Polycycles

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Dimerization of Pyramidalized 3,4,8,9-Tetramethyltetracyclo[4.4.0.0^{3,9}.0^{4,8}]dec-1(6)-ene to a Hydrocarbon Featuring Four Cyclohexane Rings in Boat Conformations[**]

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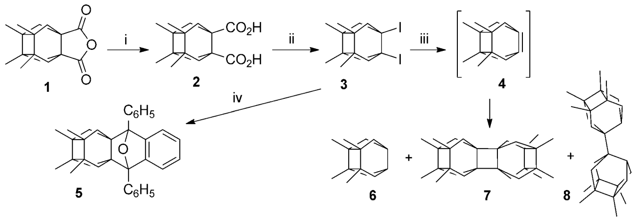
Dedicated to Professor Pelayo Camps

Abstract: *The synthesis, chemical trapping, and dimerization of a highly pyramidalized alkene is reported. Its dimer is a unique nonacycle featuring three planar cyclobutane rings, four cyclopentane rings, and four cyclohexane rings in boat conformations. The X-ray diffraction analysis showed a H–H distance between the flagpole hydrogen atoms of 1.999 Å and a separation of 2.619 Å between the two flagpole carbon atoms. The three cyclobutane rings of the dimer were thermally stable.*

Pyramidalized alkenes are compounds containing carbon–carbon double bonds in which one or both of the sp^2-carbon atoms do not lie in the same plane as the attached atoms.[1] We have reported the generation, trapping, and dimerization of several highly pyramidalized alkenes and the first cross-coupling of two different pyramidalized alkenes leading to a tetrasecododecahedradiene derivative.[1c,2,3] Herein, we report the generation of **4** (Scheme 1), a novel highly pyramidalized alkene, its trapping with 1,3-diphenylisobenzofuran, and its dimerization to a unique polycyclic hydrocarbon, **7**, which features three planar cyclobutane rings, four cyclopentane rings, and four cyclohexane rings in a boat conformations.



Scheme 1. Synthesis, trapping, and dimerization of alkene **4**. a) aq. NaOH, reflux, then conc HCl, 70% yield; b) 1,3-diiodo-5,5-dimethylhydantoin, 1,2-dichloroethane, 27% yield; c) Na, 1,4-dioxane, reflux, 4 h; d) *t*BuLi, 1,3-diphenylisobenzofuran, THF, −67 °C, 37% yield.

Theoretical calculations using B3LYP/6-31G(d) showed us that the alkene **4** should be an accessible target.[4] Its calculated pyramidalization angle ($\Phi = 47.5°$),[5] carbon–carbon double bond length (1.360 Å), heat of hydrogenation (−63.7 kcal mol^{-1}), HOMO–LUMO gap (5.64 eV), and predicted ^{13}C NMR chemical shift ($\delta = 148.4$ ppm) were in line with the values calculated for previously synthesized highly pyramidalized alkenes.[1c,6]

It is known that vicinal diiodo compounds are suitable precursors of highly pyramidalized alkenes, so the generation of **4** was envisioned from the diiodo derivative **3** (Scheme 1), whose preparation from the known anhydride **1**[7] was carried out in just two steps. Saponification of **1** gave the dicarboxylic acid **2** in 70% yield. The diiodo compound **3** was obtained in 27% yield by using a iododecarboxylation procedure recently reported by Gandelman and co-workers.[8] Previous attempts to carry out the iododecarboxylation of **2** using iodosobenzene diacetate or lead tetraacetate gave even lower yields of **3**. Reaction of **3** with *tert*-butyllithium in THF at −67 °C in the presence of 1,3-diphenylisobenzofuran furnished the expected Diels–Alder adduct **5** in 37% yield. Finally, reaction of **3** with a large excess of molten sodium in 1,4-dioxane at reflux for 4 hours gave a mixture of three products (GC/MS): the reduced product **6**, the expected dimer **7**, and the dihydrodimer **8**. From this mixture, **6** was isolated by sublimation (100 °C at 1 Torr), **7** was obtained by crystallization from *n*-pentane, and **8** was obtained from the mother liquors. X-Ray diffraction analysis unequivocally established the structures of **7** and **8**.[9]

