Synthesis, Structure, and Electronic Properties of Bis(tetramethylcyclopropylidene)methane and Bis(cyclopropylidene)methane

Mirjana Eckert-Maksić*[a], Stephan Zöllner[b], Wolfgang Göthling[b], Roland Boese[c], Ljiljana Maksimović[a], Reinhard Machinek[d], and Armin de Meijere*)*[b]

Ruder Bošković Institute, Department of Organic Chemistry and Biochemistry[a],
Bijenička 54, YU-41001 Zagreb, Croatia, Yugoslavia

Institut für Organische Chemie der Universität Hamburg[b],
Martin-Luther-King-Platz 6, W-2000 Hamburg 13, FRG

Institut für Anorganische Chemie der Universität-GH Essen[c],
Universitätsstraße 3–5, W-4300 Essen, FRG

Institut für Organische Chemie der Universität Göttingen[d],
Tammannstraße 2, W-3400 Göttingen, FRG

Received December 13, 1990

Key Words: Allenes, highly strained / Strain–structure correlation / Hybridization effects, $^{13}C,^{13}C$ coupling constants / Calculations

Bis(tetramethylcyclopropylidene)methane (**5**) was prepared by treating 1-(dichloroethenylidene)-2,2,3,3-tetramethylcyclopropane (**3**) with *tert*-butyllithium in the presence of 2,3-dimethyl-2-butene. The parent allene **6** was obtained along a new route from bis(1-bromocyclopropyl) ketone (**11**) with low-valent titanium. Both **5** and **6** show unusually intense allene stretching bands in the IR spectra, and the signals of their central carbon atoms appear at remarkably high field in the ^{13}C-NMR spectra. The unique structural features of **5** and **6**, as evidenced by an X-ray crystal structural analysis of **5** and $^{1}J_{CC}$ values, agree remarkably well with theoretical predictions made by semiempirical (MNDO) and ab initio (4-31G) calculations and on the basis of the simple picture offered by the hybridization model using the iterative maximum overlap (IMO) approach.

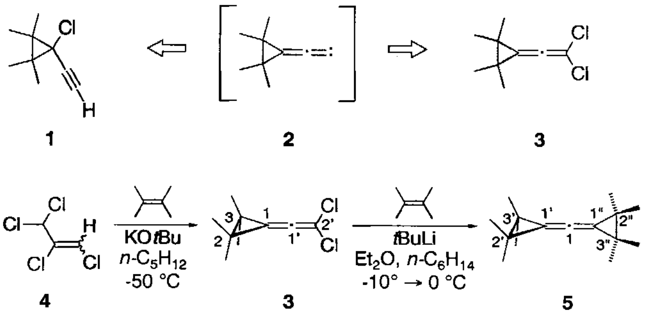
Small cyclic and polycyclic compounds attract continous attention of theoretically, physically as well as synthetically oriented organic chemists in view of their peculiar electronic properties, their inherent angular strain and enhanced reactivity[1)]. Systems containing double bonds emanating from small rings are particularly interesting since multiply bound centers in small rings increase the strain incorporated. Theoretical considerations have shown that carbon atoms at junctions between double bonds and small rings undergo substantial rehybridization with a shift of s character from the ring bonds towards the semicyclic double bond yielding changes of its properties relative to those of a normal double bond as in ethylene[2)]. For example, semicyclic double bonds linked to small rings are shortened, whereas their bond energies and stretching force constants are increased[3)].

Here we present the synthesis of bis(tetramethylcyclopropylidene)methane (**5**) and its parent compound **6** as well as the crystal structure of **5** and the results of ^{13}C-NMR as well as photoelectron spectroscopic measurements. Experimental data are discussed and interpreted in terms of theoretical calculations obtained at the semiempirical and ab initio SCF level.

Synthesis of Title Compounds

Two routes are conceivable from readily available materials to (tetramethylcyclopropylidene)ethenylidene (**2**), the carbene precursor to a whole series of bis(cyclopropylidene)methane derivatives. Treatment of 1-chloro-1-ethyl-2,2,3,3-tetramethylcyclopropane, which is easily prepared from the adduct of ring-opened tetrachlorocyclopropene onto 2,3-dimethyl-2-butene[4)], with a strong base under aprotic conditions should lead to **2** and – in the presence of alkenes – its trapping products. An alternative route starts from 1-(dichloroethenylidene)-2,2,3,3-tetramethylcyclopropane (**3**), which is readily obtained from 1,1,3,3- or 1,2,3,3-tetrachloropropene and 2,3-dimethyl-2-butene[5)].

