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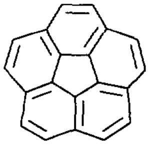
2,5,8,11,14,17-Hexa-*t*-butyldecacyclene and 1,7,13-/1,6,12 -Tri-*t*-butyldecacyclene: Possible Precursors for Bowl-shaped Polycyclic Arenes[1]

Klaus Zimmermann, Richard Goddard, Carl Krüger and Matthias W. Haenel*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Federal Republic of Germany

Abstract: Decacyclene (**2**) was converted into 2,5,8,11,14,17-hexa-*t*-butyldecacyclene (**4**) by Friedel-Crafts alkylation using *t*-butylchloride/aluminium chloride in 1,2-dichlorobenzene. Dehydrogenating cyclotrimerization of 5-*t*-butylacenaphthene by reaction with elemental sulfur resulted in 1,7,13- and 1,6,12-tri-*t*-butyldecacyclene (**6a/6b**) in the expected statistical 1:3 isomeric ratio. Single crystal X-ray structure analysis showed **4** to possess a non-planar, non-propeller C_i conformation in the crystal. According to molecular modelling (force field calculations) this non-propeller conformation is 12.7 kJ mol^{-1} higher in energy than the expected D_3 propeller conformation. The observation of the energetically unfavourable non-propeller molecular conformation in the crystal is attributed to favourable crystal packing of the bulky *t*-butyl substituents. Copyright © 1996 Elsevier Science Ltd

Inserting five-membered rings into polycyclic aromatic frameworks consisting of *peri*-condensed six-membered rings results in the formation of molecules that exhibit non-planar, bowl-shaped topologies. These compounds with their simplest representative corannulene (**1**)[2] have attracted considerable interest in recent years, because, among other things, they are considered to be possible intermediates in the synthesis of buckminsterfullerenes.[3] Decacyclene (**2**), a commercially available hydrocarbon $C_{36}H_{18}$, may serve as a potential precursor for the bowl-shaped polycyclic aromatic hydrocarbon **3**. Thus, replacing the C-H bonds in the 3, 4, 9, 10, 15 and 16 positions of **2** by intramolecular C_{aryl}-C_{aryl} bonds results in the condensed polycyclic hydrocarbon $C_{36}H_{12}$,[4] which contains three five-membered rings completely surrounded by six-membered rings in the same manner as in C_{60}.



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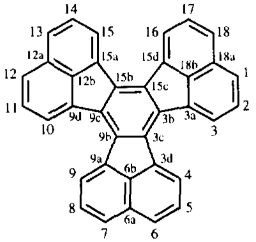

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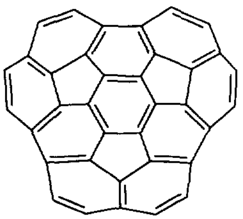
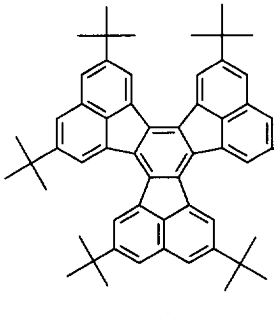


3

We first attempted the chemical transformation **2** → **3** using flash vacuum pyrolysis by applying temperatures up to 1000°C, but only unchanged educt **2** was recovered.[5] The extremely low solubility of decacyclene (**2**) makes such a conversion with chemical reagents difficult, and we hoped to overcome this problem by multiple alkylation. In the patent literature the synthesis of a mixture of mono- to hexa-*t*-butyldecacyclenes by Friedel-Crafts alkylation of **2** with *t*-butylchloride and aluminium chloride and the use of this mixture as a soluble fluorescent agent has been described.[6] Since the authors assumed that substitution occurs in 2,5,8,11,14 and 17 positions without giving any proofs, we reinvestigated the Friedel-Crafts butylation of **2**. A recent communication describing the preparation of 2,5,8,11,14,17-hexa-*t*-butyldecacyclene (**4**) and its use in the synthesis of a trifold phenalenyl system[7] prompts us to report briefly our syntheses of **4** and 1,7,13- and 1,6,12-tri-*t*-butyldecacyclene (**6a/6b**) as well as the X-ray structure analysis of **4**.



