Synthesis, Structure, and Properties of Twofold Bridged Sesquinorbornenes

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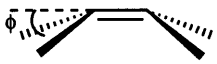
The twofold bridged sesquinorbornenes **2** and **6** were prepared using sequential [4 + 2] cycloadditions of benzoquinone with 1,5-dihydropentalenes **1** and **5**. These syntheses were improved using dilution conditions or a more reactive substituted benzoquinone. Results from semiempirical and ab initio DFT calculations indicated remarkably high pyramidalization angles (ϕ = 46–47°) for the central C–C double-bond atoms. The chemical reactivity with triplet and singlet oxygen, dimethyldioxirane and *N*-methyl-1,2,4-triazoline-3,5-dione supports these structural assignments.

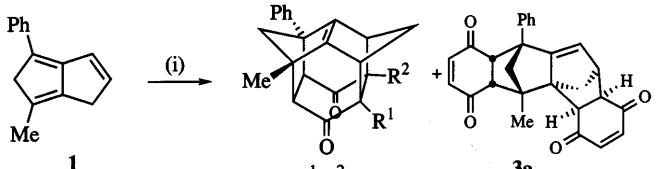
The structural properties and the chemical reactivity of *syn*-sesquinorbornes have been studied intensively[1] in the last decades. Especially the symmetric deformation of the central C−C double bond is a remarkable property which leads to an increased reactivity in comparison with norbornenes. One out of several parameters which are used to describe the out-of-plane deformation is the pyramidalization angle ϕ as defined by Borden[2] (cos ϕ = −cos (RCC)/[cos 0.5(RCR)], see Figure 1). Several *syn*-sesquinorbornes have been described with ϕ values up to 25°.[3] Much higher pyramidalization angles have been determined for the fullerene C_{60} ($\phi_{ex.}$ = 31.6°),[4] a sesquinorbornatriene ($\phi_{ex.}$ = 32.4°)[5] and a secododecahedradiene ($\phi_{ex.}$ = 35.3°).[6] The 9,9′,10,10′-tetradehydrodianthracene (**10**), prepared more than twenty years ago, has one of the highest ϕ angles for symmetrically out-of-plane bent alkenes ($\phi_{ex.}$ = 35.9°).[7] Recent studies have revealed the unusual reactivity of this compound.[8] Even higher pyramidalization values were determined for bridgehead-substituted tribenzodihydroacepentalenes ($\phi_{ex.}$ = 45.8 and 47.2°),[9] however, these molecules are asymmetrically bent, i.e. the pyramidalization angles for the second olefinic carbon atom are much lower ($\phi_{ex.}$ = 27.6 and 30.2°). In the series of *isolable* unsaturated dodecahedrane molecules, for dodecahedradiene a remarkably high pyramidalization angle was calculated ($\phi_{calc.}$ = 42.9°).[10][11] Recently, we discovered a simple reaction sequence which results in cage compounds with a twofold bridged sesquinorbornene structure.[12] We expected these compounds to exhibit an additional increase in double-bond nonplanarity compared with their unbridged analogues. Herein we describe synthetic improvements and studies on the chemical reactivity as well as theoretical investigations with these molecules.

Figure 1. Pyramidalization angle ϕ



A sequence of inter- and intramolecular Diels-Alder reactions of the dihydropentalene **1**[13] with 1 equivalent of *p*-benzoquinone gave the cage compound **2a** in relatively low yields (15−20%). The major product was the 1:2 adduct **3a** from **1** and two equivalents of *p*-benzoquinones. (Scheme 1).

Scheme 1



For other monofunctional dienophiles such as maleic anhydride, the equilibrium constant of the double-bond isomers **I** and **II** could be determined (ca. 5). This was not possible for the benzoquinone adducts **Ia** and **IIa** due to the rapid consumption of **IIa** by intramolecular cycloaddition. When the reaction of **1** and benzoquinone was performed with 0.2 equivalents of benzoquinone, the primary Diels-