Scheme 1



In fact, when **3** is treated with *tert*-butyllithium in *n*-hexane in the presence of 2,3-dimethyl-2-butene in diethyl ether, the unusual allene **5**, a trapping product of (tetramethylcyclopropylidene)ethenylidene (**2**) or a corresponding carbenoid, can be isolated as the sole low molecular mass product

---

*) New address: Institut für Organische Chemie der Universität Göttingen, Tammannstraße 2, W-3400 Göttingen, FRG.

in 40% yield. The highly symmetrical structure of **5** is evident from its NMR spectra. The ^1H spectrum exhibits a single line at $\delta = 1.33$ corresponding to all 24 methyl protons, while the ^{13}C spectrum shows four signals (see Table 1). The one at $\delta = 168.9$, which corresponds to the central carbon in **5**, occurs at an unusually high field for such carbon atoms in allenes. Pasto and Borchardt[6] have observed a similar effect – albeit less pronounced – for the central carbon atoms in substituted ethenylidenecyclopropanes such as **7**, **8**, and **9** and have attributed it to the spatial overlap between the cyclopropyl Walsh-type[7] e_A orbital and the π orbital of the terminal allenic double bond. This kind of interaction occurs twofold in **5** and its unsubstituted parent compound **6**[12,13] (see Figure 1), and consequently the signal of the central carbon in **5** and **6** is shifted upfield with respect to that in tetramethylallene (**10**) twice as much as in **7** and **9** (see Table 1).

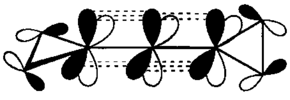


Figure 1. Orbital interactions in bis(cyclopropylidene)methane (**6**)

Table 1. Selected ^{13}C-NMR chemical shifts (δ_{TMS}) and $^{13}C,^{13}C$ coupling constants ($^1J_{C,C}$ in Hz) for bis(cyclopropylidene)methanes **5**/**6**, ethenylidenecyclopropanes **7**–**9** and tetramethylallene **10** (designation of carbon atoms according to Scheme 2)

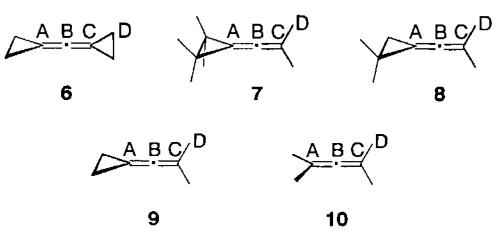
C-Atom	**5**	**6**	**7**	**8**	**9**	**10**
C(A)	101.0	80.9	98.0	87.8	77.2	92.6
⟩ $^1J_{C,C}$	142.2	151.8	–[a]	142.0	–[a]	–[a]
C(B)	169.8	177.6	184.5	185.7	183.8	200.2
⟩ $^1J_{C,C}$	142.2	151.8	–[a]	109.0	–[a]	–[a]
C(C)	(101.0)	(80.9)	97.4	98.0	97.9	(92.6)
⟩ $^1J_{C,C}$	23.0	24.6	–[a]	45.0	–[a]	–[a]
C(D)	21.8	28.2	22.6	21.5	–[b]	20.2

[a] Chemical shifts from ref.[6], $^1J_{CC}$ not reported. – [b] Not reported in ref.[6].

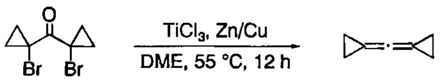
As predicted by semiempirical and ab initio MO calculations (see below), electron densities of the allenic double bonds are increased in **6** with respect to tetramethylallene (**10**), leading to a partial triple bond character. Therefore, the high-field shift of the signals of the central carbons in **5** and **6** corresponds to the typical diamagnetic shift of acetylenic carbon atoms.

The parent bis(cyclopropylidene)methane (**6**) has previously been reported without experimental details by Conia et al.[12] and a more convenient preparation of **6** has been described by Hanack et al.[13] Incidentally, we have discovered an even simpler route to **6** from easily accessible bis(1-bromocyclopropyl) ketone (**11**)[14]. When **11** is treated with titanium trichloride and zinc-copper couple[15], the only low molecular mass product is the allene **6**, isolated in 43% yield. Like its octamethyl derivative **5**, the parent **6** shows a drastic upfield shift for the signal of its central carbon atom in the ^{13}C-NMR spectrum. Both compounds also show a remarkably strong absorption at 2010 and 2060 cm^{-1}, respectively, in the IR spectrum; the unusual intensity of this C=C=C stretching vibration band may be due to an increased polarizability arising from the π to e_A orbital overlap.

Scheme 2



6 **7** **8** **9** **10**



11 **6**

Structural Properties

The geometry of **5** features several interesting structural parameters. Firstly, substantial shortening of the double bonds as predicted by IMO[16] (Iterative Maximum Overlap), MNDO[17] and 4-31G[18] methods for its unsubstituted analog **6**[2,3] are born out by the present X-ray diffraction crystal structure analysis (Figure 2 and Tables 2, 4). Furthermore, adjacent and distal C–C bonds in the three-membered rings are shortened and expanded, respectively, relative to the standard value in cyclopropane itself[3c]. This may be described in terms of a considerable rehybridization of all three carbon atoms in the allene unit (vide infra). The three-membered ring is deformed by the double bond attachment, and this is reflected in its bond angles. IMO, MNDO, and 4-31G calculations all predict a C2'–C1'–C3' angle greater than 60°, calculated values being 62, 61.7, and 62.3°, respectively. In fact, the experimental angle [60.6(9)°] is slightly greater than 60°. Concomitantly, C1'–C2'–C3'/C1'–C3'–C2' angles are smaller than 60° assuming the values 59.0, 59.1, and 58.8° [experimental value 59.0(2)°], when defining them as the angles between straight lines passing through the carbon nuclei rather than through the exocyclic points of highest electron density[19].

