Synthesis, Spectroscopic, and Structural Properties of Spirocyclopropanated Bicyclobutylidenes and Their Radical Cations

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Dedicated to Professor Edgar Heilbronner on the occasion of his 80th birthday

Abstract: The spirocyclopropanated bicyclobutylidenes **3**–**7** have been prepared by McMurry coupling of the corresponding spirocyclopropanated cyclobutanone (**3** and **5**), Staudinger–Pfenniger reaction (**4**), oxidative coupling of a Wittig ylide (**4**) or Wittig olefination of perspirocyclopropanated cyclobutanone (**6** and **7**). The structure of the parent **2a** and the perspirocyclopropanated bicyclobutylidene **5** was determined by X-ray crystallography which disclosed considerable steric congestion around the double bond. As a result **5** did undergo addition of dichlorocarbene, epoxidation with *meta*-chloroperbenzoic acid, and cyclopropanation with $CH_2I_2/ZnEt_2$, but did not add the more bulky dibromocarbene. The reaction of **5** with tetracyanoethene proceeded smoothly, but led to a formal [3+2] cycloadduct across the proximal single bond of one of the inner cyclopropane rings. The consecutive spirocyclopropanation of bicyclobutylidene led to a bathochromic shift in the UV spectra of 12 and 17 nm, respectively, for each pair of β- and α-spirocyclopropane groups. In the He(I)-photoelectron spectra of these bicyclobutylidenes, the effect of spirocyclopropanation upon their π-ionization energies (π-IE$_v$) was found to be almost additive, leading to a lowering of 0.05 eV per any additional β-spirocyclopropane, and 0.28–0.22 eV per additional α-spirocyclopropane group; this indicates an increasing nucleophilicity of the double bonds in the order **1** < **4** < **3** < **5**. Following the radical cations of the three symmetrical bicyclobutylidenes without (**2a**, **b**) and with six (**5**) spiroannelated cyclopropane rings, the radical cations of two symmetrical bicyclobutylidenes with two (**4**) and four (**3**) such rings were studied by ESR spectroscopy. Whereas **2b**$^{\bullet+}$, **3**$^{\bullet+}$, and **5**$^{\bullet+}$ could be generated by electrolytic oxidation of the corresponding hydrocarbons in solution, the spectra of **2a**$^{\bullet+}$ and **4**$^{\bullet+}$, with unsubstituted 2,2′,4,4′-positions, were observed upon radiolysis of their neutral precursors in a Freon matrix. On going from **2a**$^{\bullet+}$ to **4**$^{\bullet+}$, the coupling constant $|a_H|$ of the eight β protons in the 2,2′,4,4′-positions of bicyclobutylidene increases from 2.62 to 3.08 mT, and that of the four γ protons in the 3,3′-positions changes from 0.27 to 0.049 to 0.401 mT on passing from **2a**$^{\bullet+}$ via **2b**$^{\bullet+}$ to **3**$^{\bullet+}$. Computations by means of the density functional theory (DFT) at the B3LYP/6-311+G*//B3LYP/6-31G* level reproduce well the experimental hyperfine data.

Keywords: density functional calculations · bicyclobutylidenes · conjugation · radical ions · small ring systems

Introduction

The cyclopropyl substituent is well known to be the best nonheteroatom containing donor group for electron-deficient centers,[1] and as such it enhances the nucleophilicity of alkenes[1c] by efficiently stabilizing the incipient carbenium ion upon attack of any electrophile on the double bond. The ultimate nucleophilicity would thus be achieved for tetracyclopropylethene (**1**),[2a] if all four cyclopropyl groups were in a bisected orientation with respect to the central double bond.

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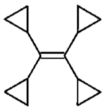
Yet, in the ground state, at least one of the four cyclopropyl groups in **1** is in a non-bisected (synclinal) orientation, a conclusion which can be drawn, for example, from its π-ionization energy derived from photoelectron spectra, in comparison to those of tri-, di-, and monocyclopropylethene.[2b,c] By proper bridging of the two pairs of cyclopropyl groups in tetracyclopropylethene (**1**), however, all four cyclopropyl groups can be rigidly held in a synplanar conformation and thus in a parallel orientation with respect to the π-orbital axis of the double bond, as realized in the tetraspirocyclopropanated bicyclobutylidene **3**. With such an orientation, the conjugative interaction attains a maximum, which is illustrated by the most pronounced decrease of the lowest ionization energy (π-IE$_v$) in the He(I)-photoelectron spectrum on going from methylenecyclopropane (9.57 eV)[3a] to methylenespiropentane (9.10 eV),[3b] and from bicyclopropylidene[4a] to its spirocyclopropanated analogues.[4b, 5] Still, the electronic structure of the double bond in bicyclobutylidene (**2a**) is closer to that in ethene and thus **3**, with its four α-spirocyclopropane groups, is a better mimic of a conformationally locked tetracyclopropylethene. An additional interesting feature of such bicyclobutylidene would be the uniquely short 1,3-diagonal distance. Due to this feature, the transannular electronic interaction in a cyclobutane ring can be quite pronounced,[6] and thus the perspirocyclopropanated bicyclobutylidene **5** should even surpass the tetraspirocyclopropanated one in its nucleophilicity.



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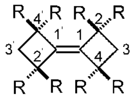
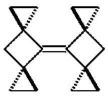


2a R = H
2b R = Me



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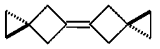

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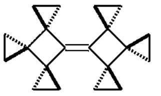

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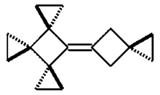

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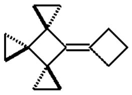

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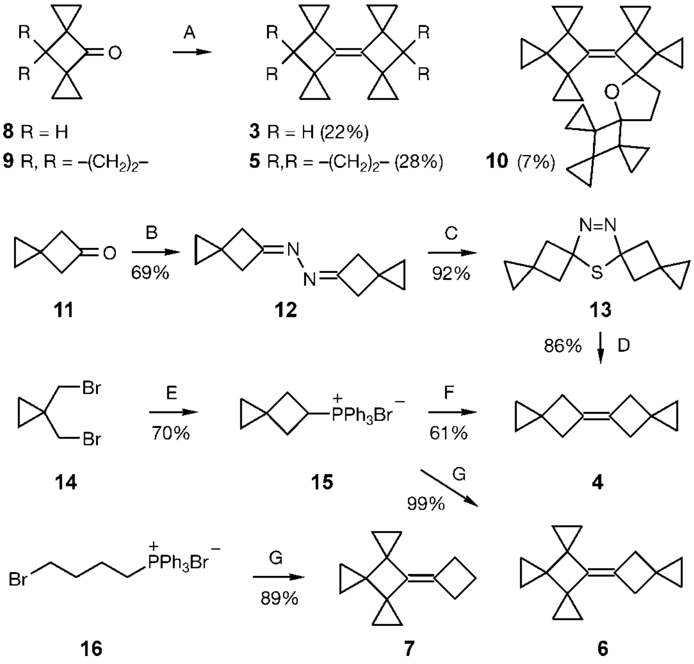
We, therefore, embarked on a project to synthesize the spirocyclopropanated bicyclobutylidenes **3**, **5** and, for a better evaluation of the effects of the two additional β-positioned spirocyclopropane groups in **5**, also the bisspirocyclopropanated analogue **4**. For comparison, the unsymmetrically oligospirocyclopropanated bicyclobutylidenes **6** and **7** were also prepared and their spectroscopic properties studied along with those of **3**–**5**. The ESR spectral features of the radical cations of **3**–**5** were of particular interest in comparison to those of the radical cations of the parent bicyclobutylidene (**2a**)[7] and its 2,2,2′,2′,4,4,4′,4′-octamethyl derivative **2b**,[8] because the coupling constants of the protons at the bicyclobutylidene core sensitively respond to the introduction of spiroannelated cyclopropane rings in the neighboring positions.