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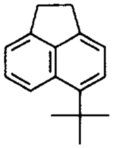

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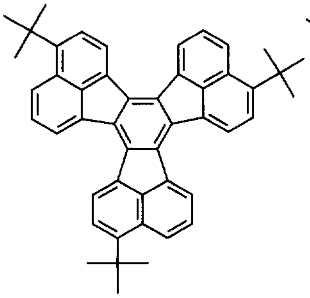
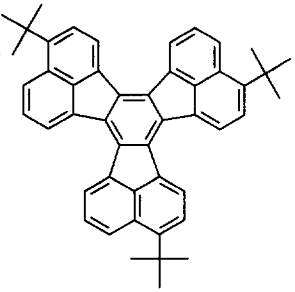


6a



6b

Following the procedure described in the patent,[6] a suspension of **2** (22.2 mmol) was stirred with a large excess of 2-chloro-2-methylpropane (*t*-butylchloride, 594 mmol) in 1,2-dichlorobenzene (1 L) at room temperature for 16 hours in the presence of aluminium trichloride (113 mmol). The solid isolated after aqueous work up contained 75 % **4** by GC. Chromatography with cyclohexane on silica gel and recrystallisation from ethyl acetate/*n*-heptane yielded yellow rhombic crystals, m.p. = 419°C (DSC).[8] The substitution pattern was unambiguously established by ^{1}H-NMR data, which showed meta coupling of $^4J = 1.4$ Hz between protons 1 and 3 (and other equivalent protons). A single crystal X-ray structure analysis reveals that **4** is considerably distorted from planarity, but surprisingly possesses a non-propeller conformation of C_i symmetry in the crystal (Figure 1).[9] The non-propeller conformation of **4** is in striking contrast to the conformation adopted by the parent hydrocarbon decacyclene (**2**) in the crystal, as found in a recently published X-ray analysis.[10] According to this, **2** is twisted into a shallow three-bladed molecular propeller of almost perfect D_3 symmetry as a result of non-bonded repulsion between the 3,4-, 9,10- and 15,16-H atoms of the peripheral naphthalene units (the angles between the mean plane of the central benzene ring and the mean planes of the naphthalene moieties vary between 7.7° and 9.3°).[10] The non-propeller C_i conformation adopted by **4** in the crystal is obtained from the propeller D_3 conformation by counter-twisting one propeller blade against the two other blades (Figure 1, left).

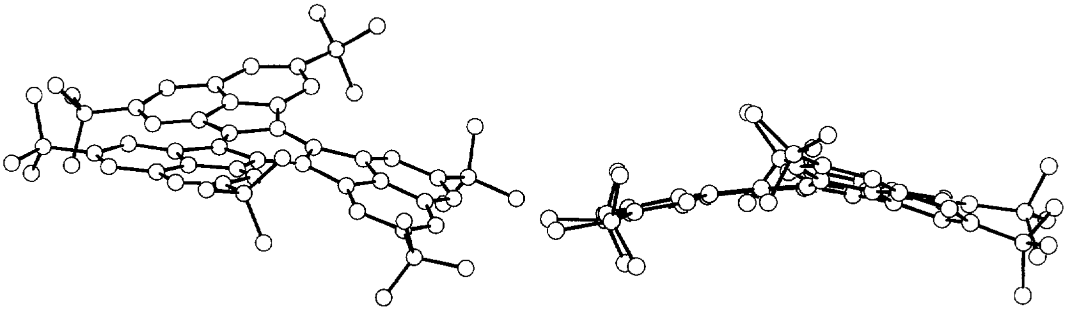


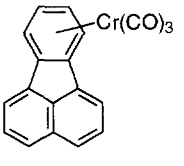
Figure 1: Molecular structure of 2,5,8,11,14,17-hexa-*t*-butyldecacyclene (**4**) in the crystal.
left: general view; right: side view