MNDO bicentric energy terms obtained by the customary energy partitioning technique[20] show that in the cyclopro-

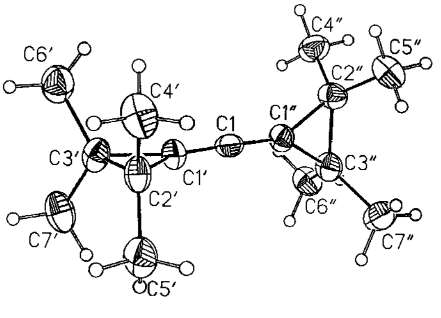


Figure 2. ORTEP plot of the crystal structure of bis(tetramethylcyclopropylidene)methane (**5**) (for structure parameters see Tables 2 and 4)

pyl fragments of **6** the C–C bonds adjacent to the allenic double bonds are indeed stronger than the distal one (Table 2). In addition, the C=C bond two-center term (–26.2 eV) is substantially lower than the corresponding value in 1,1,3,3-tetramethylallene (–25.0 eV)[2]. Therefore, shorter bonds contribute more to the molecular stability as usual. The overall pattern is easily interpreted in terms of rehybridization relative to the parent compounds cyclopropane and 1,1,3,3-tetramethylallene. This is most pronounced for the doubly bound carbon atoms in the rings. The s character in the exocyclic orbitals must be considerably increased as the p character of endocyclic bond orbitals of small rings is higher than for sp^3 orbitals (Table 2). The corresponding shortening of the C=C bond and its enhanced strength are reflected in its high stretching force constant of 10.4 mdyn · $Å^{-1}$ as predicted by the IMO method[3]. Despite the s character transfer, the hybrids placed at C1′ and directed toward apical C2′/3′ atoms possess more s character than those in cyclopropane. Hence, C1′–C2′/3′ adjacent interatomic distances are shorter. On the other hand, *d*(C2′–C3′) is larger as a consequence of the rehybridization at C1′ and a concomitant opening of the C2′–C1′–C3′ angle (vide supra). The increase in C2′–C1′–C3′ angles is plausible because it diminishes bond bending and angular strain at C1′. Additional lengthening of the C2′–C3′ bond is caused by a slight rehybridization at C2′ and C3′ as evidenced by the IMO s characters of the $\chi_{2'3'}$ (20.8%) and $\chi_{2'1'}$ (22.1%) hybrides (Table 2).

Table 2. Comparison of selected bond distances in **6** as estimated by IMO, MNDO, and 4-31G procedures with experimental data for the octamethyl derivative **5** (for further parameters see Table 4). In addition, hybridization parameters as obtained by IMO and MNDO are correlated with MNDO two-center bond energy terms E_{AB}

Method	Bond C1-C1′(1″)	C1′(1″)-C2′/3′(2″/3″)	C2′(2″)-C3′(3″)	C2′/3′(2″/3″)-CH_3
	Bond distances [pm][a]			
IMO	128.6	147.6	152.1	
MNDO	128.8	149.5	153.4	
4-31G	127.8	147.3	152.5	
Exp. for **5**	129.3(4)	148.2(3)	152.6(5)	152.6(3)
	Hybridization and bond indices[a]			
IMO	50.0-44.2	27.9-22.1	20.8-20.8	
MNDO	49.6-45.6	28.0-19.7	19.6-19.6	
E_{AB}	-26.2	-13.4	-12.5	

[a] Calculated values refer to the parent compound **6**.

This is compatible with a general rule stating that hybrids forming a bond tend to be as similar as possible[21]. Hence, the $\chi_{2'1'}$ hybrid tends to match the $\chi_{1'2'}$ hybrid as close as possible. It is interesting to note that the MNDO procedure fails to reproduce these subtle changes. Two points are noteworthy: (a) structural parameters obtained by the ab initio split-valence 4-31G basis set are very close to the simple picture offered by the hybridization model and (b) the hybridization extracted[22] from the MNDO first order density matrix is similar to the results of the localized IMO approach (Table 2). Consequently, widely different theoretical approaches yield consistent structural data and a bonding pattern which is dominated by rehybridization.

