Syntheses, Structures, and Reactions of Highly Strained Dihydro- and Tetrahydroacepentalene Derivatives

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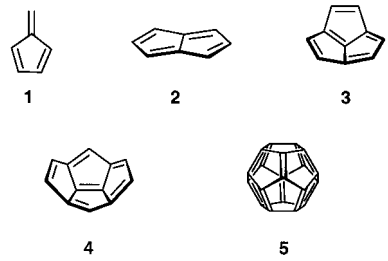
Dedicated to Professor Klaus Hafner on the occasion of his 70th birthday

Abstract: A versatile approach towards the highly strained acepentalene **3** via the readily accessible dipotassium acepentalenediide (**10a**) and the highly strained tetraenes **7** is reported. An unexpected [4+2] cycloaddition dimer **14** is formed upon protonation of the dipotassium acepentalenediide (**10a**) in 93% yield, and the monomeric 4,7-dihydroacepentalene (**7a**), as the reactive intermediate, can be trapped with anthracene to form the corresponding Diels–Alder adduct **16** in 15% yield. In contrast, the highly strained, but sterically protected monomeric bridgehead–bridgehead alkenes **7c,d** can be isolated upon reaction of **10a** or **10b** with bulky electrophiles, such as Me_3SiCl and Me_3SnCl, respectively. The X-ray crystal structure analysis of **7d** exhibits a highly pyramidalized central double bond. The bisstannane **7d** is an ideal precursor for acepentalene (**3**), which would be formed by removal of the two trimethylstannyl substituents. It can also be transmetallated to give the pure crystalline dilithium acepentalenediide (**10b**) in 78% yield. According to its ^1H, ^7Li and ^{13}C NMR spectra, the bowl-shaped 12π-dianion in **10b** is an aromatic species, and it undergoes a rapid bowl-to-bowl inversion at room temperature.

Keywords: aromaticity · acepentalene · alkenes · polyquinanes · strained molecules

Introduction

Conjugated oligoquinanes have been of experimental and theoretical interest for a long time.[1, 2] They offer a real challenge as synthetic targets due to their highly strained structures and unusual electronic bonding properties. The first and only isolable member in the series of fully unsaturated oligoquinanes is the monocyclic fulvene (**1**).[3]Compound **1** can be isolated at room temperature, but is thermally labile.[3d] However, many more stable derivatives of **1**, including metal complexes, are known.[4] Higher members of the series of fully unsaturated oligoquinanes always bear the fulvene motif with its cross-conjugated double bonds, and all of them are much less stable than **1** due to increased ring strain and electronic destabilization. The bicyclic pentalene (**2**, C_8H_6) is antiaromatic and can only be generated in a low-temperature matrix.[5] However, a number of stable derivatives of pentalene are known, such as 1,3,5-tri-*tert*-butylpentalene,[6] as well as several metal complexes.[7] The dianion of **2** is also a stable species and its dilithium derivative has been synthesized and characterized by X-ray crystallography.[8] The high stability of this dianion is explained by its favourable closed-shell electronic system, while **2** itself has a triplet ground state.[2a] Acepentalene (**3**, $C_{10}H_6$) is the third member in the series of fully unsaturated oligoquinanes and remained unobserved for a long time. Its periannelated tricyclic ring system is highly strained and calculations predict a curved molecular surface. Higher members with a curved molecular surface, such as dicyclopenta[*cd*,*gh*]pentalene (**4**) and the completely ball-shaped C_{20}-fullerene (**5**), are still unknown, although attempts to synthesise both **4**[9] and **5**[10] are in progress.



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Our interest is focused on acepentalene (**3**) with its unique tricyclic structure, its curved molecular surface, and its interesting electronic properties. According to Hückel MO theory, acepentalene should have a triplet ground state;[2] but more recent ab initio calculations have shown that the singlet ground state should be more favourable.[11, 12] However, the prohibitively large strain in the molecule makes it impossible to isolate **3** at ambient temperature. In contrast, the dianion of **3** is a closed-shell system and therefore electronically more favourable than the neutral species. In addition, it should be less strained than **3** due to its delocalized double bonds.

While **2** could be generated from monocyclic precursors,[5] similar approaches to **3** from monocyclic precursors have not yet been successful.[13] Therefore, triquinacene (**8**) has long been envisaged as the logical precursor of **3** (Figure 1).[14]

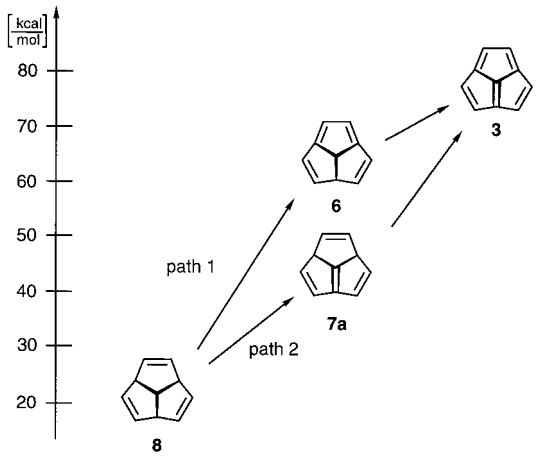
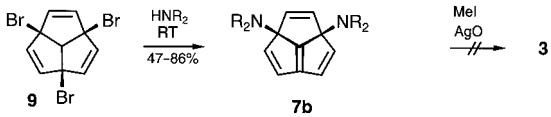