The X-ray diffraction analysis of **7** revealed several interesting features. Firstly, **7** has three planar cyclobutanes, two of them with four eclipsed methyl groups. While the central cyclobutane is not a fully perfect square, as it has two newly formed carbon–carbon bonds being slightly shorter than the other two bonds, the other two cyclobutanes are nearly perfect squares (see Figure 1). Secondly, the compound

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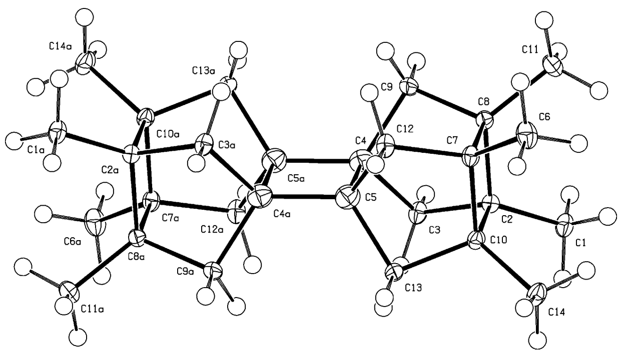
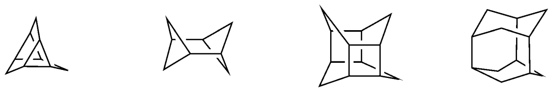


Figure 1. Crystal structure (ORTEP) of **7**. Thermal ellipsoids shown at 50% probability. Selected distances [Å] and angles [°]: C2–C8 1.5844(19), C7–C8 1.5841(19), C4–C5 1.589(2), C4–C5a 1.542(2), C8–C9 1.5376(19), C4–C9 1.543(2); C3-C2-C10 109.44(11), C3-C2-C8 105.41(11), C10-C2-C8 90.01(10), C2-C3-C4 99.61(11), H3a-C3-H3b 110.1 (15), C5a-C4-C5 90.05(11), C3-C4-C5 109.78(12), C4a-C5-C12 122.30(13), C12-C5-C13 101.86(12), C4a-C5-C4 89.95(11).

has four cyclopentane rings in a "frozen" envelope conformation. Finally, the structure features four cyclohexane rings in a boat conformation. Although there are several precedents of cyclohexane rings in boat conformations,[10] most of the known examples lack the typical H–H flagpole interaction of the boat conformation (e.g. camphor and other norbornane derivatives).[11] Some notable exceptions with frozen boat cyclohexanes, featuring a H–H flagpole interaction, are the asteranes, such as tetracyclo [3.3.1.0^{2,8}.0^{4,6}]nonane (triasterane; **9**)[12] tricyclo[3.1.1.1^{2,4}]octane (diasterane; **10**),[12d,13] and pentacyclo[6.4.0.0^{2,7}.0^{4,11}.0^{5,10}] dodecane (tetraasterane; **11**),[12a,d,14,15] and tetracyclo[5.3.1.1^{2,6}.0^{4,9}]dodecane (iceane; **12**),[16] a polycyclic compound featuring two chair and three boat cyclohexane rings (Figure 2). Interestingly, the cyclobutane rings of these polycyclic compounds can be either planar, as in **7** and **11**, or puckered as in **10**.



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

Figure 2. Known polycyclic compounds featuring boat cyclohexane rings.

According to a seminal paper by Hassel and Ottar,[17] the boat conformer of the cyclohexane ring with fixed C-C-C angles of 109.5° would have a distance between the flagpole hydrogen atoms of 1.8–1.83 Å and a separation of 2.57 Å would be expected between the flagpole carbon atoms. These distances should induce severe steric congestion given the van der Waals radius of hydrogen and carbon, 1.1–1.2 Å and 1.7–1.8 Å, respectively.[18] In fact, Sauers has found, using density functional calculations at the B3LYP/6-311++G(2d,p) level of theory, that the boat conformer of cyclohexane suffers from significant distortions from pure sp^3 hybridization, thus relieving the flagpole H–H interaction at an interatomic separation of 2.353 Å and with a distance of 2.736 Å between the two flagpole carbon atoms.[11a] In this work, for the boat conformer of cyclohexane, we have found smaller distances using MP2/6-31G(d): 2.289 Å and 2.710 Å for the flagpole H–H and C–C interatomic distances, respectively.[4]