The carbon-carbon coupling constants $^1J_{C,C}$ across the allenic double bonds in bis(cyclopropylidene)methanes **5** and **6** also reveal the consequences of rehybridization and concomitant bond shortening. The values of $^1J_{C(A),C(B)}$ are considerably larger for **5** and **6** (see Table 1 and Scheme 2) than the corresponding one across the double bonds in tetramethylallene. There is yet an influence by the methyl substitution, causing a decrease of 9.6 Hz (151.8 versus 142.2) on going from **6** to its octamethyl derivative **5**. The corresponding value for 1-(dimethylethenylidene)-2,2-dimethylcyclopropane (**8**) is, however, identical to that for **5**.

Photoelectron Spectra

The low-energy region of the PE spectrum of **5** is characterized by the presence of three distinct pairs of bands (Figure 3). The first of them exhibits the typical shape associated with a Jahn-Teller distortion[23]. The magnitude of the Jahn-Teller splitting is of the same order as that encountered in the PE spectra of allene[24] (0.57 eV) and 1,1,3,3-tetramethylallene[25] (0.49 eV). On the basis of band intensities we attribute two ionizations each to the first and second pair of bands, while four ionization events must be assigned to the third pair of bands. This is also in line with the sequence of highest occupied MO's predicted by calculations (Table 3).

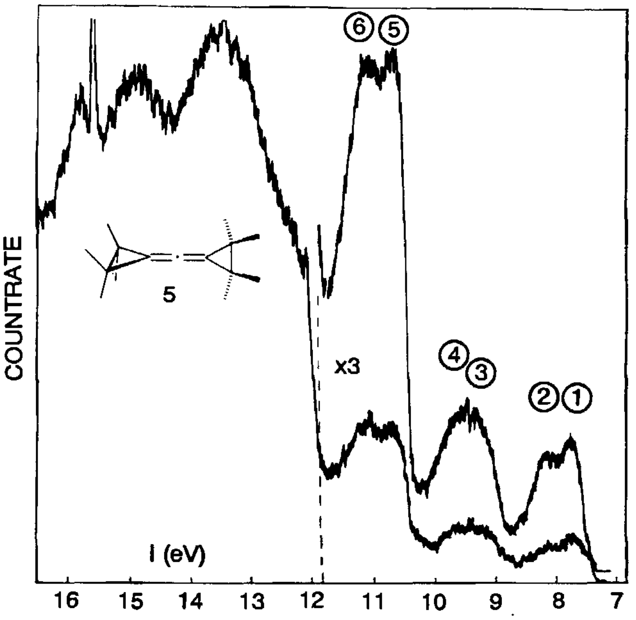
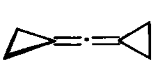
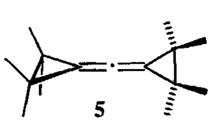


Figure 3. He(I) PE spectrum of bis(tetramethylcyclopropylidene)methane (**5**)

Assignment of the individual bands as presented in Table 3 is based on a comparison of the measured vertical ionization ($I_{v,j}$) energies with calculated orbital energies assuming the validity of Koopmans' approximation[26]. A scrutiny of the experimental data shows that theory suggests the assignment of the first two bands to ionizations out of Walsh type e_A MO's of the cyclopropane rings and nonadjacent allenic double bond π orbitals. An additional evidence for such an assignment is offered by a comparison of the observed $I_{v,j}$'s with the PE data of 1-(dimethylethenylidene)-2,2,3,3-tetramethylcyclopropane (**7**) (Figure 4) previously reported by Pasto et al.[27]. For symmetry reasons, the two allenic π-MO's belonging to the 2-e irreducible representation are not degenerate in **7** giving rise to two cleanly separated bands at 7.9 and 8.7 eV.

Table 3. Comparison of the first vertical ionization energies ($I_{v,j}$) of **5** and **6** with calculated orbital energies (ε_j) based on MNDO and 4-31G procedures

Compd.	Band	$I_{v,j}$ (eV)	Assign.	−ε (eV)	
				MNDO[a]	4–31G[a]
 **6**	①	8.52	4e	9.57	9.05
	②	9.04			
	③	11.00	$4b_2$	11.73	12.13
	④	11.50	$4a_1$	12.12	12.48
	⑤,⑥	12.07	3e	12.80	13.40
	⑦,⑧	12.99	$1a_2$, $1b_1$	13.14	13.89
 **5**	①	7.70	10e	9.57	
	②	8.10			
	③	9.20	$7b_2$	10.76	
	④	9.60	$7a_1$	11.00	
	⑤,⑥	10.70	9e	12.25	
	⑦,⑧	11.10	$4a_2$, $4b_1$	12.27	

[a] Calculations performed on parent compound **6**.