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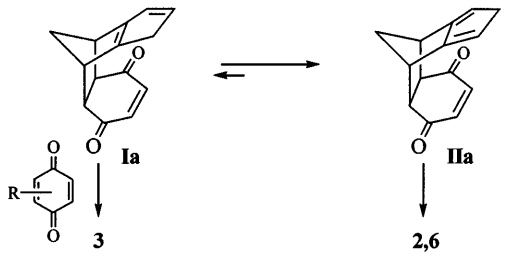
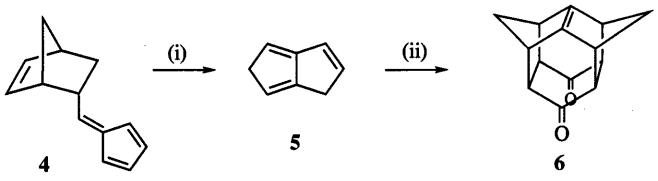
Alder cycloadduct **Ia** was detected by low-temperature ^{1}H NMR and the activation barrier for isomerization was determined to be 23 ± 2 kcal/mol (see Scheme 2).

Scheme 2



In order to improve the yield of cage compounds we examined two modifications: (a) Use of more reactive benzoquinones which should accelerate the intra- versus the intermolecular cycloaddition, and (b) application of the dilution principle in order to suppress the addition of a second equivalent of benzoquinone to the intermediate **I**. Treatment of the 1,5-dihydropentalene **1** with 2-(4-nitrophenyl)benzoquinone as bifunctional nonsymmetric dienophile resulted in two regioisomeric products **2b** and **2c** in a ratio of 57:43 (Scheme 1). The constitution of the cage products could be easily derived from the H-H coupling patterns. Surprisingly, no 1:2 cycloaddition products were isolated. As can be seen from the product substituent pattern, the primary cycloaddition exclusively involves the unsubstituted benzoquinone double bond (which can be easily derived from the H-H coupling pattern in the products). Thus, the secondary intramolecular cycloaddition must have been accelerated by the *p*-nitrophenyl group and the intermolecular reaction is widely suppressed. The second alternative was the use of dilution conditions. By slow addition of *p*-benzoquinone to a solution of **1** in dichloromethane the yield of **2a** could be raised to 52%. More important was the fact that this procedure allowed the preparation of the unsubstituted cage compound **6** from 1,5-dihydropentalene **5** (Scheme 3). The starting material **5** is easily available by thermolysis of the pentafulvene **4**.[14][15] After treatment with 1.1 equivalents of *p*-benzoquinone under dilution conditions, a 65:35 mixture of cage product **6** and a 1:2 cycloaddition product were isolated. After flash chromatography, **6** could be isolated as a colorless oil in 29% yield.

Scheme 3



Unfortunately, no X-ray analysis could be performed so far, neither from the parent compound **6** nor from its derivatives **2** due to low crystal quality. Nevertheless, we tried to gain more information on the double-bond deformation by studying the chemical behaviour and performing calculations (vide infra). A characteristic property of *syn*-sesquinorbornenes is that they readily add oxygen to give the corresponding epoxides.[16] Actually, the cage compound **2a** was quantitatively epoxidized by a variety of reagents: Dimethyldioxirane (DMD) gave the epoxides **7** already after some minutes at −20°C, singlet oxygen likewise reacted efficiently, whereas triplet oxygen needed some days for completion (Scheme 4). Oxirane **7** was crystallized as its methanol adduct and characterized by X-ray analysis.[17] It is important to mention, that no trace of 1,2-dioxetane or the corresponding cleavage products were formed in the singlet-oxygen reaction. Dioxetane formation can be found for many strained alkenes which have no properly aligned allylic hydrogen atoms.[18] Thus, the pyramidalization of the central double bond is depicted in a radical-like behaviour in its reaction with triplet oxygen as well as the unusual oxygen-atom transfer from singlet oxygen. That this behaviour is not a consequence of extreme shielding by the two flanking methylene bridges became apparent from the reaction of **2a** with *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD) in aqueous THF which led to the adduct **8**. For TAD [2 + 2] cycloaddition reactions an intermediate aziridinium imide zwitterion has been proven recently.[19] Thus, adduct **8** probably resulted from the nucleophilic ring opening of such an intermediate with substrate **2a**.