The reason for the conformational difference between **2** and **4** cannot be attributed to effects such as intramolecular steric repulsion, since the non-bonded repulsion between the 3,4-, 9,10- and 15,16-H atoms should be similar for both molecules and the bulky *t*-butyl substituents in **4** are not close enough to contribute significantly to the overall intramolecular repulsion. This view is supported by molecular modelling using force field calculations. Indeed, according to these,[11] the propeller D_3 conformation of **4** was found to be 12.7 kJ mol^{-1} lower in energy than the non-propeller C_i conformation found in the crystal (both optimised).[12] It thus appears that **4** adopts the higher energetic conformation as a result of favourable crystal packing of the bulky *t*-butyl substituents. The side view (Figure 1, right) demonstrates that the observed arrangement of the bulky *t*-butyl substituents does in fact result in a compact molecule.[13]

4 is excellently soluble in many organic solvents. However, a transformation of **4** to the corresponding *t*-butylated derivative of **3** is unlikely because the sterically demanding *t*-butyl groups clearly prevent **4** from developing the curvature necessary to form the intramolecular C_{aryl}-C_{aryl} bonds. We therefore searched for *t*-butyl derivatives of **2** carrying the substituents in the 1,6,7,12,13 or 18 positions. Since **2** can be synthesised by dehydrogenating cyclotrimerisation of acenaphthene with elemental sulfur at high temperatures,[14] this reaction was applied to 5-*t*-butylacenaphthene (**5**).[15] Heating **5** (190 mmol) with elemental sulfur (210 mmol) for 90 min at 295°C yielded a dark-brown product, containing a 1:3 mixture of 1,7,13- and 1,6,12-tri-*t*-butyl-decacyclene (**6a/6b**), which was isolated in 18 % yield by extraction with toluene and chromatography with cyclohexane/toluene (1:1) on silicagel as a bright yellow powder, m.p. 397°C (DSC).[16] The 1:3 isomer ratio **6a**:**6b** could be established from the ^{13}C-NMR spectrum ($CDCl_3$) at 150 MHz, since most signals of the aromatic C atoms are split into four closely attached lines of equal intensity.[16] One of these lines is attributed to the C_l symmetric isomer **6a**, while the other three lines belong to the asymmetric isomer **6b**. Separation of **6a** and **6b** by usual methods (crystallisation, chromatography, HPLC) has so far been unsuccessful. In contrast to **2**, the mixture **6a/6b** shows satisfactory solubility in various organic solvents.

All attempts to perform the intramolecular C_{aryl}-C_{aryl} coupling between the 3,4-, 9,10-, and 15,16-C atoms in **6a/6b** have failed so far. When oxidative coupling reagents such as CoF_3, $Tl(OCOCF_3)_3$, $Hg(OCOCF_3)_2$ or $Pb(OCOCH_3)_4$ were used, essentially only unreacted **6a/6b** could be detected by MS. The *Kovacic* method ($AlCl_3$, $CuCl_2$, CS_2),[17] which has recently been successfully applied to the synthesis of large planar condensed polycyclic aromatic hydrocarbons by similar intramolecular C_{aryl}-C_{aryl} coupling,[18] led to di- and tetra-*t*-butyl derivatives of **2** by transalkylations. An attempt at reductive coupling by treating **6a/6b** consecutively with potassium in DME and iodine in toluene[18] resulted only in products formed by the addition of 12 or 26 H atoms in Birch-Hückel type reductions (as shown by MS).