Figure 1. Strain energies of unsaturated tricyclodecanes.[16]

Abstract in German: *Ein vielseitiger Zugang zum hochgespannten Acepentalen (**3**) über das gut zugängliche Dikaliumacepentalendiid (**10a**) und den hochgespannten Tetraenen **7** wird vorgestellt. Ein unerwartetes [4+2]-Cycloadditions-Dimer **14** des Dihydroacepentalens **7a** wird durch Protonierung des Dikaliumacepentalendiids (**10a**) in 93% Ausbeute erhalten. Das monomere 4,7-Dihydroacepentalen (**7a**) als reaktives Intermediat kann auch mit Anthracen zum korrespondierenden Diels–Alder-Addukt **16** in 15% Ausbeute abgefangen werden. Dagegen sind die hochgespannten, allerdings sterisch geschützten monomeren Brückenkopf–Brückenkopf-Alkene **7c,d** durch Reaktion von **10a** oder **10b** mit Elektrophilen wie Me_3SiCl und Me_3SnCl isolierbar. Die Röntgen-Kristallstrukturanalyse von **7d** zeigt eine stark pyramidalisierte zentrale Doppelbindung. Das Bis(stannan) **7d** ist ein idealer Vorläufer für Acepentalen (**3**), welches durch Entfernen der beiden Trimethylstannylsubstituenten in einem NRMS-Experiment erzeugt und nachgewiesen werden kann. Weiterhin kann **7d** transmetalliert werden, wodurch man das reine kristalline Dilithiumacepentalendiid (**10b**) in 78% Ausbeute erhält. Gemäss den ^1H, ^7Li and ^{13}C-NMR-Spektren ist das nach Kristallstrukturanalyse schalenförmige 12 π-Dianion **10b** aromatisch und unterliegt in Lösung einer schnellen Inversion bei Raumtemperatur.*

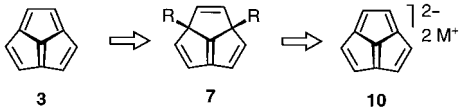
Compound **8** can be readily synthesized by a six- or seven-step procedure.[15] It incorporates the full tricyclic ring system of **3** and already has three of the five double bonds. For the stepwise introduction of the two additional double bonds into **8** (Figure 1, **8** →**3**), two different tetraene intermediates, **6** and **7a**, are conceivable. Even simple MMP2 force-field calculations[16] reveal a significant difference in the strain energies of **6** and **7a**. Among the two potential pathways from **8** to **3** only path 2 appears to have a reasonable chance for realization, as an intermediate tetraene of type **7** might be stable enough for isolation at room temperature and further elaboration.

As was reported previously, stable tetraenes of type **7**, namely 4,7-bis(dialkylamino)dihydroacepentalenes **7b,** can be obtained by threefold bromination of **8** to form the tribromide **9** followed by treatment with a secondary amine which, in a sequence of two consecutive substitution–elimination reactions and a third elimination (Scheme 1),[17] gives the tetraenes **7b**. However, the attempt to generate **3** by a single quaternisation of **7b** (NR_2 = diethylamino, piperidinyl) and subsequent elimination of both amino groups was unsuccessful.[18]



Scheme 1. Attempted synthesis of acepentalene (**3**) from **9** via **7b**. NR_2 = piperidinyl, morpholinyl, dimethylamino, diethylamino. RT = room temperature.

In this paper the syntheses of some more versatile 4,7-disubstituted dihydroacepentalenes **7** via the stable acepentalenediides **10** (Scheme 2) are reported.[19] This approach

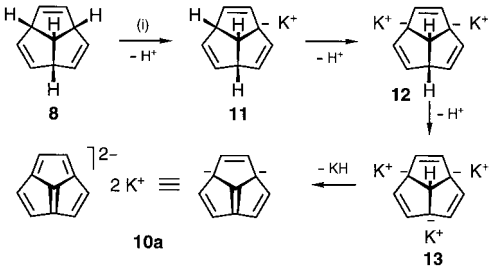


Scheme 2. Retrosynthesis of **3** from **10** via **7**.

allows the introduction of a larger variety of substituents into tetraenes **7**, including relatively weakly bonded ones which, on removal, would lead to the generation of acepentalene (**3**).

Results and Discussion

Dipotassium acepentalenediide (**10a**) was readily synthesized in a one-pot reaction: triquinacene (**8**)[20] was treated with the strongly basic mixture of *n*-butyllithium and potassium-*tert*-butoxide in *n*-hexane (Scheme 3). The original protocol required a fairly high temperature (70 °C for 24 h) and a large excess of the poorly soluble so-called Lochmann–Schlosser base, which could not be completely removed from the crude product.[21] Over the last few years various new superbasic cocktails have been developed, and the structures of the active ingredients have been determined by NMR



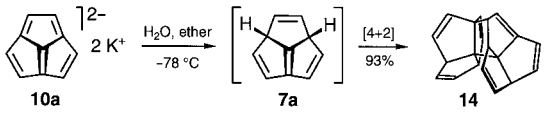
Scheme 3. One-pot synthesis of dipotassium acepentalenediide (**10a**). i) 7 equiv *n*BuLi, 7 equiv KO*t*Bu, 8 equiv TMEDA, $-30 \rightarrow 22\,^{\circ}C$, 40 h, $22 \rightarrow 60\,^{\circ}C$, 3 h, ultrasonic bath.