Results and Discussion

Preparation of spirocyclopropanated bicyclobutylidenes: Only the syntheses of the parent bicyclobutylidene **2a**[9] and its octamethyl derivative **2b**[10] have previously been reported. The titanium-mediated coupling of the correspondingly spirocyclopropanated cyclobutanones **8**[11a] and **9**[11] (McMurry coupling[12]) appeared to be the most straightforward approach to the symmetrically oligospirocyclopropanated bicyclobutylidenes **3** and **5** (Scheme 1).



Scheme 1. A: TiCl$_3$/LiAlH$_4$/**8** or **9** (2:1:1), THF, 55 °C, 12 h; B: N$_2$H$_4$, EtOH, 78 °C, 3 h; C: 1) H$_2$S, acetone/C$_6$H$_6$ 1:1, 5 °C, 23 h; 2) DDQ, Et$_2$O, 0 °C, 0.5 h, then 0 → 30 °C, 1 h; D: Ph$_3$P, 150 °C, 2 h; E: MeP$^+$Ph$_3$Br$^-$, NaNH$_2$ (2 equiv each), C$_6$H$_6$, 80 °C, 1.5 h, then 65 °C, 0.5 h; F: 1) *t*BuOK, C$_6$H$_6$, 50 °C, 2 h; 2) O$_2$, 40 °C, 20 min; G: *t*BuOK, C$_6$H$_6$, 50 °C, 2 h, then addition of **9** and heating at 65–70 °C for 2–8 h.

In a way differing from the reported method,[11a] cyclobutanone **8** was more conveniently prepared by direct oxidation of dispiro[2.1.2.1]octane[13] with ozone on silica gel[14a] or in situ generated ruthenium tetroxide (from RuCl$_3$ and sodium periodate).[14b] Bicyclobutylidenes **3** and **5** were obtained in 22 and 28 % yield, respectively, when the reductive dimerizations of **8** and **9**, respectively, were performed with TiCl$_3$/LiAlH$_4$ (2:1) in THF at 55 °C. When this transformation of **9** was carried out at room temperature, the yield of bicyclobutylidene **5** was only 8 %.[6] Other protocols for the McMurry coupling[12] applied to **8** and **9** also gave lower yields. The reductive coupling of the trispirodecanone **9** gave the interesting by-product **10** (7 %). The structure of **10**, which corresponds to that of a formal [2+2] cycloadduct of the carbonyl group of **9** across the σ bond of a proximal spirocyclopropane group in **5**, was proven by X-ray crystallography (Figure 1). It may be speculated that **10** is actually formed in a titanium-mediated reaction of **5** with **9**.

The symmetrical β,β-bisspirocyclopropanated bicyclobutylidene **4** was prepared applying the Staudinger–Pfenniger reaction[15] to spiro[2.3]hexan-5-one **11**[16] as well as by oxidative coupling of the ylide[9c, 17] generated from triphenyl(spiro[2.3]hex-5-yl)phosphonium bromide **15** (Scheme 1). Along the first route, the spiro[2.3]hexanone **11** was treated

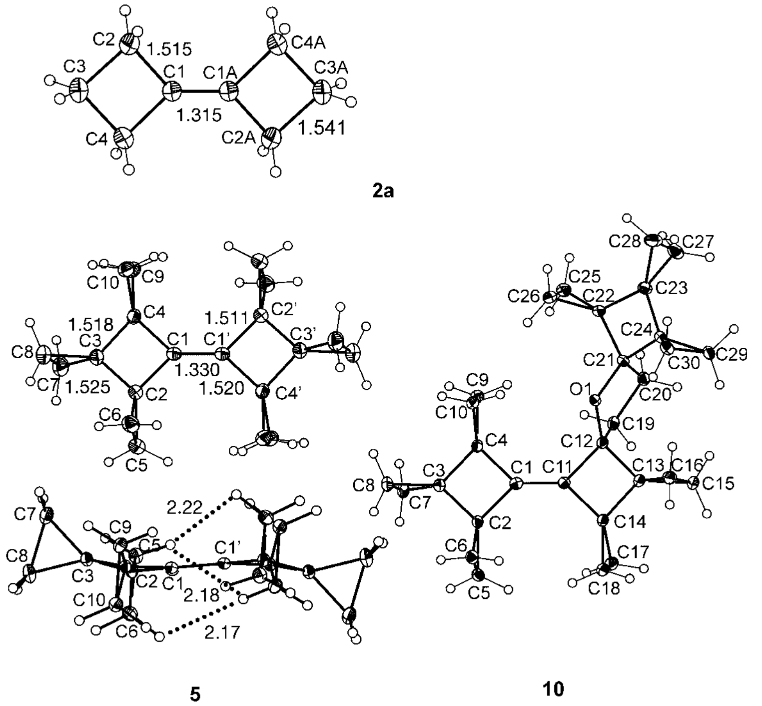
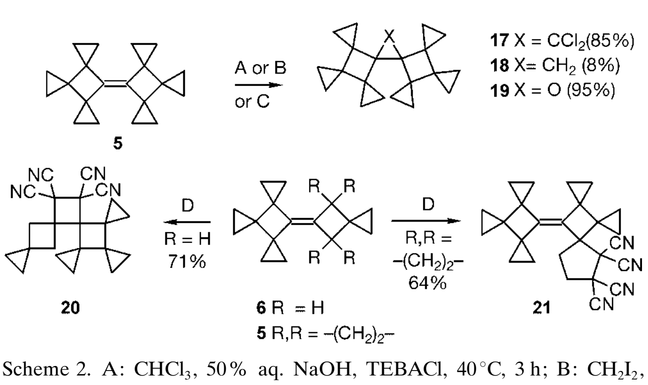


Figure 1. Structures of bicyclobutylidene **2a**, the perspirocyclopropanated bicyclobutylidene **5**, and the oxaoligospirane **10** in the crystal (bond lengths in Å).[19]

with hydrazine; the resulting ketazine **12** was converted to the thiadiazatetraspiropentadecene **13** by treatment with hydrogen sulfide followed by oxidation with dichlorodicyano-*p*-benzoquinone (DDQ). Upon heating **13** with triphenylphosphane at 150 °C, the bicyclobutylidene **4** was obtained in 86% yield (55% overall from the ketone **11**). The alternative approach by oxidation of the Wittig ylide from **15** is even more efficient, as it requires only two steps, proceeding with 70 and 61% yield, respectively, from the readily available 1,1-bis(bromomethyl)cyclopropane (**14**).[18] The unsymmetrical bicyclobutylidenes **6** and **7** with four and three spirocyclopropane groups, respectively, were prepared by Wittig olefination of the trispirodecanone **9** with ylides generated in situ from the phosphonium salts **15** and **16**, respectively (Scheme 1).

The structure of the centrosymmetrical perspirocyclopropanated bicyclobutylidene **5**, as disclosed by X-ray crystallographic analysis in comparison with those of the parent bicyclobutylidene **2a**,[19] showed a marked deviation of its bicyclobutylidene moiety from the ideally assumed planarity. While the four carbon atoms C2, C4, C2′, and C4′ and the C1–C1′ double bond form almost an undistorted plane (the angle between the two planes formed by C1, C2, C4 and C1′, C2′, C4′ is only 1.7, computed 3.8°), the cyclobutane rings are significantly puckered with a dihedral angle between the two planes formed by C1, C2, C3 and C1, C3, C4 being 14.6° (computed 10.8°). This angle is only slightly smaller than that in bicyclobutylidene (**2a**) itself in the gas phase, as determined by electron diffraction (15.6, computed 10.8°).[20] In the crystal, however, the cyclobutane rings of **2a** turned out to be only very slightly puckered with dihedral angles of 4.5 and 4.4° between the pairs of planes C2, C1, C4/C2, C3, C4 and C1, C2, C3/C1, C4, C3, respectively. The four carbon atoms C2, C4, C2A, C4A and C1, C1A of the double bond in bicyclobutylidene **2a** are completely coplanar in the crystal[19] (the interplanar angle between C2, C1, C4 and C2A, C1A, C4A is 0°). The length of the central double bond in **5** [1.330(3), computed 1.341 Å] is essentially the same as that in **2a** in the gas phase [1.338(8), computed 1.328 Å],[20, 21] but slightly longer than that in **2a** in the crystal [1.315(2) Å].[19] These significant differences in geometries of **2a** in the gas phase and in the crystal must be attributed to crystal packing effects. The bond lengths in the spiroannelated cyclopropane rings in **5** alternate in the same way as those in the oligospirocyclopropanated bicyclopropylidenes.[5] The consistent difference between longer distal and shorter proximal bonds in the spirocyclopropane moieties is due to hybridization changes of the spirocarbon atoms which also cause increased angular strain.