Since the direct C_{aryl}-C_{aryl} coupling could not be accomplished with **6a/6b**, the tricarbonylchromium(0) complexes **8** and **9a/9b** were considered as an alternative route to derivatives of **3**. The existence of fluoranthene tricarbonylchromium(0) (**7**)[19] suggested to us that a tricarbonylchromium(0) fragment might complex to the central six-membered ring of decacyclene, and by increasing the acidity in the adjacent C-H bonds, activate these for selective metalation by alkyllithium reagents. Preliminary experiments show that reactions of **4** and **6a/6b** with $Cr(CO)_6$ in di(*n*-butyl)ether/THF (10:1) at 120°C result in deep-red compounds. MS and IR spectra of the crude products indicate the presence of tricarbonylchromium(0) complexes of **4** and **6a/6b**, for which the tentative structures **8** and **9a/9b** have been assigned.[20] Experiments to isolate and fully characterise **8** and **9a/9b** are currently under way.



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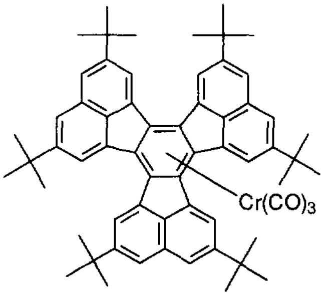

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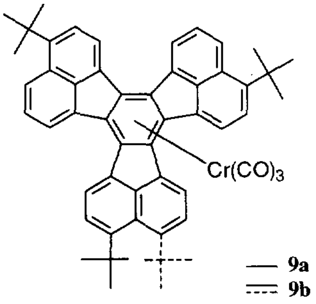

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1) The present work is part of the doctoral thesis of K. Zimmermann, University of Düsseldorf, 1996.

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4) A systematic name for the target molecule **3** is benz[1",2",3":3',4';6":9]-*as*-indaceno-[1',2',3',8':1,2,3,10;8',7',6',5'-*atuv*]acephenanthro[6,5,4,3-*opqrs*]picene.

5) Recently it was reported that traces of C_{60} were formed by pyrolysis of **2** at 1000 °C: Osterodt, J.; Zett, A.; Vögtle, F. *Tetrahedron* **1996**, *52*, 4949-4962.

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8) **4**: $C_{60}H_{66}$ (787.19), calcd. C 91.55, H 8.45, found C 91.33, H 8.47. - MS (70 eV): m/z (%) = 788 (21), 787 (66), 786 (100, M^+), 393 (12, M^{2+}), 386 (9), 378 (11), 57 (18, $C_4H_9^+$). - ^{1}H-NMR ($CDCl_3$, 300 K, 200 MHz, TMS): $\delta = 8.97$ (d, $^4J_{1\text{-H3-H}} = 1.4$ Hz, 1 H, 3-H), 7.92 (d, $^4J_{1\text{-H3-H}} = 1.4$ Hz, 1 H, 1-H), 1.66 (s, 9 H, C(C*H₃*)). - ^{13}C-NMR ($CDCl_3$, 300 K, 50 MHz, TMS): $\delta = 151.0$ (C-2), 137.1 (C-3a), 136.4 (C-3b), 131.4 (C-6b), 129.6 (C-6a), 122.2 (C-1, $^1J_{C\text{-}H} = 157$ Hz), 121.8 (C-3,$^1J_{C\text{-}H} = 154$ Hz), 35.8 (*C*(CH_3)), 32.0 (C(*C*H_3), $^1J_{C\text{-}H} = 126$ Hz); assignments by DEPT and gated decoupling).