spectroscopy and X-ray structure analysis.[22] Particular efforts have been made to improve the solubility of these superbasic mixtures. In the light of these developments, the disadvantages of the initial dipotassium acepentalenediide synthesis[19, 20] could be overcome by addition of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)[23] to the reaction mixture. Furthermore, the use of ultrasonication decreased the reaction time considerably and led to a much cleaner product (**10a**) in a very high yield (93%), as determined by the yield of the hydrolysis product (see below). The dipotassium diide **10a** can either be isolated as a red, highly pyrophoric solid or kept as a suspension in *n*-hexane for subsequent reactions. Both the solid material and the solution can be stored for several months under argon at room temperature. The structure and spectroscopic details of the dipotassium acepentalenediide (**10a**) are discussed in detail together with those of the dilithium acepentalenediide (**10b**) (see below). The dipotassium acepentalenediide (**10a**) thus prepared is sufficiently pure for most substituton reactions with electrophiles.

The details of this interesting sequence of three deprotonations and one hydride elimination which leads from **8** to **10a** have already been well studied for the tribenzotriquinacene analogue of **8**, and an analogous mechanism is assumed for the formation of **10a**.[24, 25] Stepwise deprotonation of all three allylic positions in **8** gives intermediates **11**, **12**, and **13**. Subsequent elimination of the central hydrogen as a hydride ion generates the diide **10a** (Scheme 3). The final elimination step which may, but must not necessarily be irreversible, requires elevated temperatures ($60\,^{\circ}C$)[26] and does not occur if the 1- and 10-positions in triquinacene are substituted.[24]

Treatment of dipotassium acepentalenediide (**10a**) with moist ether (1% H_2O) gave a single product in high yield (93%). The complex ^1H and ^{13}C NMR spectra of this compound were not consistent with the structure of the expected C_s-symmetric 4,7-dihydroacepentalene (**7a**) and the relative molecular mass of the product (EI-MS) clearly indicated a dimer of **7a**. An X-ray crystal structure analysis of single crystals, obtained by recrystallisation from *n*-hexane, showed the structure to be that of the dimer **14** (Scheme 4, Figure 2).

This dimer is a [4+2] cycloadduct of two molecules of **7a**. Some interesting structural features are worth mentioning. While the triquinacene fragment in **14** shows the usual bond angles and lengths,[27] the isotriquinacene moiety is highly distorted (Figure 2). The rigid framework apparently leads to



Scheme 4. Synthesis of dimer **14**.

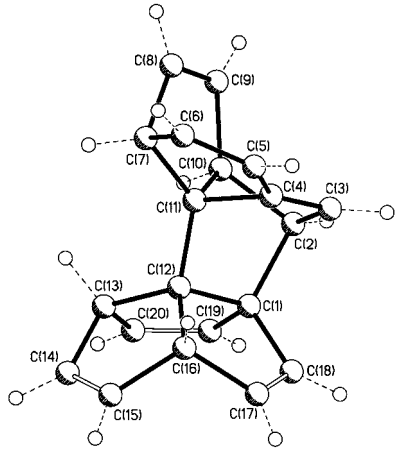


Figure 2. Structure of the 4,7-dihydroacepentalene dimer **14** in the crystal.

an unusually long $C(1)(sp^3)-C(2)(sp^3)$ single bond (159.7(3) pm) connecting the two halves. A relatively short $C(4)(sp^2)-C(5)(sp^2)$ single bond (145.2(2) pm)[28] between the two double bonds in the 1,3-diene unit of the isotriquinacene fragment is observed. This indicates significant conjugative electronic interaction in this diene system, in spite of the pyramidalized bridgehead carbon atom.

The protonation of **10a**, which produces the dimeric product **14**, can also be used to monitor the progress of the formation of diide **10a**: aliquots from a reaction mixture were quenched and subsequently analysed by gas chromatography to give the relative amounts of substrate **8** and dimer **14** formed from **10a**. By use of this monitoring method, the synthesis of the diide could be significantly improved so that gram quantities of the dimer **14** became available. In contrast to **14**, the known tribenzodihydroacepentalene dimer is a [2+2] cycloadduct across the strained bridgehead–bridgehead double bond.[25, 29] The smooth and rapid formation of the 4,7-dihydroacepentalene dimer **14** also implies that the highly strained central double bond in **7a** is not sufficiently shielded by the two hydrogens on the other bridgehead positions in the monomer **7a**. The highly reactive monomer **7a** could not be observed by NMR spectroscopy, even at $-80\,^{\circ}C$.[30] The intermediacy of the monomeric dihydroacepentalene **7a** in the formation of the dimer **14** was, however, unambiguously proved by a trapping reaction with various reactive dienes: the diide **10a** was allowed to react with cyclopentadiene and anthracene to give the respective [4+2] cycloadducts **15** and **16** (Scheme 5). The best yields were obtained with cyclopentadiene, which served simultaneously as the proton source and the diene and could therefore be used in large excess, whereas anthracene was only used in 10-fold excess (in the presence of water). Dimer **14** was obtained as a side product in all cases.