Reactivities: The nearest nonbonded H···H distances between hydrogen atoms on two spirocyclopropane moieties attached to the two different four-membered rings in α-positions of the double bond in **5** are as short as 2.17, 2.18, and 2.22 Å. Such proximity causes substantial steric congestion around the double bond, which significantly decreases the reactivity of this bond towards common reagents (electrophiles, cyclophiles, etc.), in comparison not only with the double bond in the parent bicyclobutylidene (**2a**),[22] but even with that in perspirocyclopropanated bicyclopropylidene.[4b, 23] Thus, phenylsulfenyl chloride, methyldi(methylthio)sulfonium hexachloroantimonate and dibromocarbene (see [22, 23]) did not add onto the double bond in **5**. However, with the sterically less demanding dichlorocarbene, generated from chloroform with 50% aqueous sodium hydroxide, the corresponding dichloropolyspirane **17** was obtained in excellent yield (Scheme 2). The cyclopropanation of **5** with diiodomethane/diethylzinc[24] afforded the polyspirane **18** in only



Scheme 2. A: $CHCl_3$, 50% aq. NaOH, TEBACl, 40 °C, 3 h; B: CH_2I_2, $ZnEt_2$, 20 °C, 4 d; C: *m*CPBA, $NaHCO_3$, CH_2Cl_2, 0 °C, 3 h; D: TCNE, CH_3CN, 20 °C, 54 h for **5** or THF, 50 °C, 24 h for **6**.

8% yield, but the epoxidation of **5** with *meta*-chloroperbenzoic acid gave the epoxide **19** almost quantitatively without skeletal rearrangement (Scheme 2).

The steric effect of the four three-membered rings adjacent to the double bond in **5** is evident from the outcome of its reaction with tetracyanoethene (TCNE) in comparison to that of the bicyclobutylidene **6** with only two α-cyclopropane rings. While **6** yielded the normal [2+2] cycloadduct **20**, the sterically encumbered **5** was solely attacked at one of the α-spirocyclopropane groups, as was observed for tetracyclopropylethene,[2a, 25] to give **21** (see also [26]). Bromination and acetoxymercuration of **5** also occurred with ring opening of one of the proximal spirocyclopropane groups, according to the NMR spectra of the not fully characterized products (see [5]).

Electronic interactions in spirocyclopropanated bicyclobutylidenes: The conjugation between the double bond and α-spirocyclopropane groups in the bicyclobutylidenes **3**, **5**, and **6** is evident in their UV spectra. Each α-spirocyclopropane group causes a bathochromic shift of the $\pi-\pi^*$ band compared to that of the parent bicyclobutylidene (**2a**) by about 9 nm. Although this is less than the 15 nm bathochromic shift caused by each spirocyclopropane group in dispiro[2.0.2.4]deca-7,9-diene,[27] it indicates a significant decrease in the HOMO–LUMO energy gap. Due to the short 1,3-transannular distance in a four-membered ring (e.g. 2.147 Å in **5**), there is also significant electronic interaction between the double bond and the β-spirocyclopropane groups in **4**, **5**, and **6**, as evidenced by the bathochromic shifts of 3–6 nm for each added β-spirocyclopropane group (Table 1). The four α- and two β-spirocyclopropanes in the perspirocyclopropanated bicyclobutylidene **5** in total cause a bathochromic shift of the $\pi-\pi^*$ band by 40 nm compared to that of the parent **2a**. In contrast, there is virtually no effect by the α-methyl substituents in the octamethylbicyclobutylidene **2b**. The conjugative and homoconjugative interactions with the spirocyclopropane groups are also evidenced by the shifts of the C=C stretching band in the Raman spectrum to lower wavenumbers. These shifts are nicely reproduced by the B3LYP/6-31G* computations which show the same trend.

The effect of added spirocyclopropane groups on the HOMO energies of bicyclobutylidenes can be estimated rather accurately from their He(I) photoelectron spectra, assuming the validity of Koopmans' theorem[30] (Table 1). Thus, comparing the lowest energy vertical ionization events, corresponding to π-ionization energies of the two pairs of bicyclobutylidenes **2a** (8.26 eV) and **4** (8.16 eV) as well as **3** (7.4 eV) and **5** (7.3 eV), the same difference of 0.1 eV, that is, 0.05 eV per β-spirocyclopropane group, can be derived. The quantitative effect of an α-spirocyclopropane group can be extracted from a comparison of the data for bicyclobutylidenes **4** (8.16 eV) and **6** (7.6 eV), as well as **2a** (8.26 eV) and **3** (7.4 eV). The difference of 0.56 eV in the first pair reflects the influence of two α-spirocyclopropanes with 0.28 eV per one such ring. The difference of 0.86 eV in the second pair reveals the effect of four α-spirocyclopropanes with 0.22 eV per spirocyclopropane group. These values only slightly exceed the corresponding increments for oligospirocyclopropanated bicyclopropylidenes (0.20–0.22 eV).[5] The good agreement between the experimental first ionization energies and the computed values (calculated as the energy difference between the neutral and the radical cation, Table 1) lends credibility to the density functional theory approach to these kinds of systems.

ESR Studies of the radical cation: The radical cation of 2,2,2′,2′,4,4,4′,4′-octamethylbicyclobutylidene (**2b**), generated electrochemically from its neutral precursor in a CH_2Cl_2/CF_3COOH/$(CF_3CO)_2O$ 10:1:1 mixture, was the first in the series of the bicyclobutylidene radical cations to be characterized by its ^1H-hyperfine data.[8] Some years later, a further bicyclobutylidene with six spiroannelated cyclopropane rings, 10,10′-bis(trispiro[2.0.2.0.2.1]decylidene) (**5**), was reported by us to be readily oxidized to its radical cation by electrolysis in CH_2Cl_2 (supporting salt $n$$Bu_4NClO_4$) and to exhibit a well-defined ^1H-hyperfine pattern.[6] On the other hand, because of the presence of acidic hydrogen atoms in the allylic 2,2′,4,4′-positions and the high ionization energy of the parent bicyclobutylidene (**2a**), its radical cation had to be produced by γ irradiation of **2a** in a $CFCl_3$ matrix.[7] There are six sorts of protons[31] in the radical cations of bicyclobutylidene (**2a**) and its derivatives **2b** and **3**–**5** (see pertinent formulae): i) Eight β protons in the 2,2′,4,4′-positions of the bicyclobutylidene core, present in **2a**$^{\bullet+}$ and **4**$^{\bullet+}$; ii) four γ protons in the 3,3′-positions of the bicyclobutylidene core, present in **2a**$^{\bullet+}$, **2b**$^{\bullet+}$, and **3**$^{\bullet+}$; iii) twenty-four γ' protons of the eight methyl groups in the 2,2′,4,4′-positions, present in **2b**$^{\bullet+}$ (they appear as equivalent by rotation of the substituents); iv and v) two sets, each of eight γ' protons, in the four cyclopropane rings spiroannelated to the 2,2′,4,4′-positions, present in **3**$^{\bullet+}$ and **5**$^{\bullet+}$ (the protons of the two sets differ in their orientation, *syn* or *anti*, with respect to the double bond); vi) eight δ protons in the two cyclopropane rings spiroannelated to the 3,3′-positions, present in **4**$^{\bullet+}$ and **5**$^{\bullet+}$.

The well-resolved multi-line ESR spectrum of **3**$^{\bullet+}$ (Figure 2) was observed upon electrolytic

Table 1. Selected spectroscopic data for the spirocyclopropanated bicyclobutylidenes **2**–**6** in comparison. Computed IE_v at the B3LYP/6-311+G*//B3LYP/6-31G* level of theory.