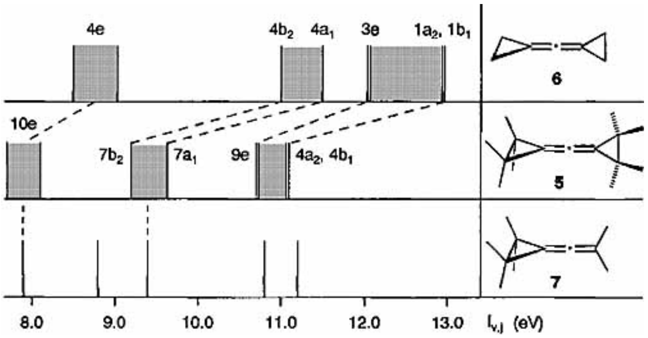


Figure 4. Comparison between the first bands in the PE spectra of bis(cyclopropylidene)methanes **5**, **6** and 1-(dimethylethenylidene)-2,2,3,3-tetramethylcyclopropane (**7**)

They are related to an ionization process out of e_A-$\pi_{C1'-C2'}$ and $\pi_{C1-C1'}$ MO, respectively. In reference to Figure 4 we note that the position of the first band in the PE spectrum of **7** coincides with the center of gravity of the first ionization event comprising bands ① and ② in **5**.

Furthermore, the second pair of bands in the PE spectrum of **5** appears at about the same energy as the third band in **7**, which is related to symmetric Walsh-type (e_S) cyclopropyl MO. Accordingly, we assign these two bands to the ionization from $7b_2$ and $7a_1$ MO's in **5**. The rather large energy splitting between $I_{v,3}$ and $I_{v,4}$ (≈ 0.4 eV) indicates that in **5** e_s MO's of the cyclopropane subunits interact to a significant extent by lower lying σ orbitals of the allenic bridge. An analysis of the calculated wave functions of **5** shows that there is indeed a significant admixture of the $3b_2$ allenic σ-MO orbital into the $7b_2$ MO, while the $7a_1$ MO is influenced by the $4a_1$ allenic σ-MO.

Finally, assignment of the ionization events at 10.7 and 11.1 eV is less straightforward. A comparison of the $I_{v,j}$'s for **5** with those of **7** suggests that the band at 10.7 eV corresponds to the bonding counterparts of the HOMO's and the one at 11.1 eV to an ionization from the symmetry-allowed linear combinations of the pseudo π orbitals of $C(CH_3)_2$ fragments located at the peripheral positions of the three-membered rings. The same ordering is predicted by the MNDO procedure, but their energy difference appears to be heavily underestimated.

The PE spectrum of unsubstituted bis(cyclopropylidene)methane (**6**) helps to clarify this point. The measured ionization energies and MO energies calculated by MNDO and 4-31G procedures are listed together with the relevant data for **5** in Table 3. In passing from **5** to **6** (see Figure 4) a strong shift of all bands toward higher energy is observed. This shift found for the first and the third ionization event is smaller than for the second and fourth pair of bands. This indicates that the bands within the second and fourth ionization features are related to MO's with large coefficients at the 2,2′,3,3′-cyclopropane carbon atoms, namely to the $4b_2$ and $4a_1$ (bands ③ and ④) and $1a_2$ and $1b_2$ (bands ⑦ and ⑧) MO's, respectively. A comparison of the $I_{v,j}$'s for **6** with the calculated ε(MO)'s listed in Table 3 reveals that both theoretical procedures in fact underestimate the energy differences between the third (bands ⑤ and ⑥) and fourth (bands ⑦ and ⑧) ionization features, with MNDO values being less accurate.

Hence, we tend to assign the ordering of levels ⑤ – ⑧ in **5** as indicated in Table 3 and Figure 4.

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. The collaboration was made possible within the framework of the agreement for scientific cooperation between the universities of Hamburg and Zagreb. We are indebted to *A. Flatow* and Prof. *R. Gleiter*, Heidelberg, for recording the PE spectrum of **6**.

Experimental

^1H NMR: Bruker AW 250 (250 MHz) and WH 270 (270 MHz), δ = 0 for tetramethylsilane, 7.15 for [D_5]benzene, 7.26 for chloroform. – ^{13}C NMR: Bruker WP 80 (20.17 MHz), WH 270 (67.93 MHz), and Varian XL 200 (50.3 MHz), δ = 0 for tetramethylsilane, 77.0 for $CDCl_3$, 128.0 for C_6D_6. Assignments were supported by DEPT spectra with a puls angle of 135°. – IR: Perkin-Elmer 399 and 1720 FT-IR. – MS: Varian MAT CH 7, MAT 112 with Varian Aerograph 1400 (GC-MS) with 25-m capillary Oribond SE 54. – Preparative GC: Varian Aerograph 920 (3/8″ teflon tubing with chromosorb W-AW DMCS 60–80 mesh, carrier gas hydrogen). – Melting points: Melting point apparatus Wagner & Munz, m.p.'s are uncorrected. – Microanalyses were performed by the Microanalytical Laboratory of the Institut für Organische Chemie, Universität Hamburg. – He(I) PE spectra of **5** and **6** were recorded on a Vacuum Generators UV-G3 and Perkin-Elmer Ltd. Model P18 (Beaconsfield, England) instrument, respectively, and calibrated with Xe and Ar. A resolution of 20 meV at $^2P_{3/2}$Ar line was achieved.

