle reflux. After the mixture had been heated under reflux for 2 h, quenched with sat. solution of Na_2SO_4 (8 mL), and filtered, the precipitate was additionally extracted overnight with Et_2O in a Soxhlet apparatus. The combined ethereal solutions were dried and concentrated under reduced pressure to give the alcohol **10** (6.37 g, 99%) as an oil, pure enough to be used without further purification. The analytical sample was obtained by column chromatography, R_f (hexane/Et_2O, 1:1) = 0.32. ^{1}H NMR: $\delta =$ 0.35−0.49 (m, 2 H, CH_2), 0.49−0.60 (m, 2 H, CH_2), 0.70−0.82 (m, 4 H, 2 CH_2), 1.56 (t, $J = 6.6$ Hz, 1 H, CH), 3.25 (s, 1 H, OH), 3.54 (d, $J = 6.6$ Hz, 2 H, CH_2O). ^{13}C NMR: $\delta = 2.7$, 4.7 (2 CH_2), 65.0 (CH_2), 23.7 (CH), 18.1 (2 C). IR: $\tilde{\nu} = 3356$ cm^{-1}, 3064, 2984, 2869, 1421, 1003. $C_8H_{12}O$ (124.18): calcd. C 77.37, H 9.74; found C 77.43, H 9.52.

Dispiro[2.0.2.1]heptane-7-carbaldehyde (11): A solution of the alcohol **10** (6.20 g, 49.93 mmol) in CH_2Cl_2 (25 mL) was added in one portion at ambient temp. to a vigorously stirred suspension of pyridinium chlorochromate (12.890 g, 59.80 mmol) in anhydrous CH_2Cl_2 (75 mL). The resulting mixture was stirred at this temp. for 3 h, diluted with anhydrous Et_2O (100 mL), additionally stirred for 10 min, and then filtered through a 3-cm pad of silica gel (50 g, 60 mm diameter). The silica gel was washed with Et_2O (3×50 mL), and the combined ethereal solutions were concentrated under reduced pressure to give **11** (5.98 g, 98%) as a colorless solid, pure enough to be used without further purification. The analytical sample was obtained by recrystallization from hexane and had m.p. 47−49 °C. ^{1}H NMR: $\delta = 0.55$−0.65 (m, 2 H, CH_2), 0.65−0.85 (m, 4 H, 2 CH_2), 0.85−0.95 (m, 2 H, CH_2), 2.09 (d, $J = 7.4$ Hz, 1 H, CH), 8.95 (d, $J = 7.4$ Hz, 1 H, CHO). ^{13}C NMR: $\delta = 3.1$, 3.6 (2 CH_2), 34.5, 202.2 (CH), 21.4 (2 C). IR: $\tilde{\nu} = 3074$ cm^{-1}, 2844, 2750, 2291, 1700, 1426, 1134. MS (CI): *m*/*z* (%) = 157 (100) [M + NH_3 + NH_4^+], 140 (10) [M + NH_4^+], 123 (5) [M + H^+]. $C_8H_{10}O$ (122.16): calcd. C 78.64, H 8.25; found C 78.41, H 8.00.

Preparation of 7-(2,2-Dibromoethenyl)dispiro[2.0.2.1]heptanes 12 and 16. − General Procedure (GP) 1: Zinc (9.141 g, 139.8 mmol), triphenylphosphane (38.09 g, 145.2 mmol), and carbon tetrabromide (48.15 g, 145.2 mmol) were mixed in anhydrous CH_2Cl_2 (300 mL) at −20 °C, and the mixture was then stirred for 30 h at room temperature. Aldehyde **11** or **15** (72.5 mmol) was added to the resulting mixture, and stirring was continued for a further 72 h. The reaction mixture was then poured into pentane (400 mL), and the insoluble materials were removed by filtration. The insoluble fraction was taken through two additional cycles of dichloromethane extraction and pentane precipitation to remove all of the olefinic product. Evaporation of the solvent under reduced pressure gave compounds **12** or **16** in almost pure form.