In order to gain more detailed information on the degree of double-bond deformation, we performed a series of semiempirical and DFT calculations for the unsubstituted cage compound **6**, its deoxygenated (hypothetical) analogue **9** (in order to exclude through-space carbonyl-carbonyl interactions) and the tetradehydrodianthracene **10** (Figure 2). Force field calculations (MM2[20]) resulted in too high values for the pyramidalization angle ϕ: e.g. for Greene's compound **10** a ϕ value of 43.3° resulted ($\phi_{ex.}$ = 35.9°). Semiempirical methods resulted in more realistic values: AM1[21] calculation gave 35.4° for **10** [for C_{60} $\phi_{calc.}$ is 31.9° ($\phi_{ex.}$ = 31.6°)]. For compound **6** the force field predicts a pyramidalization of 52.8°, the AM1 calculation gave 48.6°. To further optimize these results we performed density functional theory calculations (DFT-B3LYP[22]) with the 6-31G* basis set.[23] The GAUSSIAN94 program package was used for these calculations.[24] The results for **6** and **9** were nearly identical: for **6** a ϕ value of 46.5° (**9**: 47.1°) resulted (Table 1). Another useful parameter for the description of large symmetrical out-of-plane bending is the α_{av} value.[25][26][28] For Greene's compound **10** α_{av} is 114.8°, for C_{60} a_{av} = 116° (from X-ray data). The DFT calculations for **6** and **9** resulted in α_{av} values of 114.4° and 114.2°, respectively. These calculations lead to the suggestion that the (at room temperature stable) cage compounds **2**, **6** have remarkably high double-bond pyramidalizations. This pyramidalization results mainly from the fact that the strong compression of the α and β angles, which is typical for sesquinorbornenes, cannot be counterbalanced by expansion of the γ angle. In typical *syn*-sesquinorbornenes the γ angle can reach values up to 144°.[3a]

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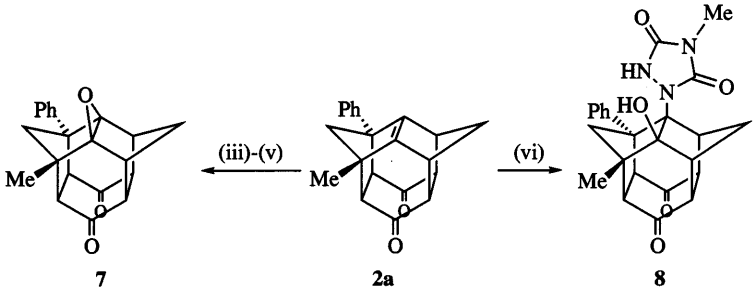
Scheme 4



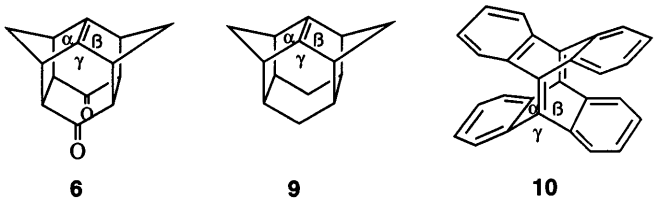
7 **2a** **8**

(iii) DMD, acetone, -30°C, 10 min; (iv) CH_2Cl_2, TPP, O_2, -10°C; (v) CH_2Cl_2, O_2, r.t., 5d; (vi) MTAD, THF-H_2O, -20°C, 1h.

Table 1. Results of calculations for **6** (**9**)

	MM2	AM1	B3LYP/6-31G*
α	107.25	106.77	107.62 (107.55)
β	107.25	106.77	107.62 (107.55)
γ	121.23	128.18	127.87 (127.53)
α + β + γ	335.73	341.72	343.11 (342.63)
ϕ	52.8	48.6	46.5 (47.1)
$\alpha_{av.}$	111.91	113.91	114.37 (114.21)

Figure 2. Pyramidalized alkenes **6**, **9**, **10**



6 **9** **10**

Experimental Section

General: The dihydropentalenes **1** and **5** were synthesized according to literature procedures.[13][14] − IR: Perkin-Elmer 1420. − ^{1}H NMR: AC 200 (200 MHz), Bruker AC 250 (250 MHz), Bruker AC 300 (300 MHz) Bruker AC 500 (500 MHz). − ^{13}C NMR: Bruker AC 200 (50.3 MHz), Bruker AC 250 (63.4 MHz), carbon multiplicities were determined by DEPT. − For ^{1}H NMR, $CDCl_3$ as solvent, TMS as internal standard; for ^{13}C NMR, $CDCl_3$ (δ_C = 77.0). − Column chromatography: Silica gel (Merck) 60−230 mesh; petroleum ether (PE, 40−60°C), ethyl acetate (EA). − Combustion analyses: Institut für Anorganische Chemie der Universität Würzburg.