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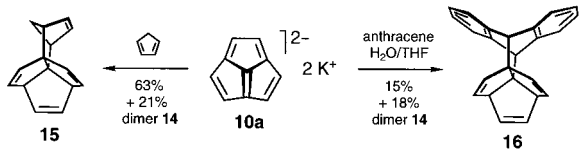


Scheme 5. Trapping reactions of **10a** with reactive dienes.

The anthracene adduct **16** is a stable crystalline solid. An X-ray crystal structure analysis confirmed its C_s-symmetrical structure (Figure 3). The structure analysis also revealed a significantly elongated C(1)–C(2) single bond (157.4(2) pm). A similar bond lengthening was observed previously for the head-to-tail [2+2] cycloadduct dimer from 4,7-dihydrotribenzoacepentalene, which was attributed to a $\pi-\sigma^*$-orbital interaction.[25]

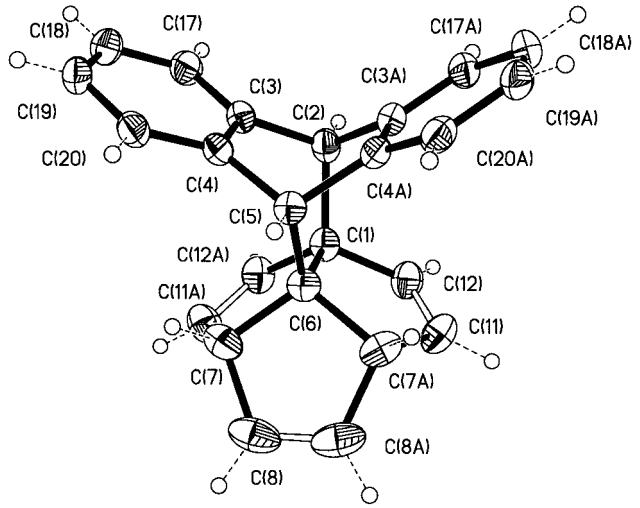
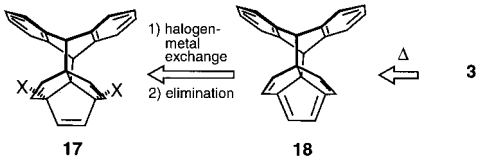


Figure 3. Structure of the 4,7-dihydroacepentalene–anthracene adduct (**16**) in the crystal. The anisotropic displacement parameters depict 50% probability levels.

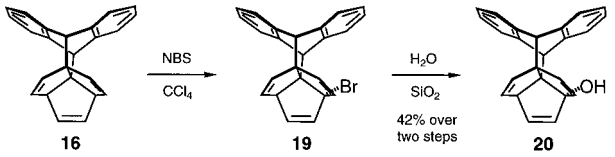
The elongation of the C(1)–C(2) single bond in **16** should also facilitate the reversal of the Diels–Alder reaction. This might allow the use of anthracene as a protecting group for the central double bond in **3**. The 9,10-dihydroanthracene moiety in an adduct of **3**, **18**, would sterically protect the remaining tetraene system, and in addition, such a potential precursor to **3** would have two sp^3 centres instead of two sp^2 centres and thus be far less strained than **3**. The reversibility of the Diels–Alder reaction for the anthracene adduct **16** was shown by differential scanning calorimetry (DSC). In addition to the melting peak at 168 °C, another endothermic peak at 291 °C was observed. In order to prove that this additional peak is due to a retro Diels–Alder reaction, a small sample of **16** was heated in an ampoule to 350 °C. The ^{1}H NMR spectrum of the crude product clearly indicated the presence of anthracene, which most likely arose from such a retro Diels–Alder reaction.

After the introduction of an additional double bond into the anthracene adduct **16** one would probably be able to generate **3** by a simple thermolysis reaction and isolate it in a matrix. Metallation and metal-halide elimination of a dihalogen derivative **17** might lead to such an anthracene-protected dihydroacepentalene **18** (Scheme 6).[31] Therefore, **16** was treated with excess *N*-bromosuccinimide (NBS), but



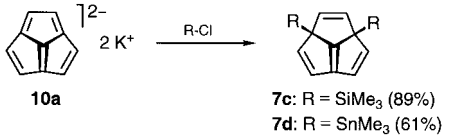
Scheme 6. Possible synthesis of anthracene-protected dihydroacepentalene **18**.

only the monobromide **19** was observed in the NMR spectrum of the crude reaction mixture. The attempted purification by column chromatography (SiO_2) gave the corresponding alcohol **20** in 42% yield (Scheme 7). The steric demand of the anthracene unit made the bridgehead position in **16** unaccessible for dibromination. Our efforts were then focussed on 4,7-disubstituted dihydroacepentalenes **7** as potential precursors for **3**.



Scheme 7. Bromination of **16** to produce **19**. Subsequent hydrolysis during an attempted chromatographic purification gave the alcohol **20**.