1-(Dichloroethenylidene)-2,2,3,3-tetramethylcyclopropane (**3**)[5]: To a suspension of 2.40 g (21 mmol) of potassium *tert*-butoxide in 5.0 g (60 mmol) of 2,3-dimethyl-2-butene and 20 ml of anhydrous and olefin-free pentane, kept at −20°C under nitrogen, was added with stirring a solution of 1.53 g (8.5 mmol) of 1,2,3,3-tetrachloro-1-propene (**4**) in 5 ml of anhydrous pentane. The mixture was then stirred at ambient temperature for 1 h, diluted with 80 ml of diethyl ether and 50 ml of water, and filtered over Celite. The organic layer was washed with two 50-ml portions of 2 N HCl, two 50-ml portions of water, one portion of 50 ml of saturated sodium chloride solution and dried with magnesium sulfate. The solvent was evaporated in a rotatory evaporator and the residue sublimed at 50°C/1 Torr, yield 782 mg (48%) of **3**, m. p. 68°C (after crystallization from ethanol). — IR (KBr): $\tilde{\nu}$ = 3005−2875 cm^{-1} (C−H), 1440, 1100, 840 (C−Cl). — ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.23 (s, CH_3). — ^{13}C NMR (20.17 MHz, $CDCl_3$): δ = 20.9 (CH_3), 31.5 [C-2(3)], 98.5 (C-1), 113.1 (C-2'), 181.1 (C-1'). — MS (70 eV): *m/z* = 194/192/190 [M$^+$], 179/177/175 [M − CH_3], 157/155 [M − Cl].

$C_9H_{12}Cl_2$ (191.1) Calcd. C 56.57 H 6.33 Cl 37.10
Found C 56.52 H 6.23 Cl 37.10

Bis(tetramethylcyclopropylidene)methane (**5**): To a solution of 955 mg (5.0 mmol) of **3** and 5.9 g (70 mmol) of 2,3-dimethyl-2-butene in 20 ml of anhydrous diethyl ether, kept at −10°C under nitrogen, was added dropwise with stirring 6.0 ml (7.2 mmol) of 1.2 N *tert*-butyllithium in *n*-hexane. The mixture was then stirred for 4 h at 0°C and diluted with 80 ml of diethyl ether and 30 ml of water. The organic phase was separated and washed with three 30-ml portions of 10% ammonium chloride solution, three 30-ml portions of water and dried with magnesium sulfate. The solvents were removed by trap-to-trap distillation at 30°C/100 Torr, and the residue was filtered over 40 g of alumina (neutral, activity III) with *n*-pentane/dichloromethane (9:1). After removal of the solvents, crystalline **5** remained, yield 402 mg (40%), m.p. 175−178°C (after sublimation and crystallization from diethyl ether). — IR (KBr): $\tilde{\nu}$ = 3000−2855 cm^{-1} (C−H), 2010 (C=C=C), 1450, 1370, 1100, 1002, 935. — ^{1}H NMR (270 MHz, C_6D_6): δ = 1.32 (s). — ^{13}C NMR (50.3 MHz, C_6D_6, 60°C, undecoupled): δ = 21.8 (q, CH_3), 28.2 [C_{quat}, C-2'(3',2'',3''), $^1J_{C,C}$ = 23.0 Hz], 101.0 [C_{quat}, C-1'(1''), $^1J_{C,C}$ = 142.2 and 23.0 Hz], 169.8 (C_{quat}, $^1J_{C,C}$ = 142.2 Hz). — MS (70 eV): *m/z* = 204 [M$^+$], 189 [M − CH_3], 161 [M − C_3H_7].

$C_{15}H_{24}$ (204.4) Calcd. C 88.16 H 11.84
Found C 88.39 H 11.79

Bis(cyclopropylidene)methane (**6**): 2.32 g (8.0 mmol) of titanium trichloride−1,2-dimethoxyethane complex [$TiCl_3(dme)_{1.5}$][15] and 2.20 g (31 mmol) of zinc-copper couple[15] were transferred under argon to a flask containing 60 ml of anhydrous DME, and the mixture was heated under reflux for 2 h to yield a black suspension. A solution of 536 mg (2.0 mmol) of bis(1-bromocyclopropyl) ketone (**11**)[14] in 6 ml of DME was added dropwise with stirring within 30 min at 0°C, the mixture was then stirred at 24°C for 1 h and at 55°C for 12 h. After having been cooled down to 0°C, it was diluted with 60 ml of pentane and filtered through a pad (2 × 8 cm) of florisil to remove all salts. The florisil was washed with an additional 60 ml of pentane, and the combined pentane layers were washed under argon with four 60-ml portions of cold water, then dried with Na_2SO_4 and concentrated at −15°C. Separation of the residue by preparative GC (1.5 m 13% silicone DSFS, 50°C) gave 79 mg (43%) of **6** as a colorless liquid. — IR (film): $\tilde{\nu}$ = 3055 cm^{-1}, 2974, 2060 (s, C=C=C), 1430, 1413, 1127, 1046, 996, 798. — ^{1}H NMR (250 MHz, C_6D_6): δ = 1.35 (s). — ^{13}C NMR (50.3 MHz, C_6D_6, 22°C, undecoupled): δ = 7.20 [t, C-2'(3',2'',3''), $^1J_{C,C}$ = 24.6 Hz], 80.90 [C_{quat}, C-1'(1''), $^1J_{C,C}$ = 151.8 and 24.6 Hz], 177.56 (C_{quat}, C-1, $^1J_{C,C}$ = 151.8 Hz).