Compound	Ionization energies $IE_{j,v}$ [eV] first	second	Computed vertical IE_v [eV]	$\pi-\pi^*$ in the UV spectrum [λ_{max} (lg ε)]	$\tilde{\nu}$ (C=C) in the Raman spectrum [cm^{-1}] (computed value, unscaled)
1	7.90[a]	9.4	–[b]	217 (4.08)[c]	–[d]
2a	8.26	10.0	8.2	203 (4.01)[e]	1742 (1809)
2b	8.05[f]		8.3	204.5 (4.15)[g]	1670[g] (1727)
4	8.16	9.5	8.0	215 (3.31)	–[d]
6	7.6	9.2	7.1	233 (3.24)	1738 (1797)
3	7.4	9.0	7.0	237 (3.18)	–[d]
5	7.3	9.0	6.7	243 (3.10)	1710 (1745)

[a] See also ref. [2c]. [b] Not calculated. [c] Ref. [28]. [d] Not measured. [e] Ref. [9b]. [f] W. Rüger, *Dissertation*, Universität Hamburg, **1981**. [g] Refs. [10, 29].

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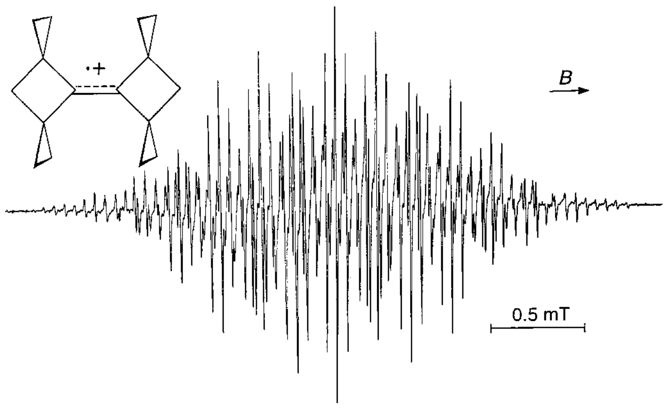

Figure 2. ESR spectrum of the radical cation $\mathbf{3}^{\cdot+}$. Solvent CH_2Cl_2, counterion ClO_4^-, $T = 203$ K.

Table 2. Observed ^{1}H-coupling constants, $|a_H|$ in mT, for the radical cations $\mathbf{2}^{\cdot+}-\mathbf{5}^{\cdot+}$; computed B3LYP/6-311G*//B3LYP/6-31G* values in parentheses.

Radical cation	Number and sort of protons 8 β	4 γ	24 γ'-Me	8 γ'-*syn*	8 γ'-*anti*	8 δ	Ref.
2a$^{\cdot+}$	2.62 (2.76)[a]	0.27 (0.34)[a]					[7]
2b$^{\cdot+}$		0.049 (0.047)	0.123 (0.102)				[8]
3$^{\cdot+}$		0.401 (0.540)		0.056 (0.040)	0.222 (0.266)[a]		this work
4$^{\cdot+}$	3.08 (3.24)					<0.1[b] (0.090)	this work
5$^{\cdot+}$				0.048[c] (0.049)	0.207 (0.288)	0.014[c] (0.050)	[6]

[a] Averaged value. [b] Not observed. [c] This assignment differs from that made previously in ref. [6].

oxidation of **3** in CH_2Cl_2 at 203 K, with 0.1M nBu$_4$NClO$_4$ as the supporting salt.[32] The spectrum was simulated using the ^{1}H-coupling constants $|a_H|$ 0.401, 0.222, and 0.056 mT, due to four, eight, and eight equivalent protons, respectively (exptl error: ±1%). The largest $|a_H|$ value (0.401 mT) must belong to the four γ protons in the 3,3′-positions of this bicyclobutylidene, while the remaining ones arise from two sets, each of eight γ' protons, in the four cyclopropane rings spiroannelated to the 2,2′,4,4′-positions. Of these two values, the larger one (0.222 mT) is assigned to the γ' protons with the *anti*-orientation, leaving the smaller one (0.056 mT) for their *syn*-counterparts. These assignments are confirmed by density functional theory (DFT) computations at the B3LYP/6-311G*//B3LYP/6-31G* level (see below).

The ESR spectrum of $\mathbf{4}^{\cdot+}$, which was obtained at 125 K upon γ irradiation (^{60}Co probe) of **4** in the "mobile" $CF_2ClCFCl_2$ matrix at 77 K,[33, 34] exhibits a nonet spaced by 3.08 ± 0.02 mT due to the eight equivalent β protons in the 2,2′,4,4′-positions (Figure 3). The coupling constant of the eight δ protons in the two cyclopropane rings spiroannelated to 3,3′-positions is too small to be detected for a radical cation in a rigid medium.

Table 2 lists the observed ^{1}H coupling constants for **2a**, **b**$^{\cdot+}$ and $\mathbf{3}^{\cdot+}-\mathbf{5}^{\cdot+}$, along with their computed counterparts. Evidently, the coupling constants of the protons at the bicyclobutylidene core are sensitive to the spiroannelation of cyclopropane rings in the neighboring positions. Thus, on going from $\mathbf{2a}^{\cdot+}$ to $\mathbf{4}^{\cdot+}$, the $|a_H|$ value of the eight β protons in the 2,2′,4,4′-positions of bicyclobutylidene increases from 2.62 to 3.08 mT. An analogous effect on the coupling constants of the four γ protons in the 3,3′-positions of bicyclobutylidene is even more striking: on passing from $\mathbf{2a}^{\cdot+}$ via $\mathbf{2b}^{\cdot+}$ to $\mathbf{3}^{\cdot+}$, the corresponding value changes from 0.27 to 0.049 to 0.401 mT. This behavior must be due to sensitivity of the 1,3-interaction in the four-membered ring to structural modifications.[35] On the other hand, the coupling constants of the protons in the spirocyclopropane rings are affected little by such modifications. Hence, those of the eight γ'-*syn*- and the eight γ'-*anti* protons in the four cyclopropane rings spiroannelated to the 2,2′,4,4′-positions are quite similar for $\mathbf{3}^{\cdot+}$ and $\mathbf{5}^{\cdot+}$; their average is comparable to the corresponding value of the twenty-four γ' protons in the eight freely rotating 2,2′,4,4′-methyl substituents of $\mathbf{2b}^{\cdot+}$.

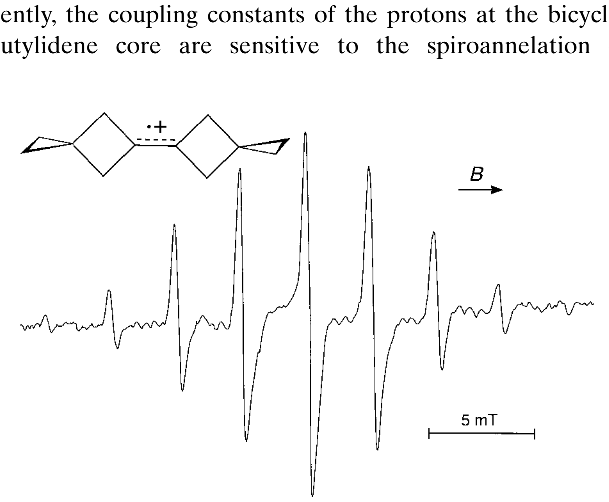

Figure 3. ESR spectrum of the radical cation $\mathbf{4}^{\cdot+}$. Solvent $CF_2ClCFCl_2$ (matrix), $T = 125$ K.