4,7-Disubstituted dihydroacepentalenes **7** are readily obtained by reaction of the diide **10a** with electrophiles (Scheme 8). Appropriately pure dipotassium acepentalenediide (**10a**) is essential to obtain high yields without tedious



Scheme 8. Reaction of the diide **10a** with electrophiles to give 4,7-disubstituted dihydroacepentalenes **7**.

purifications of the highly reactive bridgehead–bridgehead alkenes **7**.[20, 32] With the optimized preparation of dipotassium acepentalenediide (**10a**) (see above) the 4,7-bis(trimethylsilyl)-4,7-dihydroacepentalene (**7c**) was isolated in 89% yield after distillation. The bulky trimethylsilyl substituents provide sufficient steric congestion to protect the highly reactive central double bond and prevent the molecule from undergoing dimerization. Nevertheless, organic acids readily add to give 1,4,7-trisubstituted triquinacene derivatives. Alcohols and water can likewise be added under conditions of acid catalysis (see below).

In order to obtain 4,7-disubstituted dihydroacepentalenes **7** with substituents labile to homolysis (see Scheme 2), the diide **10a** was treated with phenylselenyl chloride and trimethylstannyl chloride. While the 4,7-bis(phenylselenyl)dihydroace-

pentalene could not be isolated, 4,7-bis(trimethylstannyl)dihydroacepentalene (**7d**) was obtained in 61% yield. The purification of **7d** was impeded by the presence of *tert*-butyl trimethylstannyl ether, which came from the LiO*t*Bu impurity in dianion **10a**. By applying the optimized procedure or, if necessary, after repeated distillation, the highly air- and moisture-sensitive bisstannane **7d** was obtained as a colourless crystalline material (m.p. 35 °C).

Analogous to the 4,7-bis(trimethylsilyl) derivative **7c**, the bisstannane **7d** is protected against dimerization by the bulky substituents. In order to determine the degree of pyramidalization of the central double bond in compounds of type **7** in comparison to other highly strained alkenes,[33] the structure of the crystalline bisstannane **7d** was determined by X-ray crystallography (Figure 4). On account of its low melting point, a suitable single crystal could only be obtained by the previously described capillary zone melting procedure.[34]

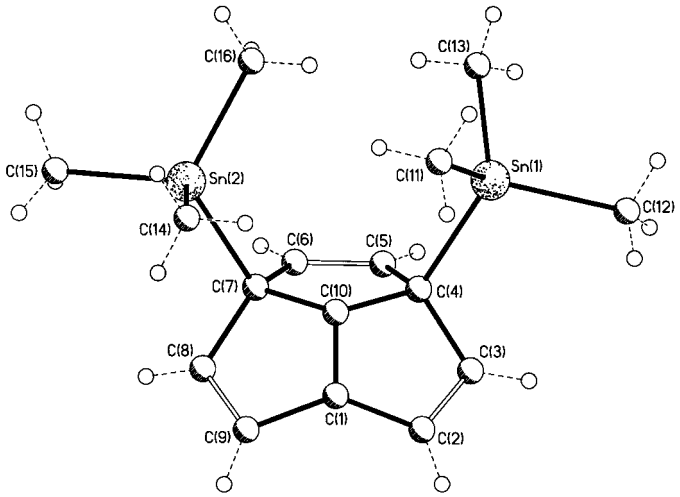


Figure 4. Structure of **7d** in the crystal.

The structural data of **7d** correlate well with those reported for the tribenzodihydroacepentalene derivatives;[25, 29] however, **7d** shows the largest out-of-plane deformation ($\psi = 36.8^\circ$) of any of the bent double bonds in this series. The pyramidalization of double bonds has best been characterized by Haddon[35] with the definition of the two angles ψ and Φ (see Figure 5). Angle ψ describes the out-of-plane bending

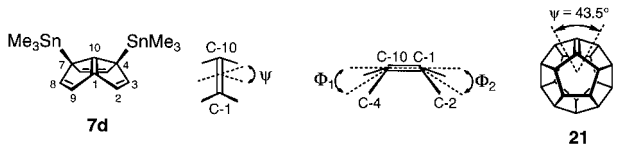
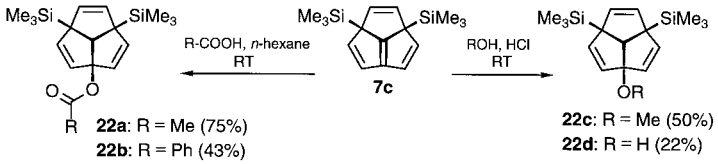


Figure 5. Definition of angles ψ and ϕ for pyramidalized double bonds.[35]

angle of the double bond, and Φ is the angle between the double bond axis and the neighbouring triangles. Since the double bond in **7d** is unsymmetrically tetrasubstituted there are two different angles $\Phi_1 = 43.5^\circ$ and $\Phi_2 = 34.6^\circ$. In **7d** Φ_1 is even larger than that reported for dodecahedrene **21** ($\Phi_1 = \Phi_2 = 42.9^\circ$),[10] whereas the sum of the angles $\Phi_1 + \Phi_2 = 78.1^\circ$ in **7d** falls short of $\Phi_1 + \Phi_2 = 85.8^\circ$ in **21**.

The structural analysis of **7d** also disclosed a slightly enlongated C(1)–C(10) double bond (134.8(6) pm),[36] as previously observed for the corresponding bond in the tribenzodihydroacepentalene derivative.[25, 29] In contrast to the latter which possess C_s symmetry, the C(1)–C(2) and C(1)–C(9) bond lengths in **7d** are different, 144.4(6) and 150.4(7) pm, respectively. Also, the C(4)–C(5) (154.3(6) pm) and C(6)–C(7) (149.1(7) pm) are unequal in length. This distortion from symmetry might be due to the differently oriented trimethylstannyl groups. The tin d orbitals could interact to a different extent with the neighbouring π orbitals causing the distortion of the skeleton.