X-Ray Crystal Structure Determination of Bis(tetramethylcyclopropylidene)methane (**5**)[28]: A crystal with the approximate dimensions of 0.10 × 0.08 × 0.04 mm^3 was measured on a Nicolet R3m/V diffractometer with Mo-K_α radiation at 200 K. Cell dimensions, refined from the diffractometer angles of 25 centered reflections, are a = 774.7(2), b = 952.9(3), c = 975.5(3) pm, α = 86.69(2), β = 89.39(2), γ = 68.50(2)°, V = 6.689(3) · 10^8 pm^3; Z = 2, $d_{cal.}$ = 1.015 g · cm^{-3}, μ = 0.05 mm^{-1}, space group $P\bar{1}$, data collection of 1760 unique intensities (2Θ$_{max}$ = 45°), 737 observed ($F_o \geq 4\sigma(F)$), structure solution with direct methods and refinement with full matrix least squares (rigid groups for hydrogen atoms; common isotropic U values and isotropic U values for C atoms), 137 parameters, R = 0.043, R_w = 0.040. The maximum difference electron density, based on the final model, was 0.14 e · pm^{-6}. Atomic coordinates and U_{eq} values are listed in Table 5.

Table 4. Bond lengths [pm] and angles [°], averaged according to the D_{2d} symmetry of **5**

C1 - C1'(1")	129.3(4)
C1'(1") - C2'/3'(2"/3")	148.2(3)
C2'(2") - C3'(3")	152.6(5)
C(ring) - C(methyl)	152.6(3)
C1' - C1 - C1"	179.3(4)
C1'(1") - C2'/3'(2"/3") - C3'/2'(3"/2")	59.0(2)
C2'(2") - C1'(1") - C3'(3")	60.6(9)
C1'(1") - C(ring) - C(methyl)	118.4(2)
C2'/3'(2"/3") - C3'/2'(3"/2") - C(methyl)	118.9(2)

Table 5. Atomic coordinates (× 10^4) and equivalent isotropic displacement factors [pm^2]

	x	y	z	U_{eq}
C(1)	2422(5)	4983(4)	7473(4)	288(6)*
C(1')	2946(5)	3844(4)	8368(4)	301(6)*
C(2')	3812(5)	3166(4)	9709(4)	354(6)*
C(3')	3140(5)	2267(4)	8748(4)	334(6)*
C(4')	2691(5)	3727(4)	11007(4)	466(6)*
C(5')	5883(5)	2770(4)	9914(4)	442(6)*
C(6')	1371(5)	1963(4)	9099(4)	483(6)*
C(7')	4561(5)	1004(4)	7999(4)	457(6)*
C(1")	1921(5)	6117(4)	6584(4)	296(6)*
C(2")	498(5)	7570(4)	6079(4)	339(6)*
C(3")	2400(5)	6962(4)	5403(4)	349(6)*
C(4")	-1190(5)	7544(4)	5295(4)	447(6)*
C(5")	44(5)	8910(4)	6968(4)	434(6)*
C(6")	2529(5)	6346(4)	3975(3)	411(6)*
C(7")	3788(5)	7717(4)	5636(4)	465(6)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

CAS Registry Numbers

3: 94106-62-4 / **4**: 20589-85-9 / **5**: 132723-92-3 / **6**: 50874-22-1 / **11**: 60538-60-5 / 2,3-dimethyl-2-butene: 563-79-1

[1] Cf. *Strain and its Implications in Organic Chemistry — Organic Stress and Reactivity* (A. de Meijere, S. Blechert, Eds.), NATO ASI Series C, Vol. 273, Kluwer Academic Publications, Dordrecht 1989.

[2] M. Eckert-Maksić, Z. B. Maksić, A. Skancke, P. N. Skancke, *J. Phys. Chem.* **91** (1987) 2786; *Modelling of Structure and Properties of Molecules* (Z. B. Maksić, Ed.), p. 67, Ellis Horwood, Chichester 1987; *J. Mol. Structure (Theochem)* **164** (1988) 25.