The observed ^{1}H-coupling constants are consistent with an effective D_{2h} symmetry, as previously pointed out for $\mathbf{2a}^{\cdot+}$.[7] The apparent planar geometry of **2a**, **b**$^{\cdot+}$ and $\mathbf{3}^{\cdot+}-\mathbf{5}^{\cdot+}$ contrasts with that found for the radical cation of bicyclopropylidene,[36] in which case removal of an electron from the double bond of the neutral compound leads to a twisting about this bond and, as a consequence, to a lowering of the symmetry from D_{2h} to D_2. The ground-state geometries of the symmetrical bicyclobutylidenes **2a**, **b** and **3**–**5** and their radical cations **2a**, **b**$^{\cdot+}$ and $\mathbf{3}^{\cdot+}-\mathbf{5}^{\cdot+}$, as determined by the DFT calculations, are summarized in Table 3. Obviously, the symmetry of these species should be reduced by twisting from D_{2h} to C_{2h} or D_2. However, the barriers to planarization are expected to be very low (less than 1 kcal mol^{-1}), so that ^{1}H-hyperfine patterns of the radical cations exhibit effective D_{2h} symmetries. Accordingly, the computed coupling constants $|a_H|$, which are compared in Table 2 with their experimental counterparts, represent averaged values mimicking such symmetry. It is gratifying to note how faithfully these theoretical values reproduce the experimental data.

Experimental Section

ESR Measurements: The experimental conditions, under which the radical cations $\mathbf{3}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$ were generated and their ESR spectra recorded, are

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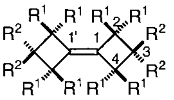
Table 3. Selected bond lengths (in Å) and puckering angles of cyclobutane rings (α in degrees) for all optimized structures **2a**, **b** and **3**–**5** and their radical cations **2a**, **b**$^{\cdot+}$ and **3**$^{\cdot+}$–**5**$^{\cdot+}$, as determined by DFT calculations.

Species 	R^1,R^1	R^2,R^2	Symmetry	$C^1-C^{1'}$	C^1-C^2	C^1-C^3	α
2a	H,H	H,H	$\approx C_{2h}$	1.328	1.525	2.147	14.0
2a$^{\cdot+}$	H,H	H,H	$\approx C_{2h}$	1.405	1.495	2.132	7.2
2b	Me,Me	H,H	D_2	1.339	1.552	2.169	0.0
2b$^{\cdot+}$	Me,Me	H,H	D_2	1.388	1.535	2.160	0.0
3	-CH_2CH_2-	H,H	D_2	1.338	1.535	2.160	0.0
3$^{\cdot+}$	-CH_2CH_2-	H,H	D_2	1.403	1.476	2.154	0.0
4	H,H	-CH_2CH_2-	D_2	1.327	1.527	2.127	0.0
4$^{\cdot+}$	H,H	-CH_2CH_2-	D_2	1.389	1.499	2.111	0.0
5	-CH_2CH_2-	-CH_2CH_2-	$\approx C_{2h}$	1.341	1.517	2.146	15.3
5$^{\cdot+}$	-CH_2CH_2-	-CH_2CH_2-	D_2	1.395	1.480	2.132	0.0

indicated in the text. The spectrometers used were a Varian-E9 instrument and a Bruker-ESP-300 system.

PES Measurements: The He(I) photoelectron spectra of **1**–**6** were recorded with a Perkin–Elmer PS18 spectrometer at the following temperatures: **2** and **4** at ambient temperature, **3** at 75 °C, **5** at 108 °C, and **6** at 55 °C. The calibration was performed with Ar and Xe. A resolution of 20 meV on the $^2P_{3/2}$ Ar line was obtained.

Computations: Geometries of all stationary points were optimized with analytical energy gradients.[37] Becke's three-parameter exchange-correlation functional[38, 39] including the nonlocal gradient corrections described by Lee–Yang–Parr (LYP),[40] as implemented in Gaussian 94,[41] was utilized. All geometry optimizations were performed with the 6-31G* basis set;[42] stationary structures were characterized by harmonic frequency computations, where true minima have only real values number of imaginary frequencies, Nimag = 0). Single-point energies were evaluated using a standard 6-311G* basis set;[42] final energies thus refer to B3LYP/6-311G*//B3LYP/6–31G*. Standard notation is used, that is, // means energy computed at // geometry.[43]

Synthesis

General aspects: ^{1}H and ^{13}C NMR: Spectra were recorded at 250, 400 (^{1}H), and 62.9, 100.6 [^{13}C, additional DEPT (distortionless enhancement by polarization transfer)] MHz on Bruker AM 250 and WM 400 instruments in $CDCl_3$ solution if not otherwise specified, $CHCl_3/CDCl_3$ as internal reference; δ in ppm, J in Hz. IR spectra were recorded on Perkin–Elmer 298 and Bruker IFS 66 (FT-IR) instruments, measured as KBr pellets, oils between KBr plates. Mass spectra were measured at 70 eV with a Finnigan MAT 95 spectrometer (EI). Melting points were determined on a Büchi 510 capillary melting point apparatus and are uncorrected. GC analyses were carried out with a Siemens Sichromat 1-4, 25 m capillary column CP-SIL-5-CB, and GC separations with an Intersmat 130 instrument, 20% SE-30 on Chromaton W-AW-DMCS, 1500 × 8.2 mm Teflon column. TLC analyses were performed using Macherey–Nagel precoated sheets, 0.25 mm Sil G/UV_{254}, and column chromatography using Merck silica gel, grade 60, 230–400 mesh. Starting materials: Anhydrous diethyl ether, benzene, and THF were obtained by distillation from sodium/benzophenone, ethanol from CaH_2, and acetone from K_2CO_3. Compounds **8**,[14a] **9**,[11b] **11**,[16], and **14**[18b] were prepared according to published procedures. All other chemicals were used as commercially available (Merck, Acros, BASF, Bayer, Hoechst, Degussa AG, and Hüls AG). All reactions were performed under an Ar atmosphere. Organic extracts were dried over $MgSO_4$.

General procedure (GP 1) for the preparation of 3, 5, and 10: Anhydrous THF was added dropwise at 0 °C to a stirred mixture of $TiCl_3$ (2 equiv) and $LiAlH_4$ (1 equiv). The mixture was stirred at this temperature for 0.5 h, then at 65 °C for 2 h, and cooled again to 0 °C. To the resulting black suspension, a solution of the respective ketone **8** or **9** (1 equiv) in anhydrous THF was added at this temperature over a period of 20 min. The resulting mixture was stirred for 1 h at 0 °C, then at 55 °C for 2 d, cooled to 0 °C, hydrolyzed with H_2O (1 mL), 15% aqueous NaOH solution (1 mL), and H_2O again (3 mL, quantities are given per 1 g $LiAlH_4$) and filtered. The precipitate was thoroughly washed with THF, and the organic solution was washed with sat. NH_4Cl solution. The aqueous phase was re-extracted with Et_2O (4 × 5 mL), and the combined organic solutions were washed with sat. $NaHCO_3$ solution, brine, dried, and finally concentrated under reduced pressure. The product was isolated by column chromatography on silica gel.

8,8'-Bis(dispiro[2.1.2.1]octylidene) (3): From a solution of **8** (183 mg, 1.5 mmol) in THF (4 mL) and McMurry reagent prepared from $TiCl_3$ (463 mg, 3 mmol) and $LiAlH_4$ (57 mg, 1.5 mmol) in THF (15 mL), compound **3** (35 mg, 22%) was obtained according to GP 1 after column chromatography (20 g silica gel, column 15 × 1.5 cm, pentane). $R_f = 0.74$; m.p. 131 °C; UV (hexane): λ_{max} (lg ε) = 237 (3.18) nm; IR (KBr): $\tilde{\nu} = 3090$, 3020, 2970, 2940, 2870, 1455, 1425, 1257, 1205, 1055, 1012, 970, 938, 890, 805 cm^{-1}; ^{1}H NMR (250 MHz, 25 °C): $\delta = 1.94$ (s, 4H; 2CH_2), 0.77, 0.63 (2m, AA'BB', 16H; 8CH_2); ^{13}C NMR (62.9 MHz, 25 °C): $\delta = 16.4$ (8CH_2), 24.0 (4C), 39.9 (2CH_2), 137.4 (2C); MS (EI): m/z (%): 212 (41) $[M]^+$, 169 (19) $[M - C_3H_7]^+$, 168 (11) $[M - C_3H_8]^+$, 167 (20) $[M - C_3H_9]^+$, 155 (54) $[M - C_4H_9]^+$, 153 (39) $[M - C_4H_{11}]^+$, 141 (74) $[M - C_5H_{11}]^+$, 128 (100) $[M - C_6H_{12}]^+$, 115 (77), 91 (61), 77 (41); elemental analysis calcd (%) for $C_{16}H_{20}$ (212.3): C 90.51, H 9.49; found: C 90.58, H 9.43.