The highly pyramidalized double bonds in **7c,d** are responsible for their sensitivity towards air. In addition, **7d** is a bisallylstannane and as such extremely sensitive towards water. It must therefore be handled exclusively under argon. To explore the reactivity of the central double bond in the bis(trimethylsilyl) derivative **7c**, it was treated with organic acids (HOAc and HOBz). Rapid addition occurred at room temperature, and the corresponding trisubstituted triquinacenes **22a,b** were obtained in yields of 75 and 43%, respectively. The regioselectivity of these additions is in accord with an initial protonation at the central carbon atom to form the more stable bisallylic cation, which is then trapped by the respective carboxylate anion (Scheme 9).



Scheme 9. Reaction of **7c** with organic acids.

Attempts to cleave the trimethylstannyl residues from **7d** homolytically, either by irradiation or heating, and subsequent matrix isolation of the thus formed **3** (see Scheme 2) were unsuccessful.[37] Nevertheless, the $SnMe_3$ residues of **7d** are cleaved upon chemical ionization (using N_2O as the reagent gas) in the mass spectrometer to generate the anion radical $C_{10}H_6^{-\cdot}$ of **3**. Selection of the acepentalene anion radical, neutralisation and reionisation to the radical cation proved the existence of the neutral **3**, at least for a microsecond, in the gas phase in this neutralisation–reionisation mass spectrometric (NRMS) experiment.[11, 38]

The 4,7-bis(trimethylstannyl)dihydroacepentalene (**7d**) also proved to be perfectly suited for the transformation into dilithium acepentalenediide (**10b**). Whereas an attempted direct transmetallation between **10a** and LiBr[39] did not work, the bisstannane **7d** (prepared from **10a**) was cleanly transmetallated with salt-free methyllithium to give pure **10b** in high yield (Scheme 10). The lithium derivative **10b** can readily be crystallized at lower temperatures from dimethoxyethane (DME). The low-temperature crystal structure analysis revealed an interesting dimer–sandwich structure (Figure 6).[40] A similar dimeric structure has been proposed for

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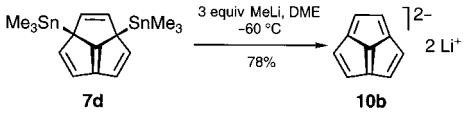


Scheme 10. Transmetallation of **7d** to give **10b**.

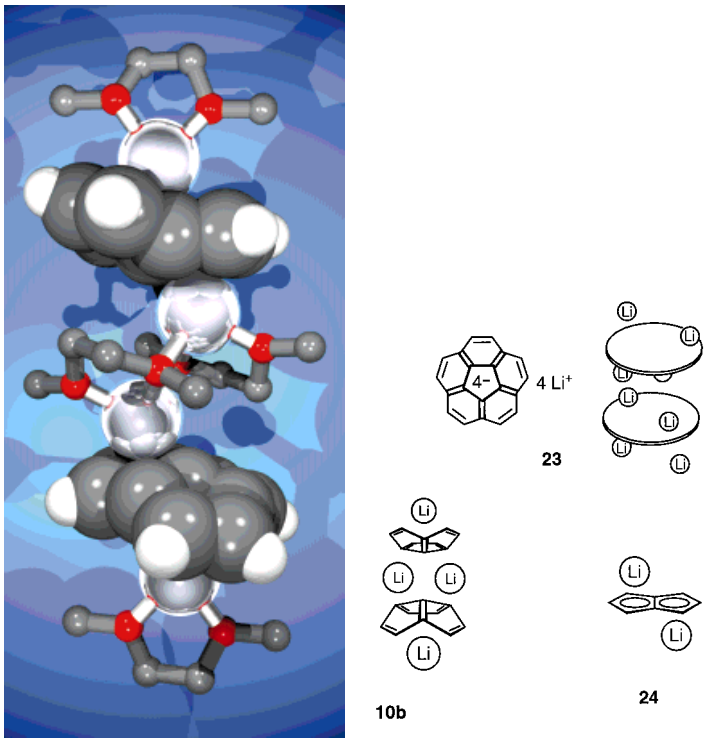


Figure 6. Sandwich structures of **10b**, **23** and **24**.

the tetralithium corannulenetetraide (**23**) in solution, although no X-ray data have been reported so far.[41] On the other hand, the dilithium pentalenediide (**24**), which can be considered to be a subunit of **10b**, does not form a dimer,[8] but remains as a monomeric ion triplet[42] with the two lithium ions on opposite sides of the planar hydrocarbon skeleton.