However, in the polycyclic compounds shown in Scheme 1 the ability of the boat cyclohexanes to relieve the flagpole H–H interaction is severely limited. Thus, the X-ray diffraction analysis of **7** revealed a distance between the flagpole hydrogen atoms of only 1.999 Å and a separation of 2.619 Å between the flagpole carbon atoms. We have optimized the structure of **7** at the MP2/6-31G(d) level of theory and found distances of 2.042 Å and 2.668 Å for the flagpole H–H and C–C distances, respectively, and they are in reasonable agreement with the experimental values. At this level, these distances are shorter than the corresponding values found in **9**, **11**, and **12**, but longer that those of **10** (Table 1).[4]

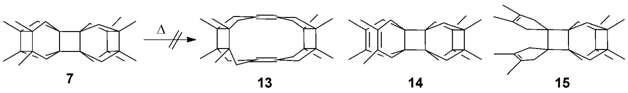
Table 1: H–H and C–C distances between the flagpole hydrogen atoms and the flagpole carbon atoms in boat cyclohexane and hydrocarbons **6**–**7** and **9**–**12**.

Compound	H–H distance [Å]		C–C distance [Å]	
	B3LYP/ 6-31G(d)	MP2/ 6-31G(d)	B3LYP/ 6-31G(d)	MP2/ 6-31G(d)
Cyclohexane	2.349	2.289	2.739	2.710
6	2.035	2.027	2.655	2.639
7[a]	2.054	2.042	2.684	2.668
9[b]	3.252	3.238	2.990	2.979
10	1.861	1.856	2.625	2.610
11	2.505	2.488	2.814	2.800
12	2.126	2.120	2.668	2.652

[a] The H–H and the C–C distances in the crystal structure of **7** were 1.999(2) Å and 2.619(1) Å, respectively. [b] The C–C distance obtained for **9** by gas-phase electron diffraction was 2.973(6).[12d]

Regarding the X-ray diffraction analysis of **8** two features are worthy of comment. Firstly, values between 1.93 and 2.03 Å were found for the distance between the flagpole hydrogen atoms, while an average value of 2.64 Å was found between the flagpole carbon atoms, very similar to the values found for **7**. These values are also very similar in the X-ray diffraction structures found for **1**, **3**, and **5**.[9] Secondly, the exocyclic intercage C−C bond length of **8** is 1.539(3) Å, the normal length for a C−C single bond, midway between the very short intercage C−C bond found in tetrahedranyltetrahedrane and bicubyl derivatives, which feature significantly shorter distances (around 1.44–1.46 Å),[19] and that of the 1-(1-adamantyl)adamantine (1.578(2) Å).[20]

Previously, we had observed that several cyclobutane dimers of highly pyramidalized alkenes underwent an exothermic [2+2] retrocycloaddition process to their corresponding diene isomers.[1,3d] However, the three cyclobutane rings in **7** were thermally stable. In fact, the only process that was observed when a sample of **7** was heated up to 500 °C was the melting process at 380 °C. MP2/6-311++G(d,p)//MP2/6-31G(d) calculations carried out on **7** and its three theoretical diene isomers, **13**, **14**, and **15**, predicted endothermic processes for all the ring-opening reactions, with the transformation of **7** into **13** being more endothermic, 17.8 kcal mol^{-1}, than the opening to **14** or **15**, 11.5 and 11.4 kcal mol^{-1}, respectively, thus probably reflecting the increase in the strain in **13** as a consequence of the approaching of the eclipsed methyl groups (Scheme 2).[4]



Scheme 2. Hypothetical [2+2] cycloreversion of **7** into the dienes **13**, **14**, and **15**.

In summary, we have presented here the synthesis, chemical trapping, and dimerization of a highly pyramidalized alkene. Its dimer features three planar cyclobutane rings and four cyclohexane rings in boat conformations. X-ray structural studies and theoretical calculations showed that the distances between the flagpole hydrogen atoms and the flagpole carbon atoms are smaller than the sum of the van der Waals radius of the involved atoms. Finally, in spite of the three cyclobutane rings, and in sharp contrast with the behavior of previously described dimers of highly pyramidalized alkenes, the nonacycle **7** is thermally stable.