1-Methyl-8-phenyl-hexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione (**2a**): A solution of 1.95 g (18.0 mmol) of *p*-benzoquinone in 100 ml of CH_2Cl_2 was added under nitrogen at room temp. to a solution of 3.50 g (18.0 mmol) of **1** in 1000 ml of CH_2Cl_2 by means of a motor-driven syringe during 24 h. After evaporation of the solvent, column chromatography (CH_2Cl_2/EA, 5:1, R_f = 0.45) resulted in 2.83 g (52%) of **2a** as a colorless powder, m.p. 108−109°C (ref.[12] 106−108°C).

1-Methyl-5-(4-nitrophenyl)-8-phenylhexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione (**2b**) *and 1-Methyl-4-(4-nitrophenyl)-8-phenylhexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione* (**2c**): A solution of 2.60 g (11.3 mmol) of 2-(4-nitro-phenyl)benzoquinone in 150 ml of CH_2Cl_2 was added under nitrogen at room temp. to a solution of 2.20 g (11.3 mmol) of **1** in 600 ml of CH_2Cl_2 by means of a motor-driven syringe during 24 h. After evaporation of the solvent, column chromatography resulted in 1.90 g (40%) of a mixture of **2b** and **2c** as a brown solid which was recrystallized several times from cyclohexane to give 1.20 g (25%) of a 1.3:1 mixture of **2b** and **2c** as a colorless powder. − IR (CCl_4, mixture): $\tilde{\nu}$ = 3010 cm^{-1}, 2940, 1695, 1590, 1510, 1340, 1250, 1130. − **2b**: ^{1}H NMR ($CDCl_3$): δ = 1.55 (s, 3H), 1.73 (d, *J* = 10.1 Hz, 1 H, 11-H$_{anti}$), 1.93 (d, *J* = 10.3 Hz, 1 H, 14-H$_{anti}$), 2.19 (m, 2 H, 11-H$_{syn}$, 14-H$_{syn}$), 2.96 (dd, *J* = 2.9, 8.0 Hz, 1 H, 2-H), 3.08 (dd, *J* = 2.9, 3.5 Hz, 1 H, 4-H), 3.52 (d, *J* = 8.0 Hz, 1 H, 7-H), 3.65 (m, 1 H, 12-H), 4.03 (s, 1 H, 10-H), 7.20−7.51 (m, 7 H, Ar.-H), 8.10−8.20 (m, 2 H, Ar.-H). − ^{13}C NMR ($CDCl_3$): δ = 15.1 (q), 41.8 (t), 51.5 (d), 55.0 (d), 56.2 (t), 60.2 (s), 62.4 (d), 65.4 (d), 65.6 (d), 68.8 (s), 70.0 (s), 123.3 (d), 127.3 (d), 127.6 (d), 128.8 (d), 129.7 (d), 136.4 (s), 137.2 (s), 146.7 (s), 157.7 (s), 160.3 (s), 208.5 (s), 209.4 (s). − **2c**: ^{1}H NMR ($CDCl_3$): δ = 1.54 (s, 3H), 1.75 (d, *J* = 10.6 Hz, 1 H, 11-H), 1.94 (d, *J* = 10.3 Hz, 1 H, 14-H), 2.19 (m, 2 H, 11′-H, 14′-H), 3.01 (d, *J* = 8.0 Hz, 1 H, 2-H), 3.02 (dd, *J* = 2.8, 3.6 Hz, 1 H, 5-H), 3.46 (dd, *J* = 2.8, 8.0 Hz, 1 H, 7-H), 3.65 (m, 1 H, 10-H), 4.03 (s, 1 H, 12-H), 7.20−7.51 (m, 7 H, Ar.-H), 8.10−8.20 (m, 2 H, Ar.-H). − ^{13}C NMR ($CDCl_3$): δ = 15.1 (q), 41.8 (t), 52.2 (d), 54.0 (d), 55.9 (t), 60.7 (s), 63.2 (d), 65.1 (d), 65.2 (d), 68.3 (s), 69.6 (s), 123.4 (d), 127.3 (d), 127.6 (d), 128.8 (d), 129.7 (d), 136.4 (s), 137.2 (s), 147.0 (s), 154.8 (s), 157.4 (s), 208.5 (s), 209.4 (s).

Hexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione (**6**): A solution of 1.36 g (12.65 mmol) of *p*-benzoquinone in 100 ml of CH_2Cl_2 was added under nitrogen at room temp. to a solution of 1.20 g (11.5 mmol) of **5** in 1000 ml of CH_2Cl_2 by means of a motor-driven syringe during 24 h. After evaporation of the solvent, flash chromatography resulted in 0.71 g (29%) of **6** as a colorless oil. − IR (CCl_4): $\tilde{\nu}$ = 2975 cm^{-1}, 1725, 1685, 1265, 1090. − ^{1}H NMR ($CDCl_3$): δ = 1.35 (d, *J* = 10.2 Hz, 2 H, 11-H$_{anti}$, 14-H$_{anti}$), 1.84 (d, *J* = 10.2 Hz, 2 H, 11-H$_{syn}$, 14-H$_{syn}$), 2.64 (s, 4H), 3.35 (s, 4H). − ^{13}C NMR ($CDCl_3$): δ = 42.3 (t, C-11, C-14), 52.3 (d, 4C), 56.6 (d, 4C), 154.9 (s, C-9, C-13), 211.7 (s, 2 C=O). − $C_{14}H_{12}O_2$ (212.2): calcd. C 79.21, H 5.70; found C 79.40, H 5.64.

1-Methyl-8-phenyl-9,13-epoxyhexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradeca-3,6-dione (**7**): A solution of 80 mg (0.27 mmol) of compound **2a** in 2 ml of CH_2Cl_2 and 1 mg of tetraphenylporphine (TPP) was irradiated with a 150-W sodium lamp at −10°C under constant purging with dry oxygen (syringe needle). After evaporation of the solvent, the residue was chromatographed which resulted in 60 mg (71%) of colorless needles, m. p. 115−117°C. − IR (CCl_4): $\tilde{\nu}$ = 3020 cm^{-1}, 2920, 1700, 1680, 1425, 1255. − ^{1}H NMR ($CDCl_3$): δ = 1.33 (dd, *J* = 1.3, 10.7 Hz, 1 H, 11-H$_{anti}$), 1.39

(s, 3H), 1.55 (d, J = 10.7 Hz, 1 H, 14-H$_{anti}$), 2.19 (dd, J = 1.6, 10.7 Hz, 1 H, 11-H$_{syn}$), 2.36 (d, J = 10.7 Hz, 1 H, 14-H$_{syn}$), 2.93 (dd, 1 H, J = 2.8, 9.7 Hz, 1 H, 2-H), 3.02 (m, 2 H, 4-H, 5-H), 3.21 (m, 2 H, 10-H, 12-H), 3.43 (dd, J = 2.8, 9.7 Hz, 1 H, 7-H), 7.28−7.42 (m, 5 H, Ph.-H). − ^{13}C NMR ($CDCl_3$): δ = 14.6 (q), 37.4 (t), 45.6 (d), 45.9 (d), 51.3 (t), 53.9 (s), 57.2 (d), 57.6 (d), 60.8 (s), 62.1 (s), 62.2 (d), 62.9 (s), 64.7 (d), 126.6 (d), 127.6 (d), 128.8 (d), 137.0 (s), 208.3 (s), 208.4 (s). − $C_{21}H_{18}O_3$ (318.4): calcd. C 79.20, H 5.70; found C 78.67, H 5.60. − Crystallization of the crude material from methanol resulted in a methanol addition product in 96% yield.[17]