10,10'-Bis(trispiro[2.0.2.0.2.1]decylidene) (5) and 20-oxa-21-(10'-trispiro-[2.0.2.0.2.1]decylidene)heptaspiro[2.0.2.0.2.0.2.0.2.0.2.0.1.1]heneicosane (10): From a solution of **9** (518 mg, 3.5 mmol) in THF (10 mL) and McMurry reagent prepared from $TiCl_3$ (1.08 g, 7 mmol) and $LiAlH_4$ (133 mg, 3.5 mmol) in THF (36 mL), compounds **5** (129 mg, 28%) and **10** (35 mg, 7%) were obtained according to GP 1 after column chromatography (50 g silica gel, column 24 × 2 cm, pentane, then MeOH for **10**).

Compound **5**: $R_f = 0.50$; m.p. 193 °C; UV (hexane): λ_{max} (lg ε) = 243 (3.10) nm; IR (KBr): $\tilde{\nu} = 3160$, 3010, 2870, 1460, 1425, 1010 cm^{-1}; Raman (powder): $\tilde{\nu} = 1710$, 1462, 1306, 984, 870, 840, 456 cm^{-1}; ^{1}H NMR (400 MHz, 25 °C): $\delta = 0.66$, 0.52 (2m, AA'BB', 16H; 8CH_2), 0.10 (s, 8H; 4CH_2); ^{13}C NMR (100.6 MHz, 25 °C): $\delta = 5.3$ (4CH_2), 12.6 (8CH_2), 29.8 (2C), 30.4 (4C), 136.2 (2C); elemental analysis calcd (%) for $C_{20}H_{24}$ (264.4): C 90.85, H 9.15; found: C 90.82, H 9.14.

Compound **10**: $R_f = 0.40$; m.p. 141 °C; IR (KBr): $\tilde{\nu} = 3060$, 2990, 1450, 1425, 1090, 1068, 1038, 1010, 1000, 867, 795 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): $\delta = 2.33$, 2.25 (2m, CD part of ABCD spectrum, 2H), 1.94 (m, AB part of ABCD spectrum, 2H), 1.79 (m, 1H), 1.62 (m, 1H), 1.28 (m, 1H), 0.86 (m, 1H), 0.77 (m, 1H), 0.69 – −0.25 (m, 26H), −0.35 (m, 1H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): $\delta = 26.9$, 26.8, 14.9, 14.3, 14.2, 11.8, 11.3, 9.4, 8.6, 8.0, 7.2, 6.7, 4.4, 3.6, 3.3, 0.6 (CH_2); 140.8, 134.1, 89.3, 87.0, 38.2, 37.6, 37.0, 36.4, 35.6, 30.6, 29.4 (C); exact mass measurement: calcd for $C_{30}H_{36}O$: 412.2766; found: 412.2794.

Spiro[2.3]hexan-5-one azine (12): A solution of anhydrous hydrazine (160 mg, 5 mmol) in anhydrous ethanol (1 mL) was added with stirring to a solution of spiro[2.3]hexan-5-one (**11**; 960 mg, 10 mmol) in anhydrous EtOH (2 mL) at ambient temperature, stirred under reflux for an additional 3 h, then cooled to ambient temperature and poured into Et_2O (50 mL). The organic solution was washed with H_2O (20 mL), brine (20 mL), dried and concentrated under reduced pressure. Column chromatography (80 g silica gel, column 40 × 3 cm, pentane/Et_2O 1:1) furnished **12** (649 mg, 69%) as a yellow solid. $R_f = 0.45$; m.p. 75 °C; IR (KBr): $\tilde{\nu} =$ 3085, 3015, 2910, 1702 (C=N), 1410, 1240, 1120, 1060, 1015, 970 cm^{-1}; ^{1}H NMR (250 MHz, 25 °C): $\delta = 3.10$ (m, AA'BB', 8H; Cbut), 0.66 (s, 8H; Cpr); ^{13}C NMR (62.9 MHz, 25 °C): $\delta = 11.5$ (4CH_2), 14.5 (2C), 41.7 (2CH_2), 42.3 (2CH_2), 167.6 (2C); elemental analysis calcd (%) for $C_{12}H_{16}N_2$ (188.3): C 76.56, H 8.57, N 14.88; found: C 76.82, H 8.58, N 14.96.

6-Thia-13,14-diazatetraspiro[2.1.1.1.2.1.2.1]pentadec-13-ene (13): A solution of the ketazine **12** (376 mg, 2 mmol) in an acetone/benzene mixture (6 mL, 1:1) was stirred under an atmosphere of H_2S at 5 °C. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 23 h, the solvent was evaporated under reduced pressure to give 6-thia-13,14-diazatetraspiro[2.1.1.1.2.1.2.1]pentadecane (444 mg, 100%) as a yellow solid. M.p. 86 °C; IR (KBr): $\tilde{\nu}$ = 3285, 3080, 3010, 2980, 2940, 1425, 1240, 1160, 1115, 1055, 1010, 915, 932, 782 cm^{-1}; ^{1}H NMR (250 MHz, 25 °C): δ = 3.90 (br s, 2H; 2NH), 2.50 (m, AA'BB', 8H; Cbut), 0.50 (s, 8H; Cpr). To a solution of this compound (444 mg, 2 mmol) in anhydrous Et_2O (30 mL), was added at 0 °C a solution of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (454 mg, 2 mmol) in Et_2O (150 mL) over a period of 0.5 h. The resulting solution was stirred at 0 °C for 0.5 h and then at ambient temperature for an additional 0.5 h, washed successively with 37% $NaHSO_3$ solution (3 × 30 mL), 5% $NaHCO_3$ solution (3 × 20 mL), water (3 × 20 mL), dried, and concentrated under reduced pressure to give **13** (405 mg, 92%) as a yellow solid. M.p. 68 °C; IR (KBr): $\tilde{\nu}$ = 3080, 3000, 2980, 2935, 1560, 1450, 1420, 1265, 1190, 1110, 1095, 1055, 885, 800 cm^{-1}; ^{1}H NMR (250 MHz, 25 °C): δ = 2.93, 2.69 (2m, AA'BB', 8H; Cbut), 0.73, 0.57 (2m, AA'BB', 8H; Cpr); ^{13}C NMR (62.9 MHz, 25 °C): δ = 12.1, 11.4 (2CH$_2$), 14.9 (2C), 45.3 (4CH$_2$), 125.0 (2C). This compound was used without further purification.