At least in the solid state of **10b**, two ion triplets with one lithium each on the convex and on the concave side are held together with the convex sides facing each other by two DME ligands shared by the two sandwiched lithium atoms. These lithium cations are located off the threefold axis of the carbon skeleton centered over two different five-membered rings of each monomer unit in the solid state. But the effect of the coordinated lithium counterions is minimal as the structural parameters of the uncoordinated five-membered rings are basically the same. Therefore the $C_{10}H_6$ fragment in **10b** is essentially C_3 symmetric, even in the solid state. According to the NMR spectroscopic data, the compound is C_3 symmetric in solution, as there must be a rapid exchange between the inside and the outside of the sandwich, even if it is dimeric. The ^{7}Li NMR spectrum shows a singlet, even at $-110\,^\circ$C in [D$_8$]THF solution, whereas two lines are observed in the solid-state ^{7}Li CP-MAS NMR spectrum (Table 1).[40]

NMR spectroscopy and ab initio calculations are two reliable tools for proving aromaticity in organic molecules.[43] The ^{1}H NMR chemical shifts are diagnostic for a diamagnetic

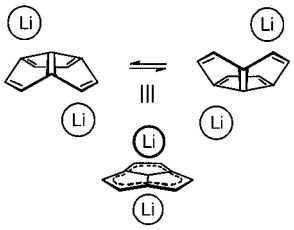
Table 1. Selected chemical shifts [δ] of acepentalenediides **10a**,**b** in [D$_8$]THF at $-60\,^\circ$C or as indicated.

Dianion	^{13}C NMR Central carbon	α-carbon	^{1}H NMR all protons	^{7}Li NMR ^{7}Li shift
10a	158.6	121.3	6.09 (s)	–
10b	151.8	116.2	6.16 (s)	-8.2[a]

[a] At 25 °C.

ring current by which protons in the plane of the molecule are deshielded and protons above or below the plane of the molecule are additionally shielded. Taking into account the shielding effect of the two negative charges in the diides **10a** and **10b**, the ^{1}H chemical shifts $\delta = 6.09$ and 6.16, respectively, suggest an aromatic system. The related dianionic aromatic hydrocarbon, dilithium pentalenediide (**24**), shows similar ^{1}H shifts of $\delta = 5.73$ (t, 2H) and 4.98 (d, 4H).[8] The aromatic behaviour of **10** becomes even more obvious if one compares the ^{7}Li chemical shifts of **10b** ($\delta = -8.2$) to that of the aromatic corannulene **23** ($\delta = -8.1$).[41b] In both molecules the lithium counterions are located in the anisotropic region of the ring current induced field (see Figure 6). Therefore a strong highfield shift is observed for the ^{7}Li signals.

The fact that **10b** has a bowl-shaped negatively charged carbon skeleton for which only one singlet can be observed in the ^{7}Li NMR spectrum at 25 °C, suggests that it must undergo a rapid bowl-to-bowl inversion (Scheme 11). Ab initio calculations at the B3LYP/6-311 + G//B3LYP/6-31G+/sp level of theory predict an inversion barrier of 5.4 kcal mol^{-1} for the acepentalene dianion in solution and with the two lithium counterions present this barrier rises to 9.8 kcal mol^{-1}.[44] An experimental value for the energy barrier of such an inversion has been reported for the neutral corannulene (10.2 ± 0.2 kcal mol^{-1}).[45] Accordingly, the acepentalene dianion must undergo a fast equilibration at room temperature so that its average geometry appears as if it had a planar aromatic π-system (Scheme 11).



Scheme 11. Bowl-to-bowl inversion and transition structure of the acepentalenediide in **10b**.

Experimental Section

General: All reactions were carried out under an atmosphere of argon with freshly distilled solvents under anhydrous conditions, unless otherwise noted. Any remaining olefins in commercial *n*-hexane were removed by standard procedures prior to drying. Triquinacene (**8**) was prepared according to the published procedure.[15b] NMR spectra were recorded at ambient or specified temperatures on Varian VXR 200, Varian VXR 500 S, Bruker AM 250 or Bruker AMX 400 instruments and calibrated with the solvent as the internal reference. The following abbreviations are used to indicate multiplicities: s singlet; d doublet; t triplet; q quartet; qi quintet; br broad; m multiplet; m$_c$ centered multiplet. The multiplicities of the ^{13}C signals were determined by the DEPT recording technique (DEPT = distortionless enhancement by polarisation transfer). The following symbols are used to indicate the DEPT signals: (+) primary or tertiary; (–) secondary and (C_{quat}) quaternary carbon atoms. Mass spectra were recorded on Varian 311 A or Finnigan MAT 95 equipment. Elemental

analyses were performed by the Mikroanalytisches Laboratorium of the Institut für Organische Chemie, Universität Göttingen (Germany). Melting points were determined with a Büchi apparatus and are uncorrected. Analytical gas chromatography (GC) was performed on a Siemens Sichromat 4 equipped with a 25 m capillary column CP-Sil-5-CB with hydrogen as the carrier gas. Silica gel (60, particle size 0.040–0.063 mm, Merck) was used for column chromatography.