13-Hydroxy-1-methyl-9-(4-methyl-3,5-dioxo-1,2,4-triazolin-1-yl)-8-phenylhexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione (**8**): A solution of 1.00 g (3.3 mmol) of **2a** in 100 ml of aqeous THF was precooled to −20°C and a solution of 0.38 g (3.3 mmol) of MTAD in 20 ml of THF was added within 10 min. After stirring for 16 h at room temperature, the solvent was evaporated and the residue dissolved in 5 ml of acetone. After cooling to −10°C, 0.48 g (35%) of **8** crystallized as colorless needles m.p. 279−280°C. − IR (CCl_4): $\tilde{\nu}$ = 3280 cm^{-1}, 2920, 1735, 1670, 1090, 1070. − ^{1}H NMR ($CDCl_3$): δ = 0.72 (s, 3H), 1.39 (d, J = 11.0 Hz, 1 H, 11-H$_{anti}$), 1.49 (d, J = 11.3 Hz, 1 H, 14-H$_{anti}$), 2.31 (d, J = 12.2 Hz, 1 H, 2-H), 2.46 (d, J = 12.2 Hz, 1 H, 7-H), 2.50 (mc, 1 H, 11-H$_{syn}$), 2.56 (s, 2 H, 4-H, 5-H), 2.63 (s, 3 H), 2.70 (s, 1 H, 12-H), 3.18 (d, J = 11.3 Hz, 1 H, 14-H$_{syn}$), 4.69 (s, 1 H, 10-H), 5.72 (s, 1 H, OH), 6.72−6.96 (m, 5 H, Ph.-H), 8.44 (s, 1 H, NH). − ^{13}C NMR ($CDCl_3$): δ = 15.9 (q), 24.7 (q), 43.3 (t), 50.3 (d), 52.3 (d), 52.7 (d), 53.5 (d), 54.2 (t), 57.4 (s), 57.8 (d), 60.0 (d), 63.9 (s), 80.1 (s), 91.3 (s), 126.9 (d), 127.6 (d), 128.0 (d), 138.3 (s), 153.3 (s), 153.4 (s), 208.5 (s), 210.7 (s). − $C_{24}H_{23}N_3O_4$ (417.5): calcd. C 69.05, N 10.07, H 5.55; found C 68.93, N 9.93, H 5.70.

[1] [1a] W. Luef, R. Keese, *Top. Stereochem.* **1991**, *20*, 231−318. − [1b] P. D. Bartlett, A. J. Blakeney, G. L. Combs, J. M. Galloy, A. A. M. Roof, R. Subramanyan, W. J. Winter, C. Wu, in *Stereochemistry and Reactivity of Systems Containing π-Electrons* (Ed.: W. H. Watson), VCH, Deerfield Beach, FL, **1983**, p. 75.

[2] W. T. Borden *Chem. Rev.* **1989**, *89*, 1095−1109.

[3] [3a] W. H. Watson, J. Galloy, P. D. Bartlett, A. A. M. Roof, *J. Am. Chem. Soc.* **1981**, *103*, 2022−2031. − [3b] L. A. Paquette, P. Charumilind, M. C. Böhm, R. Gleiter, L. S. Bass, J. Clardy, *J. Am. Chem. Soc.* **1983**, *105*, 3136−3147.

[4] R. C. Haddon, *Science* **1993**, *261*, 1545−1550.

[5] L. A. Paquette, C.-C. Shen, J. A. Krause, *J. Am. Chem. Soc.* **1989**, *111*, 2351−2352.

[6] R. Pinkos, J.-P. Melder, K. Weber, D. Hunkler, H. Prinzbach, *J. Am. Chem. Soc.* **1993**, *115*, 7173−7191.

[7] [7a] R. L. Viavatenne, F. D. Greene, L. D. Cheung, R. Majeste, L. M. Trefonas, *J. Am. Chem. Soc.* **1974**, *96*, 4342−4343. − [7b] Second X-ray analysis: S. Kammermeier, P. G. Jones, R. Herges, *Angew. Chem.* **1996**, *108*, 2834−2836; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2669−2671.

[8] [8a] R. Herges, H. Neumann, F. Hampel, *Angew. Chem.* **1994**, *106*, 1024−1026; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 993−995. − [8b] R. Herges, H. Neumann, *Liebigs Ann.* **1995**, 1283−1289. − [8c] R. Herges, S. Kammermaier, H. Neumann, F. Hampel, *Liebigs Ann.* **1996**, 1795−1800.