Experimental Section

3,4,8,9-Tetramethyltetracyclo[$4.4.0.0^{3,9}.0^{4,8}$]decane-1,6-dicarboxylic acid (**2**): A solution of the anhydride **1** (270 mg, 1.03 mmol) in 1 N NaOH (10 mL) was heated to reflux for 18 h. The suspension was allowed to cool down to room temperature, was acidified with 6 N HCl, and extracted with EtOAc (3 × 50 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give **2** (203 mg, 70% yield) as a colorless solid, m.p. 209–210 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 0.92$ (s, 12 H, 3(4,8,9)-CH_3], 0.98 [d, $J = 11.6$ Hz, 4 H, 2(5,7,10)-H$_a$], 1.97 ppm [d, $J = 11.6$ Hz, 4 H, 2(5,7,10)-H$_b$]; ^{13}C NMR (100.6 MHz, CD_3OD): $\delta =$ 15.7 [CH_3, 3(4,8,9)-CH_3], 43.5 [CH_2, 2(5,7,10)-CH_2], 46.4 [C, 3(4,8,9)-C], 53.7 [C, 1(6)-C], 179.1 ppm (C, CO_2H); IR (KBr): $\nu = 3000$–2400 (2953, 2921, 2867, 2673, 2570), 1717, 1429, 1299, 1218, 1176, 1116, 1061, 1030, 1013, 877, 771, 720 cm^{-1}; GC/MS (70 eV): m/z (%): 260 [$(M-H_2O)^{\cdot+}$, 5], 232 (51), 187 (100), 173 (73), 163 (19), 159 (15), 145 (34), 131 (23), 119 (37), 105 (17), 91 (36), 82 (37), 77 (31), 67 (17); Accurate mass [ESI(−)]: m/z calcd for $C_{16}H_{21}O_4$: 277.1445 $[M-H]^-$; found: 277.1448.

1,6-Diiodo-3,4,8,9-tetramethyltetracyclo[$4.4.0.0^{3,9}.0^{4,8}$]decane (**3**): 1,3-Diiodo-5,5-dimethylhydantoin (7.17 g, 18.9 mmol) was added to a solution of the diacid **2** (2.10 g, 7.54 mmol). The resulting orange solution was irradiated (2 × 60 W tungsten bulb) at reflux for 24 h. The suspension was cooled to room temperature and washed with 10% aqueous $NaHSO_3$ (50 mL). The aqueous layer was extracted with CH_2Cl_2 (25 mL) and the combined organic layers were washed with saturated aqueous solution of $NaHCO_3$ (2 × 25 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum to obtain 1.4 g of a mixture of starting **2**, **3** and the corresponding iodoacid. Purification by column chromatography (silica gel, *n*-hexane) gave **3** as a colorless solid (900 mg, 27% yield), m.p. 234–235 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.92$ (s, 12 H, 3(4,8,9)-CH_3], 1.62 [d, $J = 12.0$ Hz, 4 H, 2(5,7,10)-H$_a$], 2.69 ppm [d, $J = 12.0$ Hz, 4 H, 2(5,7,10)-H$_b$]; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.3$ [CH_3, 3(4,8,9)-CH_3], 47.0 [C, 3(4,8,9)-C], 48.7 [C, 1(6)-C], 53.7 ppm [CH_2, 2(5,7,10)-CH_2]; IR (KBr): $\nu =$ 2923, 2859, 1717, 1448, 1384, 1369, 1298, 1270, 1208, 1187, 1102, 935, 820, 790, 708, 654 cm^{-1}; GC/MS (70 eV): m/z (%): 442 ($M^{\cdot+}$, 2), 315 (46), 187 (100), 173 (46), 159 (13), 145 (34), 131 (16), 119 (23), 105 (11), 91 (20), 77 (12); Anal calcd for $C_{14}H_{20}I_2$: C 38.94%; H 4.49%; calcd for $C_{14}H_{20}I_2\cdot0.1$ hexane: C: 38.91%, H 4.79%; found C: 38.94, H 4.49%.