9) X-ray analysis of **4**: $C_{60}H_{66}$, $M_r = 787.2$ g · mol^{-1}, yellow crystals, crystal size 0.12 x 0.32 x 0.36 mm, orthorhombic, a = 39.163(1), b = 11.804(1), c = 21.137(1) Å, V = 9771.3(6) Å^3, T = 293 K, Z = 8, $d_{cal} = 1.07$ g · cm^{-3}, $\mu = 0.06$ mm^{-1}, space group Pbcn [No. 60], Siemens SMART diffractometer, $\lambda = 0.71073$ Å, CCD ω-scan, 34583 measured reflections, $[(\sin\theta)/\lambda]_{max} = 0.57$ Å^{-1}, 7513 independent reflections (R_{av} =0.095), 5693 observed reflections [$I>2\sigma(I)$], structure solved by direct methods (SHELXS-86, Sheldrick, G.M. *Acta Cryst.* **1990**, A46, 467-473), final refinement by least-squares (on F_o^2, SHELXL-93, Sheldrick, G.M., University of Göttingen, 1993), H riding, $R = 0.075$ (obs. data), $wR = 0.1963$ for 542 refined parameters [$w = 1/(\sigma^2(F_o^2) + (0.0643P)^2 + 7.6743P)$, where $P = (F_o^2+2F_c^2)/3$], S = 1.18, final shift/error 0.001, residual electron density 0.48 eÅ^{-3}. Atomic coordinates and e.s.d.'s have been deposited at the Cambridge Crystallographic Data Centre.

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11) Program SYBYL 6.2 (Tripos Associates, Inc., St. Louis, MO, USA); force field: Tripos version 5.2; minimisation algorithm: BFGS; convergence criterion: RMS gradient < 0.001 kcal mol^{-1}; non-bonded cutoff: 8 Å.

12) The ^{1}H-NMR-spectrum (CD_2Cl_2, 400 MHz) did not show a splitting for the singlet at $\delta = 1.66$ of the *t*-butyl groups and for other signals at - 90 °C.

13) Packing coefficient of **4**: 0.644 (**2**: 0.825). Van der Waals radii used: C, 1.80 Å; H, 1.17 Å. Close-packing was found to dominate the crystallisation of large polycyclic aromatic hydrocarbons: Goddard, R.; Haenel, M.W.; Herndon, W.C.; Krüger, C.; Zander, M. *J. Am. Chem. Soc.* **1995**, *117*, 30-41.

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16) **6a/6b**: $C_{42}H_{48}$ (618.82), calcd. C 93.16, H 6.84, found C 92.83, H 7.10. - MS (70 eV): m/z (%) = 620 (15), 619 (53), 618 (100, M^+), 604 (22, M^+ - CH_3), 603 (41), 531 (11), 491 (16), 490 (11). - ^{1}H-NMR ($CDCl_3$, 300 K, 600 MHz, TMS): δ = 8.68 - 8.66 (m, 1 H), 8.58 - 8.56 (m, 1 H), 8.47 - 8.45 (m, 1 H), 7.73 -7.69 (m, 2 H), 1.76 (s, 9 H). - ^{13}C-NMR ($CDCl_3$, 300 K, 150 MHz, TMS): δ = {147.58, 147.55, 147.51, 147.49}, {138.37, 138.36, 138.34, 138.33}, {136.01, 136.00, 135.98, 135.97}, {135.76, 135.68, 135.57, 135.48}, {135.48, 135.46, 135.45}, {135.09, 135.01, 134.91, 134.82}, {129.21, 129.20, 129.18}, {126.72, 126.69, 126.67, 126.64}, {126.27 126.25}, 124.46 (br.), {123.26, 123.24, 123.22, 123.19}, {122.45, 122.43, 122.41, 122.39}, 36.50, 32.65. Brackets indicate the closely attached lines, see text. We thank Dr. R. Mynott and Mrs. C. Wirtz for the NMR measurements and their help interpreting the spectra.

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20) **8**: $C_{63}H_{66}CrO_3$ (923.21). - MS (70 eV): m/z = 922 (M^+), 866 (M^+ - 2 CO), 838 (M^+ - 3 CO). - IR (KBr): 1961, 1907, 1880 cm^{-1} [$Cr(CO)_3$]. - **9a/9b**: $C_{51}H_{42}CrO_3$ (754,89). - MS(70 eV): m/z = 698 (M^+ - 2 CO), 670 (M^+ - 3 CO). - IR (KBr): 1983, 1958, 1882 cm^{-1} [$Cr(CO)_3$].

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