7-(2,2-Dibromoethenyl)dispiro[2.0.2.1]heptane (12): Dibromoalkene **12** (16.51 g, 82%) was obtained from the aldehyde **11** (8.85 g, 72.5 mmol) by GP1 as a slightly yellow oil. The analytical sample was obtained by column chromatography, R_f (hexane) = 0.59. ^{1}H NMR: $\delta = 0.58$−0.75 (m, 4 H, 2 CH_2), 0.75−1.0 (m, 4 H, 2 CH_2), 2.29 (d, $J = 8.9$ Hz, 1 H, CH), 6.17 (d, $J = 8.9$ Hz, 1 H, =CH). ^{13}C NMR: $\delta = 3.8$, 5.3 (2 CH_2), 27.1, 140.1 (CH), 21.3 (2 C), 85.4 (C). IR: $\tilde{\nu} = 3067$ cm^{-1}, 2986, 1792, 1550, 1419, 1227, 1166. $C_9H_{10}Br_2$ (277.99): calcd. C 38.88, H 3.63; found C 38.45, H 3.56.

7-(2,2-Dibromoethenyl)-7-(trimethylsilylethynyl)dispiro[2.0.2.1]heptane (16): Dibromoalkene **16** (11.80 g, 97%) was obtained from Zn (4.18 g), Ph_3P (16.77 g), CBr_4 (21.20 g) (64 mmol each), and the aldehyde **15** (7.08 g, 32.4 mmol) by GP1 as a slightly yellow oil. The analytical sample was obtained by column chromatography, R_f (hexane) = 0.40, as a colorless solid, m.p. 37−38 °C. ^{1}H NMR:

δ = 0.14 (s, 9 H, 3 CH_3), 0.71−0.84 (m, 4 H, 2 CH_2), 1.04−1.24 (m, 4 H, 2 CH_2), 6.36 (s, 1 H, =CH). ^{13}C NMR: δ = 0.3 (3 CH_3), 5.9, 6.0 (2 CH_2), 136.5 (CH), 29.8 (2 C), 24.7, 84.9, 93.0, 104.5 (C). IR: ṽ = 3071 cm^{-1}, 2958, 2897, 2160, 1248. $C_{14}H_{18}Br_2Si$ (374.19): calcd. C 44.93, H 4.85; found C 44.71, H 4.69.

Preparation of 7-(Bromoethynyl)dispiro[2.0.2.1]heptanes 13 and 17. − General Procedure (GP) 2: Sublimed potassium *tert*-butoxide (13.408 g, 119.5 mmol) was added in portions at −78 °C over a period of 2 h to a solution of dibromoalkene **12** or **16** (59.4 mmol) in anhydrous THF (750 mL). The resulting reaction mixture was stirred for an additional 5 h at −78 °C and then poured into H_2O (1 L). The aqueous layer was extracted with pentane (3 × 250 mL), and the combined extracts were washed with aqueous HCl and $NaHCO_3$ (each 5%, 400 mL) and water (3 × 250 mL), and dried. After evaporation of the solvent, the residue was used without further purification.

7-(Bromoethynyl)dispiro[2.0.2.1]heptane (13): Bromoalkyne **13** (10.73 g, 92%) was obtained from the dibromoalkene **12** (16.51 g, 59.4 mmol) by GP2, as a slightly yellow oil. The analytical sample was obtained by column chromatography, R_f (hexane) = 0.56. ^1H NMR: δ = 0.68−0.80 (m, 4 H, 2 CH_2), 0.96−1.05 (m, 4 H, 2 CH_2), 1.96 (s, 1 H, CH). ^{13}C NMR: δ = 4.4, 6.4 (2 CH_2), 14.7 (CH), 22.0 (2 C), 36.2, 80.4 (C). IR: ṽ = 3070 cm^{-1}, 2990, 1418, 1162, 1009. C_9H_9Br (197.07): calcd. C 54.85, H 4.60; found C 54.66, H 4.47.