12,13,14,17-Tetramethyl-2,9-diphenyl-19-oxaheptacyclo-[$10.3.2.1^{2,9}.1^{10,13}.0^{1,10}.0^{3,8}.0^{14,17}$]nonadec-3,5,7-triene (**5**). A solution of *tert*-butyllithium (1.6 M in pentane, 0.61 mL, 0.97 mmol) was slowly added, under stirring, to a cold (−67 °C) solution of **3** (252 mg, 0.6 mmol) and 1,3-diphenylisobenzofuran (186 mg, 0.68 mmol) in anhydrous THF (10 mL). The reaction mixture was kept at this temperature for 30 min and then it was allowed to warm to room temperature. Methanol (5 mL) and water (10 mL) were added dropwise and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo to dryness to give a yellow oil. Purification by column chromatography (EtOAc/*n*-hexane mixtures) gave **5** (96 mg, 37% yield) as a pale yellow solid, m.p. 182–183 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.42$ [d, $J = 11.5$ Hz, 2 H, 11(16)-H$_a$], 0.80 (s, 6 H) and 0.85 (s, 6 H) [C12(17)-CH_3 and C13(14)-CH_3], 0.94 [dd, $J = 11.0$ Hz, $J' = 2.5$ Hz, 2 H, 15(18)-H$_b$], 1.06 [d, $J = 11.0$ Hz, 2 H, 15(18)-H$_a$], 1.51 [dd, $J = 11.5$ Hz, $J' = 2.5$ Hz, 2 H, 11(16)-H$_b$], 7.15 [m, 2 H, 5(6)-H], 7.32 [m, 2 H, 4(7)-H], 7.37 (tt, 2 H, $J = 7.5$ Hz, $J' =$ 1.5 Hz, Ar-H$_{para}$), 7.49 (broad t, $J = 7.5$ Hz, 4 H, Ar-H$_{meta}$), 7.78 ppm (d, $J = 8.0$ Hz, $J' = 1.5$ Hz, 4 H, Ar-H$_{ortho}$); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 15.6$ (CH_3) and 15.8 (CH_3) [C12(17)-CH_3 and C13(14)-CH_3], 39.2 [CH_2, C11(16)], 41.0 [CH_2, C15(18)], 44.6 [C, C12(17)], 45.4 [C, C13(14)], 55.3 [C, C1(10)], 88.8 [C, C2(9)], 119.6 [CH, C4(7)], 125.0 (CH, C$_{ortho}$-C_6H_5), 126.1 [CH, C5(6)], 127.0 (CH, C$_{para}$-C_6H_5), 128.2 (CH, C$_{meta}$-C_6H_5), 138.3 (C, C$_{ipso}$-C_6H_5), 146.7 ppm [C, C3(8)]; IR (KBr): $\nu = 3061$, 3024, 2943, 2913, 2860, 1597, 1457, 1446, 1370, 1342, 1302, 1272, 1217, 1178, 1155, 1119, 1021, 1001, 975, 936, 839, 745, 712, 698, 674 cm^{-1}; GC/MS (70 eV): m/z (%): 458 ($M^{\cdot+}$, 1), 353 (36), 270 (100), 241 (13), 193 (5), 165 (8), 105 (5), 77 (4); Accurate mass [ESI(+)]: m/z calcd for $C_{34}H_{35}O$: 459.2682 $[M+H]^+$; found: 459.2680; Anal calcd for $C_{34}H_{34}O$: C 89.04%; H 7.47%; calcd for $C_{34}H_{34}O\cdot0.05CH_2Cl_2$: C: 88.35%, H 7.43%; found C: 88.10, H 7.63%.