[3] [3a] For calculations see: A. Skancke, P. N. Skancke, M. Eckert-Maksić, Z. B. Maksić, *J. Mol. Structure (Theochem)* **150** (1987) 259. — [3b] For experimental evidence on methylenecyclopropane and its derivatives see: R. Boese, D. Bläser, N. Niederprüm, T. Miebach, *Proceedings of the Seventh Symposium on Organic Crystal Chemistry*, Poznan, Oxford Univ. Press, in press. — [3c] For a survey on cyclopropane bond lengths see: F. H. Allen, *Tetrahedron* **38** (1982) 645.

[4] T. Liese, A. de Meijere, *Chem. Ber.* **119** (1986) 2995.

[5] S. Keyaniyan, W. Göthling, A. de Meijere, *Tetrahedron Lett.* **25** (1984) 4105.

[6] D. J. Pasto, J. K. Borchardt, *J. Org. Chem.* **41** (1976) 1061.

[7] It should be emphasized here that the bent bond picture[8] offered by hybrid AOs is by far superior to Walsh's[9] original suggestion[10,11]. We make use of the Walsh model (a) because our discussion is given only in qualitative terms and (b) for the sake of brevity, since it provides a compact terminology.

[8] Th. Förster, *Z. Phys. Chem.*, Abt. B, **43** (1939) 58; C. A. Coulson, W. E. Moffit, *J. Chem. Phys.* **15** (1947) 151; *Philos. Mag.* **40** (1949) 1.

[9] A. D. Walsh, *Trans. Faraday Soc.* **45** (1949) 179.

[10] E. Honegger, E. Heilbronner, A. Schmelzer, *Nouv. J. Chim.* **6** (1982) 519.

[11] M. Eckert-Maksić, Z. B. Maksić, R. Gleiter, *Theoret. Chim. Acta* **66** (1984) 193.

[12] L. Fitjer, J. M. Conia, *Angew. Chem.* **85** (1973) 832; *Angew. Chem., Int. Ed. Engl.* **12** (1973) 761.

[13] R. Kopp, M. Hanack, *Angew. Chem.* **87** (1975) 874; *Angew. Chem., Int. Ed. Engl.* **14** (1975) 821.

[14] L. Fitjer, *Chem. Ber.* **115** (1982) 1035.

[15] Cf. J. E. McMurry, T. Lectka, J. G. Rico, *J. Org. Chem.* **54** (1989) 3748.

[16] K. Kovačević, Z. B. Maksić, *J. Org. Chem.* **39** (1974) 539; Z. B. Maksić, A. Rubčić, *J. Am. Chem. Soc.* **99** (1977) 4233.

[17] M. J. S. Dewar, W. Thiel, *J. Am. Chem. Soc.* **99** (1977) 4899, 4907; P. Bischof, G. Friedrich, *J. Comput. Chem.* **3** (1982) 486.

[18] E. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **54** (1971) 724; Gaussian 82, Release A. J. S. Binkley, R. Seeger, J. A. Pople, Carnegie Mellon University, 1985.

[19] The existence of bent bonds in cyclopropanes has been experimentally verified. Cf. A. Hartmann, F. L. Hirschfeld, *Acta Cryst.* **20** (1966) 80; R. Boese, T. Miebach, A. de Meijere, *Abstracts of Papers Presented at the Hauptversammlung der Gesellschaft Deutscher Chemiker*, Bonn 18.-22.09.1989; R. Boese, T. Miebach, A. de Meijere, *J. Am. Chem. Soc.* **113** (1991), in press.

[20] J. A. Pople, D. P. Santry, G. A. Segal, *J. Chem. Phys.* **43** (1965) S129; H. Fischer, H. Kollmar, *Theoret. Chim. Acta* **16** (1970) 163.

[21] M. Eckert-Maksić, Z. B. Maksić, *J. Mol. Structure (Theochem)* **86** (1982) 325.

[22] C. Trindle, O. Sinanoglu, *J. Am. Chem. Soc.* **91** (1969) 853; Z. B. Maksić, M. Randić, *ibid* **85** (1973) 6522.

[23] Cf. D. W. Turner, A. D. Baker, C. Baker, C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley Interscience, New York 1970.

[24] C. Baker, D. W. Turner, *J. Chem. Soc., Chem. Commun.* **1969**, 480.

[25] F. Brogli, J. K. Crandall, E. Heilbronner, E. Kloster-Jensen, S. A. Sojka, *J. Electron Spectrosc. Rel. Phenomena* **2** (1973) 455.

[26] T. Koopmans, *Physica* **1** (1934) 104.

[27] D. J. Pasto, T. P. Fehlner, M. E. Schwartz, H. F. Baney, *J. Am. Chem. Soc.* **98** (1976) 530; see also: W. Runge in *The Chemistry of Allenes* (S. R. London, Ed.), Academic Press, London 1982.

[28] Further details of this crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, DW-7514 Eggenstein-Leopoldshafen 2, FRG, on quoting the deposition number CSD-320247, the authors, and the journal citation.

[414/90]