7-(Bromoethynyl)-7-(trimethylsilylethynyl)dispiro[2.0.2.1]heptane (17): Bromoalkyne **17** (7.53 g, 81%) was obtained from the dibromoalkene **16** (11.80 g, 31.53 mmol) and *t*BuOK (7.12 g, 63.4 mmol) by GP2, as a slightly yellow oil, m.p. ca. 10 °C. The analytical sample was obtained by column chromatography, R_f (hexane) = 0.34, as a colorless solid, m.p. 61−63 °C. ^1H NMR: δ = 0.13 (s, 9 H, 3 CH_3), 0.82−0.91 (m, 4 H, 2 CH_2), 1.11−1.22 (m, 4 H, 2 CH_2). ^{13}C NMR: δ = 0.1 (3 CH_3), 6.4, 6.6 (2 CH_2), 31.2 (2 C), 16.3, 38.3, 78.4, 84.2, 103.5 (C). IR: ṽ = 3074 cm^{-1}, 2994, 2963, 2898, 2164, 1252, 1152. $C_{14}H_{17}BrSi$ (293.27): calcd. C 57.33, H 5.84; found C 57.17, H 5.77.

7-(Trimethylsilylethynyl)dispiro[2.0.2.1]heptane (14): A solution of 7-(bromoethynyl)dispiro[2.0.2.1]heptane (**13**) (12.97 g, 65.8 mmol) in anhydrous THF (100 mL) was treated with *n*BuLi (69.1 mmol, 29.65 mL of a 2.33 M solution in hexane) at −60 °C. After further stirring for 30 min at this temp., the solution was cooled to −78 °C and Me_3SiCl (9.18 mL, 72.38 mmol) was added dropwise. The resulting mixture was allowed to warm to ambient temperature, poured into ice-cold water (500 mL), and extracted with Et_2O (3 × 100 mL). The combined organic solutions were washed with brine (100 mL), dried, and concentrated under reduced pressure to give acetylene **14** (12.40 g, 99%) as a colorless oil. The analytical sample was obtained by column chromatography, R_f (hexane) = 0.46. ^1H NMR: δ = 0.14 (s, 9 H, 3 CH_3), 0.66−0.80 (m, 4 H, 2 CH_2), 0.95−1.05 (m, 4 H, 2 CH_2), 1.98 (s, 1 H, CH). ^{13}C NMR: δ = 0.3 (3 CH_3), 4.3, 6.5 (2 CH_2), 14.55 (CH), 22.4 (2 C), 83.12, 107.1 (C). IR: ṽ = 3070 cm^{-1}, 2991, 2961, 2898, 2179, 2146, 1419, 1250. $C_{12}H_{18}Si$ (190.35): calcd. C 75.71, H 9.53; found C 75.80, H 9.60.

7-(Trimethylsilylethynyl)dispiro[2.0.2.1]heptane-7-carbaldehyde (15): *n*BuLi (88 mmol, 36.7 mL of a 2.4 M solution of in hexane) was added to a solution of the alkyne **14** (16.62 g, 87.32 mol) in anhydrous ether (160 mL). The reaction mixture was stirred for 24 h at ambient temperature and then cooled to 0 °C. Anhydrous DMF (16.1 mL) was added dropwise. This solution was allowed to warm to 20 °C and was then poured into ice-cold water (200 mL). The layers were separated, and the aqueous layer was extracted with ether (2 × 50 mL). The combined organic layers were washed with H_2O (2 × 500 mL) and dried. After evaporation of the solvent, the residue was recrystallized from hexane to give the aldehyde **15** (15.26 g, 80%) as a colorless solid, m.p. 140 °C. ^1H NMR: δ = 0.17 (s, 9 H, 3 CH_3), 0.79−0.88 (m, 2 H, CH_2), 1.02−1.15 (m, 4 H, 2 CH_2), 1.17−1.23 (m, 2 H, CH_2), 9.11 (s, 1 H, CHO). ^{13}C NMR: δ = 0.1 (3 CH_3), 3.5, 6.4 (2 CH_2), 197.9 (CH), 30.86 (2 C), 27.2, 88.8, 100.7 (C). IR: ṽ = 3072 cm^{-1}, 2964, 2843, 2176, 1708, 1252, 1129. $C_{13}H_{18}OSi$ (218.36): calcd. C 71.50, H 8.31; found C 71.18, H 8.10.