3,4,8,9-Tetramethyltetracyclo[$4.4.0.0^{3,9}.0^{4,8}$]decane (**6**), 4,5,6,7,12,-13,16,17-octamethylnonacyclo[$8.4.4.1^{2,5}.1^{6,9}.0^{1,10}.0^{2,9}.0^{4,7}.0^{12,17}.0^{13,16}$]-eicosane (**7**), and 3,4,8,9-tetramethyl-1-[3,4,8,9-tetramethyltetracyclo[$4.4.0.0^{3,9}.0^{4,8}$]dec-1-yl]-tetracyclo[$4.4.0.0^{3,9}.0^{4,8}$]decane (**8**). Finely cut sodium (0.49 g, 21.5 mmol) was added to boiling anhydrous 1,4-dioxane (25 mL) and the mixture was heated with stirring under an argon atmosphere until the metal melted. Then, solid **3** (0.95 g, 2.15 mmol) was added and the mixture was heated under reflux for 4 h. The reaction mixture was cooled to room temperature and filtered through Celite®. The solid residue was washed with diethyl ether and *n*-pentane, and the combined filtrate and washings were concentrated under reduced pressure to give a solid white residue (151 mg, aprox. 35% yield). GC/MS spectrometry showed the presence of three main components with the following retention times, m/z of the molecular ions and relative areas (12.3 min, 190, 20.8%; 24.2 min, 376, 11.5%; 25.1 min, 378, 45.6%). By sublimation (100 °C/1 atm), pure tetracycle **6** was obtained (19 mg, 5% yield), m.p. 189–190 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.56$ [d, $J = 11.0$ Hz, 4 H, 2(5,7,10)-H$_a$], 0.93 (s, 12 H, 3(4,8,9)-CH_3], 1.70 [d, $J = 11.0$ Hz, 4 H, 2(5,7,10)-H$_b$], 2.24 ppm [s, 2 H, 1(6)-H]; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 15.8$ (CH_3), 32.9 (CH), 38.1 (CH_2), 45.3 ppm (C); IR (KBr): $\nu = 3447$, 2946, 2864, 1458, 1381, 1369, 1323, 1116, 1096, 1028, 927 cm^{-1}; GC/MS (70 eV): m/z (%): 190 ($M^{\cdot+}$, 43), 120 (100), 119 (30), 108 (31), 107 (34), 105 (51), 95 (16), 93 (39), 91 (34), 77 (19). By recrystallization of the remaining mixture from *n*-pentane, pure dimer **7** (36 mg, 9% yield) was isolated by filtration, m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.64$ [d, $J = 13.5$ Hz, 8 H, 3(8,11,14,15,18,19,20)-H$_a$], 0.91 (s, 24 H, 4(5,6,7,12,13,16,17)-CH_3], 1.97 ppm [d, $J = 13.5$ Hz, 8 H, 3(8,11,14,15,18,19,20)-H$_b$]; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 15.8$ (CH_3), 38.9 (CH_2), 45.3 [C, 4(5,6,7,12,13,16,17)-C], 47.0 ppm [C, 1(2,9,10)-C]; IR (KBr): $\nu =$

2945, 2860, 1699, 1445, 1382, 1297, 1215, 1115 cm^{-1}; GC/MS (70 eV): m/z (%): 376 ($M^{\cdot+}$, 12), 190 (24), 189 (17), 188 (69), 187 (100), 186 (55), 185 (15), 173 (71), 171 (34), 145 (21), 131 (16), 119 (42), 105 (17), 91 (19), 79 (15); Anal calcd for $C_{28}H_{40}$: C 89.29 %; H 10.71 %; found C: 89.07, H 10.71 %. The solid remaining after concentration of the mother liquors was washed with dichloromethane to give the pure dihydrodimer **8** (37 mg, 9 % yield), m.p. 199–200 °C. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.62$ [d, $J = 11.6$ Hz, 4 H, 2(2′,10,10′)-H$_a$], 0.69 [dd, $J = 11.2$ Hz, $J' = 2.8$ Hz, 4 H, 5(5′,7,7′)-H$_a$], 0.91 (s, 12 H) and 0.93 (s, 12 H) [3(3′,9,9′)-CH$_3$, and 4(4′,8,8′)-CH$_3$], 1.62 [d, $J = 11.2$ Hz, 4 H, 2(2′,10,10′)-H$_b$], 1.71 [dd, $J = 11.2$ Hz, $J' = 1.4$ Hz, 4 H, 5(5′,7,7′)-H$_b$], 2.31 ppm [m, 2 H, 6(6′)-H]; ^{13}C NMR (100.6 MHz, CDCl$_3$): $\delta =$ 15.8 (CH$_3$), 16.1 (CH$_3$), 36.9 [CH, 6(6′)-C], 39.2 [CH$_2$, 2(2′,10,10′)-C], 39.4 [CH$_2$, 5(5′,7,7′)-C], 44.8 (C), and 45.3 (C) [3(3′,9,9′)-C and 4(4′,8,8′)-C], 47.5 ppm [C, 1(1′)-C]; IR (KBr): $\nu = 2943$, 2861, 1457, 1381, 1371, 1324, 1258, 1224, 1095, 1061, 1033, 799 cm^{-1}; GC/MS (70 eV): m/z (%): 378 ($M^{\cdot+}$, 21), 296 (49), 214 (18), 189 (65), 188 (68), 187 (20), 173 (33), 133 (21), 120 (25), 119 (100), 107 (50), 105 (29), 95 (54), 93 (16), 91 (34), 80 (19), 67 (20); Anal calcd for $C_{28}H_{42}$: C 88.82 %; H 11.18 %; calcd for $C_{28}H_{42}\cdot 0.1CH_2Cl_2$: C 87.18 %; H 10.99 %; found C: 87.43, H 11.11 %.