(Spiro[2.3]hex-5-yl)triphenylphosphonium bromide (15): A mixture of methyltriphenylphosphonium bromide (14.3 g, 40 mmol), sodium amide (1.8 g, 46 mmol), freshly prepared from sodium in liquid ammonia under $Fe(NO_3)_3$ catalysis, and anhydrous benzene (50 mL) was stirred under reflux for 1.5 h. After this, a solution of dibromide **14** (4.56 g, 20 mmol) in benzene (5 mL) was added over a period of 0.5 h at 65 °C, the resulting mixture was stirred for an additional 0.5 h at the same temperature and cooled to 0 °C. The brown precipitate was filtered off, washed with benzene (10 mL) and EtOAc (2 × 10 mL), dried under reduced pressure (0.1 Torr) and recrystallized twice from EtOH/H_2O 1:1 to give **15** (5.9 g, 70%) as a colorless powder. M.p. 238 °C; IR (KBr): $\tilde{\nu}$ = 3040, 3000, 2920, 2860, 1590, 1485, 1442, 1343, 1318, 1118, 1018, 1000, 940, 765, 734, 719, 700 cm^{-1}; ^{1}H NMR (250 MHz, 25 °C): δ = 7.84 – 7.68 (m, 15H; 3C$_6$H$_5$), 5.70 – 5.55 (m, 1H; Cbut), 3.28 – 3.12 (m, 2H; Cbut), 2.20 (dd, J = 6.0, 13.3 Hz, 1H; Cbut), 2.09 (dd, J = 7.3, 13.3 Hz, 1H; Cbut), 0.44 (dd, J = 8.5, 10.3 Hz, 2H; Cpr), −0.19 (dd, J = 6.3, 8.5 Hz, 2H; Cpr); ^{13}C NMR (62.9 MHz, 25 °C): δ = 12.2, 12.7 (CH$_2$), 16.9 (d, $^3J_{C,P}$ = 5.8 Hz, C), 21.3 (d, $^1J_{C,P}$ = 23.8 Hz, CH), 31.1 (d, $^2J_{C,P}$ = 2.6 Hz, 2CH$_2$), 118.2 (d, $^1J_{C,P}$ = 42.7 Hz, 3C), 130.4 (d, $^2J_{C,P}$ = 6.2 Hz, 6CH), 133.8 (d, $^3J_{C,P}$ = 4.7 Hz, 6CH), 135.0 (d, $^4J_{C,P}$ = 1.5 Hz, 3CH); MS (EI): m/z (%): 424/422 (0.1/0.1) $[M]^+$, 342 (3.2) $[M - HBr]^+$, 262 (100) $[Ph_3P]^+$, 183 (70), 108 (44) $[PhP]^+$, 79 (62).

5,5'-Bis(spiro[2.3]hexylidene) (4): a) A suspension of the phosphonium salt **15** (424 mg, 1 mmol) in anhydrous benzene (3 mL) was treated with potassium *tert*-butoxide (112 mg, 1 mmol), and the resulting mixture was then stirred at 50 °C for 2 h. After this, a stream of dry oxygen was passed through the mixture maintaining the temperature at 40 °C, until the intensive red color turned to light yellow. After an additional stirring for 20 min at this temperature, the mixture was poured into ice-cold water (5 mL), the water layer was extracted with pentane (3 × 5 mL), the combined organic phases were washed successively with water (2 × 5 mL) and brine (2 × 5 mL), dried, and concentrated at ambient pressure to a volume of about 2 mL. Bulb-to-bulb distillation of the residue (80 °C at 1 Torr) followed by GC separation at 90 °C furnished **4** (49 mg, 61%).

b) A mixture of the heterocyclic oligospirane **13** (405 mg, 1.84 mmol) and triphenylphosphane (524 mg, 2 mmol) was heated without solvent at 150 °C for 2 h. After cooling to ambient temperature, the reaction mixture was stirred with pentane (10 mL) for 1 h and filtered. The precipitate was washed with pentane (2 × 5 mL), the combined pentane solutions were concentrated at ambient pressure and purified by column chromatography (40 g silica gel, column 40 × 2 cm, pentane) to give **4** (253 mg, 86%) as an oil. R_f = 0.80; m.p. ≈ −10 °C; UV (cyclohexane): λ_{max} (lg ε) = 215 (3.31) nm; IR (film): $\tilde{\nu}$ = 3068, 2994, 2897, 1422, 1008 cm^{-1}; ^{1}H NMR (250 MHz, C$_6$D$_6$, 25 °C): δ = 2.71 (s, 8H; 4CH$_2$, Cbut), 0.47 (s, 8H; 4CH$_2$, Cpr); ^{13}C NMR(62.9 MHz, C$_6$D$_6$, 25 °C): δ = 12.0 (4CH$_2$), 16.3 (2C), 37.4 (4CH$_2$), 124.8 (2C); MS (EI): m/z (%): 160 (3) $[M]^+$, 117 (100) $[M - C_3H_7]^+$, 91 (95) $[M - C_5H_9]^+$, 79 (56), 77 (45), 65 (24); elemental analysis calcd (%) for $C_{12}H_{16}$ (160.3): C 89.94, H 10.06; found: C 89.62, H 10.24.

General procedure (GP 2) for the preparation of 6 and 7: A suspension of the respective phosphonium salt **15** or **16** (1 mmol) in anhydrous benzene (3 mL) was treated with potassium *tert*-butoxide (1 or 2 equiv), and the resulting mixture was then stirred at 50 °C for 2 h. After this, a solution of the ketone **9** (148 mg, 1 mmol) in anhydrous benzene (1.5 mL) was added over a period of 10 min, and stirring was continued at 65 – 70 °C for 2 h. The reaction mixture was cooled, poured into ice-cold water (5 mL), the water layer was extracted with pentane (2 × 5 mL), the combined organic phases were washed successively with water (5 mL) and brine (5 mL), dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, eluting with pentane.

10-(5-Spiro[2.3]hexylidene)trispiro[2.0.2.0.2.1]decane (6): From the salt **15** (424 mg, 1 mmol) and potassium *tert*-butoxide (112 mg, 1 mmol), compound **6** (210 mg, 99%) was obtained according to GP 2 after column chromatography (20 g silica gel, column 20 × 2 cm) as a colorless solid. R_f = 0.78; m.p. 65 °C; UV (hexane): λ_{max} (lg ε) = 233 (3.24) nm; IR (KBr): $\tilde{\nu}$ = 3070, 3000, 2900, 2820, 1420, 1220, 1118, 1045, 1038, 1000, 990, 970, 875 cm^{-1}; Raman (powder): $\tilde{\nu}$ = 1738, 1420, 1384, 971, 644, 446 cm^{-1}; ^{1}H NMR (400 MHz, 25 °C): δ = 2.57 (s, 4H; 2CH$_2$, Cbut), 0.92, 0.47 (2m, AA'BB', 8H; 4CH$_2$, Cpr), 0.43 (s, 4H; 2CH$_2$, Cpr), 0.18 (s, 4H; 2CH$_2$, Cpr); ^{13}C NMR (100.6 MHz, 25 °C): δ = 9.0, 5.5 (2CH$_2$), 12.2 (4CH$_2$), 29.3, 18.0 (C), 30.5 (2C), 37.2 (2CH$_2$), 137.9, 117.7 (C); elemental analysis calcd (%) for $C_{16}H_{20}$ (212.3): C 90.51, H 9.49; found: C 90.43, H 9.56.

10-(Cyclobutylidene)trispiro[2.0.2.0.2.1]decane (7): From the salt **16** (614 mg, 1.28 mmol), potassium *tert*-butoxide (287 mg, 2.56 mmol) and the ketone **9** (148 mg, 1 mmol), compound **7** (165 mg, 89%) was obtained according to GP 2 after column chromatography (35 g silica gel, column 30 × 2 cm) as a colorless solid. R_f = 0.51; m.p. 58 °C; UV (hexane): λ_{max} (lg ε) = 231 (3.22) nm; Raman (powder): $\tilde{\nu}$ = 1731, 1426, 1387, 1007, 965, 845, 643, 447 cm^{-1}; ^{1}H NMR (250 MHz, 25 °C): δ = 2.58 (m, 2H; CH$_2$, Cbut), 2.01 (m, 4H; 2CH$_2$, Cbut), 0.93, 0.48 (2m, AA'BB', 8H; 4CH$_2$, Cpr), 0.18 (s, 4H; 2CH$_2$, Cpr); ^{13}C NMR (62.9 MHz, 25 °C): δ = 5.5 (2CH$_2$), 9.1 (4CH$_2$), 19.2 (CH$_2$), 28.9 (2CH$_2$), 29.2 (C), 30.4 (2C), 137.0, 123.6 (C); elemental analysis calcd (%) for $C_{14}H_{18}$ (186.3): C 90.26, H 9.74; found: C 90.15, H 9.68.