[9] [9a] R. Haag, B. Ohlhorst, M. Noltemeyer, A. Schuster, D. Kuck, A. de Meijere, *J. Chem. Soc., Chem. Commun.* **1993**, 1727−1729. − [9b] R. Haag, B. Ohlhorst, M. Noltemeyer, R. Fleischer, D. Stalke, A. Schuster, D. Kuck, A. de Meijere, *J. Am. Chem. Soc.* **1995**, *117*, 10474−10485.

[10] J.-P. Melder, R. Pinkos, H. Fritz, H. Prinzbach, *Angew. Chem.* **1990**, *102*, 105−109; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 95−99.

[11] A variety of *non-isolable* highly pyramidalized alkenes have been trapped by Diels-Alder reactions, e.g. cubene with $\phi_{calc.} \approx 85°$: [11a] P. Eaton, M. Maggini, *J. Am. Chem. Soc.* **1988**, *110*, 7230−7232. − [11b] K. Lukrin, P. Eaton, *J. Am. Chem. Soc.* **1995**, *117*, 7652−7656.

[12] W. Adam, T. Deufel, R. Finzel, A. G. Griesbeck, J. Hirt, *J. Org. Chem.* **1992**, *57,* 3991−3994.

[13] A. G. Griesbeck, *Chem. Ber.* **1990**, *123*, 549−554.

[14] A. G. Griesbeck, *Synthesis* **1990**, 144−147.

[15] Recent application of this dihydropentalene-synthesis have been described: [15a] K. Jonas, B. Gabor, R. Mynott, K. Angermund, O. Heinemann, C. Krüger, *Angew. Chem.* **1997**, *109*, 1790−1793; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1710−1714. − [15b] K. Jonas, P. Kolb, G. Kollbach, B. Gabor, R. Mynott, K. Angermund, O. Heinemann, C. Krüger, *Angew. Chem.* **1997**, *109*, 1793−1796; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1714−1718.

[16] P. D. Bartlett, A. J. Blakeney, M. Kimura, W. H. Watson, *J. Am. Chem. Soc.* **1980**, *102*, 1383−1390.

[17] K. Peters, E.-M. Peters, H. G. von Schnering, A. G. Griesbeck, T. Deufel, *Z. Kristallogr.* **1996**, *211*, 435−436.

[18] A. L. Baumstark, A. Rodriguez, in *Handbook of Organic Photochemistry and Photobiology* (Eds.: W. Horspool, P.-S. Song) CRC, Boca Raton, **1995**, p. 335−345.

[19] [19a] T. H. W. Poon, S. H. Park, Y. Elemes, C. S. Foote, *J. Am. Chem. Soc.* **1995**, *117*, 10468−10473. − [19b] I. Smounou, S. Khan, C. S. Foote, Y. Elemes, I. M. Mavridis, A. Pantidou, M. Orfanopoulos, *J. Am. Chem. Soc.* **1995**, *117*, 7081−7087.

[20] N. L. Allinger, X. Zhou, J. Bergsma, *J. Mol. Struct. (Theochem)* **1994**, *312*, 69.

[21] J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 209, 221−264.

[22] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652.

[23] P. C. Hariharan, J. A. Pople, *Theoret. Chim. Acta* **1973**, *28*, 213−222.

[24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Alaham, V. G. Zakrzewski, V. G.; J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Derees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94, Revision B.1*, Gaussian Inc., Pittsburgh, PA, USA, **1995**.

[25] $\alpha_{av} = (\Sigma\theta_{ij})/3$: S. F. Nelson, T. B. Frigo, Y. Kim, *J. Am. Chem. Soc.* **1989**, *111*, 5387−5397.

[26] The out-of-plane deformation of a double bond can also be described using the flap or hinge angle:[27] 180° − χ = 141° (χ = 39°) for **6**, for the tetradehydrodianthracene **10** χ = 45°, for C_{60} χ = 41°.

[27] Ermer, C.-D. Bödecker, *Helv. Chim. Acta* **1983**, 943−959.

[28] POAV analysis[29] gives a $\theta_{\sigma\alpha}$ value of 103.3° (**9**: 103.0°) for compound **6**.

[29] R. C. Haddon, *J. Am. Chem. Soc.* **1990**, *112*, 3385−3389.

[98186]