7-(Bromoethynyl)-7-ethynyldispiro[2.0.2.1]heptane (18): The trimethylsilylalkyne **17** (4.67 g, 15.91 mmol) was added to a solution of $KF·2H_2O$ (4.46 g, 47.4 mmol) in DMF (80 mL), and the reaction mixture was stirred for 3 h at room temperature. The resulting mixture was poured into water (200 mL) and extracted three times with Et_2O (3 × 100 mL). The combined organic layers were washed with 5% aqueous HCl and $NaHCO_3$ solutions and H_2O (50 mL each), dried, and concentrated under reduced pressure to give the diyne **18** (3.45 g, 98%) as a light yellow oil. The analytical sample was obtained by column chromatography, R_f (hexane) = 0.37, as a colorless solid, m.p. 48−48 °C. ^1H NMR: δ = 0.83−0.93 (m, 4 H, 2 CH_2), 1.13−1.28 (m, 4 H, 2 CH_2), 2.13 (s, 1 H, ≡CH). ^{13}C NMR: δ = 6.4, 6.6 (2 CH_2), 81.92 (CH), 30.67 (2 C), 15.9, 38.7, 67.8, 78.0 (C). IR: ṽ = 3298 cm^{-1}, 3276, 3059, 2989, 2107, 1413, 1262, 1153. $C_{11}H_{19}Br$ (221.09): calcd. C 59.75, H 4.10; found C 60.02, H 4.00.

7,7-Diethynyldispiro[2.0.2.1]heptane (6): MeLi (43 mmol, 28.3 mL of a 1.52 M solution in Et_2O) was added dropwise at 0 °C over 30 min to a solution of the bromodiyne **18** (4.77 g, 21.58 mmol) in anhydrous Et_2O (100 mL). After further stirring for 30 min at this temp., the solution was cooled to −10 °C and carefully quenched with H_2O (5 mL). The resulting mixture was poured into ice-cold water (200 mL) and extracted with Et_2O (3 × 50 mL). The combined organic solutions were washed with brine (100 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography (180 g of silica gel, 5 × 20 cm column, hexane/benzene, 10:1) to give the diyne **6** (2.89 g, 94%) as a colorless solid, m.p. 82−84 °C (MeOH), R_f = 0.32. ^1H NMR: δ = 0.82−0.99 and 1.13−1.29 (m, AA′BB′, 8 H, 4 CH_2), 2.14 (s, 2 H, 2 ≡CH). ^{13}C NMR: δ = 6.5 (4 CH_2), 82.3 (2 CH), 30.6, 67.4 (2 C), 14.6 (C).

1,4,8-Tris(trimethylsilyl)-3-(trimethylsilylethynyl)octa-1,5,7-triyn-3-ene (20): A solution of 1,1-bis(trimethylsilylethynyl)cyclopropane (**4**) (1.0 g, 4.26 mmol) and bicyclopropylidene (**19**) (4.5 g, 5.27 mL, 56.16 mmol) in olefin- and water-free hexane (100 mL) was irradiated with an internal 450-W medium-pressure Hanovia mercury lamp in a Pyrex reactor at 0 °C for 5 h. The dark-brown reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography (80 g of silica gel, 3 × 15 cm column, hexane), followed by crystallization from a small quantity of hexane to give the tetrayne **20** (215 mg, 24%) as a colorless solid, m.p. 169−171 °C (dec.), R_f = 0.41. ^1H NMR: δ = 0.20 (br. s, 18 H, 6 CH_3), 0.24 (s, 9 H, 3 CH_3), 0.28 (s, 9 H, 3 CH_3). ^{13}C NMR: δ = −1.5, −0.6, −0.4, −0.3 (3 CH_3), 78.9, 88.2, 91.0, 97.1, 101.4, 102.6, 102.9, 104.4, 125.3, 142.6 (C).