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[9] a) Crystal structure analysis of **7**: a translucent colorless prism-like specimen of **7**, approximate dimensions 0.071 mm × 0.093 mm × 0.109 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a Multilayer monochromator and a Mo microfocus ($\lambda = 0.71073$ Å). A total of 1473 frames were collected. The total exposure time was 4.09 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 34804 reflections to a maximum θ angle of 28.57° (0.74 Å resolution), of which 2683 were independent (average redundancy 12.972, completeness = 100.0 %, $R_{\text{int}} = 5.79$ %) and 2224 (82.89 %) were greater than $2\sigma(F^2)$. The final cell constants of $a = 6.978(6)$, $b = 11.110(10)$, $c = 14.848(13)$ Å, $\beta = 113.90(4)°$, volume = 1052.4(16) Å^3, are based upon the refinement of the XYZ-centroids of 87 reflections above 20 σ(I) with $7.348° < 2\theta < 54.87°$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.955. The structure was solved and refined using the Bruker SHELXTL Software Package, with $Z = 2$ for the formula unit, $C_{28}H_{40}$. The final anisotropic full-matrix least-squares refinement on F^2 with 155 variables converged at $R1 =$ 5.13 %, for the observed data and $wR2 = 14.36$ % for all data. The goodness-of-fit was 1.065. The largest peak in the final difference electron density synthesis was 0.571 e$^-$ Å^{-3} and the largest hole was –0.444 e$^-$ Å^{-3} with an RMS deviation of 0.068 e$^-$ Å^{-3}. On the basis of the final model, the calculated density was 1.188 g cm^{-3} and F(000), 416 e$^-$. 8 H atoms were located from a difference synthesis and refined with an isotropic temperature factor equal to 1.2 time the equivalent temperature factor of the atom which are linked and 12 H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 time the equivalent temperature factor of the atom which are linked; b) crystal structure analysis of **8**: a colorless Prism-like specimen of **8**, approximate dimensions 0.090 mm × 0.209 mm × 0.623 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus ($\lambda = 0.71073$ Å). A total of 1064 frames were collected. The total exposure time was 17.73 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 40995 reflections to a maximum θ angle of 28.33° (0.75 Å resolution), of which 5377 were independent (average redundancy 7.587, completeness = 98.8 %, $R_{\text{int}} = 5.79$ %, $R_{\text{sig}} = 3.37$ %) and 5037 (93.23 %) were greater than $2\sigma(F^2)$.The final cell constants of $a = 22.792(3)$, $b = 7.8099(8)$, $c = 12.4331(15)$ Å, $\beta = 100.517(4)°$, volume = 2176.0.(4) Å^3, are based upon the refinement of the XYZ-centroids of 143 reflections above 20 σ(I) with $7.142° <$ $2\theta < 52.43°$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.775. The structure was solved and refined using the Bruker SHELXTL Software Package, with $Z = 4$ for the formula unit, $C_{28}H_{42}$.The final anisotropic full-matrix least-squares refinement on F^2 with 322 variables converged at $R1 = 8.25$ %, for the observed data and $wR2 = 21.75$ % for all data. The goodness-of-fit was 1.071. The largest peak in the final difference electron density synthesis was 0.426 e$^-$ Å^{-3} and the largest hole was –0.428 e$^-$ Å^{-3} with an RMS deviation of 0.099 e$^-$ Å^{-3}. On the basis of the final model, the calculated density was 1.156 g cm^{-3} and F(000), 840 e$^-$. 22 H atoms were located from a difference synthesis and refined with an isotropic temperature factor equal to 1.2 time the equivalent temperature factor of the atom which are linked and 20 H atoms were computed and refined, using a riding model, with an

isotropic temperature factor equal to 1.2 time the equivalent temperature factor of the atom which are linked; c) the structures of **1**, **3** and **5** were also established by X-Ray diffraction analysis. See supporting information for details. CCDC 994900, 994901, 994902, 994903 and 994904 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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