11,11-Dichlorooctaspiro[2.0.2.0.2.0.1.0.2.0.2.0.2.0]heneicosane (17): A mixture of the bicyclobutylidene **5** (26 mg, 0.098 mmol), TEBACl (2 mg), EtOH (one drop) in CHCl$_3$ (1 mL) and 50% aqueous NaOH (1 mL) was vigorously stirred at 40 °C for 3 h. After cooling to ambient temperature, the mixture was poured into ice-cold water (10 mL) and extracted with CHCl$_3$ (2 × 10 mL). The combined organic solutions were washed with H$_2$O (2 × 10 mL), brine (5 mL), dried, and concentrated under reduced pressure. Column chromatography (40 g silica gel, column 35 × 1.8 cm, pentane) furnished **17** (29 mg, 85%) as a colorless solid. R_f = 0.62; m.p. 167 °C; ^{1}H NMR (250 MHz, 25 °C): δ = 1.20 (m, 4H), 0.71 (m, 4H), 0.38 – 0.17 (m, 16H); ^{13}C NMR (62.9 MHz, 25 °C): δ = 6.4, 6.1 (4CH$_2$), 4.3, 3.8 (2CH$_2$), 31.2 (4C), 47.3, 32.6 (2C), 73.1 (C).

Octaspiro[2.0.2.0.2.0.1.0.2.0.2.0.2.0]heneicosane (18): A solution of the bicyclobutylidene **5** (39.7 mg, 0.15 mmol) in anhydrous diethyl ether (6 mL) was treated with diethylzinc (0.15 mmol, 123 µL of 1.22 M solution in Et$_2$O) and CH$_2$I$_2$ (0.22 mmol, 18 µL), and the resulting solution was stirred at ambient temperature for 4 d. After this, the solution was diluted with Et$_2$O (10 mL) and washed with sat. NH$_4$Cl solution (2 × 5 mL), H$_2$O (2 × 5 mL), dried, and concentrated under reduced pressure. Column chromatography (10 g silica gel, column 15 × 0.5 cm, pentane) furnished **18** (3.5 mg, 8%) as an oil. R_f = 0.68; ^{1}H NMR (250 MHz, C$_6$D$_6$, 25 °C): δ = 0.66 – 0.58 (m, 4H), 0.39 (s, 2H), 0.29 – 0.02 (m, 20H); ^{13}C NMR (62.9 MHz, C$_6$D$_6$, 25 °C): δ = 5.0, 4.9 (2CH$_2$), 8.1, 6.0 (4CH$_2$), 14.3 (CH$_2$), 30.3 (4C), 40.0, 31.1 (2C). The starting material **5** (35 mg, R_f = 0.40) was also isolated.

11-Oxaoctaspiro[2.0.2.0.2.0.1.0.2.0.2.0.2.0]heneicosane (19): A solution of the bicyclobutylidene **5** (28.7 mg, 0.11 mmol) in anhydrous CH$_2$Cl$_2$ (2 mL) was added at 0 °C over a period of 15 min to a well-stirred suspension of NaHCO$_3$ (55 mg, 0.65 mmol) in a solution of 85% *m*CPBA (33.5 mg, 0.17 mmol) in CH$_2$Cl$_2$ (1 mL). After additional stirring for 3 h at 0 °C, the mixture was poured into concentrated NH$_4$OH solution (5 mL), the inorganic phase was extracted with CH$_2$Cl$_2$ (3 × 3 mL), the combined organic solutions were washed with sat. NH$_4$Cl solution (2 × 2 mL), dried and concentrated under reduced pressure. The residue was sublimed in a Kugelrohr apparatus (150 – 220 °C at 0.05 Torr) to give **19** (29 mg, 95%) as a colorless solid. M.p. 89 °C; IR (KBr): $\tilde{\nu}$ = 3060, 2980, 2920, 2850, 1760, 1660, 1460, 1370, 1280, 1255, 1100, 1010, 1000, 985, 940, 920, 870, 850, 700, 610 cm^{-1}; ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 1.10 (m, 2H), 0.77 (m, 4H), 0.65 (m, 2H), 0.31 (m, 4H), 0.13 (m, 4H), 0.02 (m, 2H), −0.13 (m, 4H), −0.31 (m, 2H); ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 25 °C): δ = 6.2, 4.7 (4CH$_2$), 6.7, 6.4 (2CH$_2$), 30.7 (4C), 60.6, 26.6 (2C); MS (EI): m/z (%): 280 (3) $[M]^+$, 265 (25) $[M-CH_3]^+$, 252 (21) $[M-C_2H_4]^+$, 251 (37), 209 (69), 139 (100); exact mass measurement: calcd for $C_{20}H_{24}O$: 280.1827; found: 280.1747).

General procedure (GP 3) for the preparation of TCNE adducts 20 and 21: A solution of the bicyclobutylidene **5** or **6** in an appropriate solvent was stirred with 2 equiv TCNE for 54 h at ambient temperature for **5** (or 24 h at 50 °C for **6**). The solution was concentrated under reduced pressure, and the residue was washed with dichloromethane (2 × 3 mL) to give almost pure **20**. Compound **21** was purified by column chromatography.

11,11,12,12-Tetracyanohexaspiro[2.0.2.0.2.0.2.1.2.1]octadecane (20): From the bicyclobutylidene **6** (7 mg, 33 μmol) and TCNE (8 mg, 62 μmol) in anhydrous THF (2 mL), compound **20** (8 mg, 71 %) was obtained according to GP 3 as a colorless solid. M.p. 103 °C; IR (KBr): $\tilde{\nu}=3079$, 2999, 2963, 2931, 2249, 1428, 1262, 1101, 1019, 937 cm^{-1}; ^1H NMR (400 MHz, 25 °C): $\delta=3.12$ (m, 2H; CH_2, Cbut), 2.26 (m, 2H; CH_2, Cbut), 1.48 (m, 2H; CH_2, Cpr), 1.12 (m, 2H; CH_2, Cpr), 0.71 (m, 2H; CH_2, Cpr), 0.62–0.41 (m, 2H; CH_2, Cpr), 0.24 (s, 4H; 2 CH_2, Cpr); ^{13}C NMR (100.6 MHz, 25 °C): $\delta=37.7$, 6.6, 5.7, 5.2, 4.7 (2 CH_2), 12.4, 8.9 (CH_2); 109.8, 109.2, 32.3 (2 C); 58.5, 56.8, 30.7, 15.3 (C).

5,5,6,6-Tetracyano-9-(10-trispiro[2.0.2.0.2.1]decylidene)trispiro[2.0.4.1.2.0]-dodecane (21): From the bicyclobutylidene **5** (7.3 mg, 28 μmol) and TCNE (8.3 mg, 64.8 μmol) in anhydrous CH_3CN (1.5 mL), compound **21** (7 mg, 64 %) was obtained according to GP 3 after column chromatography (10 g silica gel, column 15 × 0.5 cm, CH_2Cl_2) as a colorless solid. $R_f=0.55$; m.p. 172 °C (decomp.); IR (KBr): $\tilde{\nu}=3040$, 2950, 2240, 1250, 1085, 1010, 860, 800, 695 cm^{-1}; ^1H NMR (250 MHz, 25 °C): $\delta=2.12$ (m, 4H; CH_2, Cpent), 1.80–0.20 (m, 20H; 10 CH_2, Cpr); ^{13}C NMR (62.9 MHz, 25 °C): $\delta=6.7$, 2.2 (2 CH_2), 30.1, 16.4, 15.0, 11.7, 10.8, 8.0, 7.9, 7.4 (CH_2); 148.8, 126.7, 111.8, 111.2, 66.4, 54.7, 44.7, 38.1, 33.3, 32.3, 31.0, 30.9, 29.5, 29.4 (C); MS (EI): m/z (%): 392 (2) $[M]^+$, 364 (9) $[M-C_2H_4]^+$, 363 (12) $[M-C_2H_5]^+$, 338 (11) $[M-NC_3H_4]^+$, 285 (32), 271 (39), 257 (40), 205 (43), 165 (63), 115 (66), 91 (89), 77 (91), 41 (100); exact mass measurement: calcd for $C_{26}H_{24}N_4$: 392.2001; found: 392.2046).

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(**2a**), CCDC-161506 (**5**) and 161507 (**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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