Crystal Structure Determinations: The crystals of compounds **5**, **6**, and **20** were grown by slow concentration of their solutions in hexane/Et_2O and pentane/MeOH mixtures, and hexane, respectively, and measured with a Nicolet R3m/V diffractometer (**5**, **6**) or SMART Bruker CCD 1K (**20**) diffractometer with graphite-monochromated Mo-K_α radiation. The crystals of 1,1- bis(trimethylsilylethynyl)cyclopropane (**4**) and ethynylcyclopropane (**21**) were grown in situ with the Optical Heating and Crystallization Device

Table 2. Crystal and data collection parameters for compounds **4**−**6**, **20**, and **21**

Compound	**4**	**5**	**6**	**20**	**21**
Empirical formula	$C_{13}H_{22}Si_2$	$C_{11}H_{10}O_4$	$C_{11}H_{10}$	$C_{22}H_{36}Si_4$	C_5H_6
Molecular mass	234.48	206.19	142.19	412.85	66.10
Crystal size [mm]	ϕ 0.3	0.65 × 0.27 × 0.35	0.17 × 0.15 × 0.1	0.38 × 0.18 × 0.12	ϕ 0.3
Crystals	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	*C*2/*c*	*Fdd*2	*I*$_2$	*C c*	*Pbca*
a [Å]	26.362(8)	11.849(3)	7.3403(11)	11.9166(2)	6.402(2)
b [Å]	5.809(2)	28.740(6)	6.3766(13)	22.0673(1)	9.203(3)
c [Å]	21.384(5)	5.765(1)	9.352(2)	11.8199(2)	14.609(4)
β [°]	103.89(2)	−	95.94(3)	114.36(1)	−
V [Å^3]	3179.1(10)	1963.09(76)	435.35(14)	2831.5(1)	860.7(5)
Z	8	8	2	4	8
F(000)	1024	864	152	856	288
D [g cm^{-3}]	0.980	1.395	1.085	0.902	1.020
μ [mm^{-1}]	0.20	0.11	0.061	0.090	0.057
T [K]	120(2)	120(2)	120(2)	120(1)	115(2)
Θ_{max} [°]	30	35	22.5	27.5	40
Refl. collected	6613	5056	1123	15932	5270
Refl. independent	4636	2158	566	6332	2677
R_{int}	0.0330	0.0434	0.0820	0.0376	0.0296
$wR_2(F^2)$	0.1178	0.0873	0.1174	0.1394	0.1390
$R(F)$	0.0469	0.0349	0.0490	0.0516	0.0484
Parameters refined	136	68	51	282	70
GOOF	1.028	1.086	1.084	1.106	1.024

(OHCD) by use of a miniature zone-melting procedure with focused IR laser light.[26] The device was mounted on a Nicolet R3m/V four-circle diffractometer, and the crystal formation was detected with graphite-monochromated Mo-K_α radiation. Correction for the cylindrical shape of the crystals (0.3 mm diameter) was applied for **4** and **21**. The structure solutions and refinements on F^2 were performed with the Bruker AXS SHELXTL program suite (Version 5.10). The hydrogen atoms were located in difference Fourier maps and refined as riding groups with the 1.2-fold isotropic displacement parameter of the corresponding C atom. Two of the four $SiMe_3$ groups of molecule **20** are disordered over two positions and were refined with equal SOF = 0.5. The modes of disorder are different; two positions of one of the disordered $SiMe_3$ groups are connected by rotation around the C(8)−Si(4) bond, disorder of another group includes two positions of the Si(1) atom. The parameters of crystal data collections and structure refinements are presented in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited as supplementary publication nos. CCDC-166836 (**4**), -166837 (**5**), -166838 (**6**), -165723 (**20**), and -166 839 (**21**) with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Electron Diffraction Structure Analysis: The details of the GED investigation will be published separately.[27]

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