Dipotassium acepentalenediide (10a): At room temperature *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (1.2 mL, 8.0 mmol) was added slowly to a stirred suspension of potassium *tert*-butoxide (784 mg, 7.0 mmol) in *n*-hexane (10 mL). The mixture was cooled to −30 °C, and a solution of *n*-butyllithium in *n*-hexane (4.38 mL, 7.0 mmol, 1.6 M) was slowly added. The resulting yellow solution was stirred for 5 min, and a solution of triquinacene (**8**)[15] (130 mg, 1.0 mmol) in *n*-hexane (1 mL) was added. The solution turned red and was allowed to warm to room temperature overnight. The resulting dark red suspension was stirred for 24 h at room temperature and then heated to 60 °C for 3 h under sonication in an ultrasound bath. When the dark red suspension settled, the supernatant solvent was removed with a syringe. Repeated washing of the reddish brown solid with *n*-hexane (3 × 20 mL) and drying at 0.01 Torr for 3 h at room temperature yielded 226 mg (approx. 95 %)[46] of **10a**, containing complexed TMEDA and some *t*BuOLi as impurities. ^{1}H NMR (400 MHz, [D$_8$]THF, −60 °C): $\delta = 6.09$ (s, 6H); signals at $\delta = 0.93$, 2.11, 2.26, 2.34 and 2.70 were assigned to the impurities; ^{13}C NMR (126.5 MHz, [D$_8$]THF, −60 °C, DEPT): $\delta = 109.5$ [+, C2(3,5,6,8,9)], 121.3 [C$_{quat}$, C1(4,7)], 158.6 (C$_{quat}$, C10); signals at $\delta = 37.4$, 46.4, 51.0, and 58.9 were assigned to the impurities.

Heptacyclo[11.5.2.0^{1,12}.0^{2,10}.0^{4,11}.0^{7,11}.0^{12,16}]eicosa-3,5,8,14,17,19-hexaene (14): A suspension of **10a** (1.13 g, 5.0 mmol) in *n*-hexane (50 mL) was slowly added to a solution of water (450 μL, 25 mmol) in diethyl ether (50 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and slowly warmed to room temperature, whereupon the colour changed from red to yellow. The mixture was diluted with ether (50 mL), extracted with saturated sodium chloride solution (3 × 20 mL), dried (MgSO$_4$) and concentrated in vacuo. Purification by column chromatography (12 g of silica gel, 0 % →5 % diethyl ether in *n*-pentane) yielded 595 mg (93 %) of dimer **14** as a colourless solid, which was recrystallized from *n*-hexane. M.p. 83 °C; ^{1}H NMR (500 MHz, CDCl$_3$, ^{1}H,^{1}H-COSY and long-range ^{1}H,^{1}H-COSY): $\delta = 3.07$ (dd, $J = 3.0$, 1.5 Hz, 1H, H2), 3.09 (qi, $J = 1.8$ Hz, 1H, H7), 3.14 (qi, $J = 2.1$ Hz, 1H, H13), 3.32 (m$_c$, 1H, H10), 3.41 (qi, $J = 2.1$ Hz, 1H, H16), 5.45 (dt, $J = 5.5$, 2.0 Hz, 1H, H9), 5.54 (dd, $J = 5.8$, 2.1 Hz, 1H, H18), 5.57 (d, $J = 3.0$ Hz, 1H, H3), 5.60 (dd, $J = 5.8$, 2.2 Hz, 1H, H17), 5.64 (dt, $J = 5.8$, 2.1 Hz, 1H, H14), 5.69 (dt, $J = 5.8$, 2.1 Hz, 1H, H15), 5.71 (dd, $J = 5.5$, 2.2 Hz, 1H, H19), 5.76 (dt, $J = 5.5$, 1.5 Hz, 1H, H8), 5.78 (dd, $J = 5.5$, 2.2 Hz, 1H, H20), 6.22 [m$_c$, 2H, H5(6)]; ^{13}C NMR [125.7 MHz, CDCl$_3$, DEPT, ^{1}H,^{13}C-correlation and COLOC (SF1 = 500 MHz, SF2 = 125.7 MHz)]: $\delta =$ 45.7 (+, C10), 52.0 (+, C2), 54.7 (+, C13), 63.5 (+, C16), 65.5 (C$_{quat}$, C1), 66.5 (+, C7), 74.5 (C$_{quat}$, C11), 86.9 (C$_{quat}$, C12), 118.1 (+, C3), 125.9 (+, C5), 128.9 (+, C8), 131.3 (+, C14), 132.3 (+, C15), 132.6 (+, C18), 133.9 (+, C20), 134.0 (+, C9), 134.6 (+, C19), 135.3 (+, C17), 140.7 (+, C6), 156.2 (C$_{quat}$, C4); MS (EI, 70 eV): *m*/*z* (%): 256 (64) [*M*$^+$], 255 (60), 241 (70), 240 (48), 239 (60), 229 (40), 228 (38), 227 (40), 226 (40), 215 (48), 202 (37), 189 (36), 153 (39), 128 (100), 127 (80), 102 (86); anal. calcd for $C_{20}H_{16}$: 256.1252 (correct MS).

Pentacyclo[5.5.2.1^{2,5}.0^{1,6}.0^{6,10}]pentadeca-3,8,11,13-tetraene (15): A suspension of **10a** (452 mg, 2.0 mmol) in *n*-hexane (40 mL) was slowly added to cyclopentadiene (20 mL) at 0 °C. The mixture was cooled to −78 °C, and methanol (1 mL) was added. The reaction mixture was allowed to warm to room temperature. The solvent was evaporated in vacuo and the remaining residue treated with toluene (20 mL). The extract was washed with saturated sodium chloride solution (3 × 20 mL), dried (MgSO$_4$) and concentrated in vacuo. Purification by column chromatography (10 g of silica gel, *n*-pentane) yielded dimer **14** (54 mg, 21 %), $R_f = 0.35$, and **15** (245 mg, 63 %) as a colourless oil, $R_f = 0.60$; IR (film): $\tilde{\nu} = 3039$, 2985, 2928, 2861, 1615, 1452, 1342, 1325, 1108, 1061, 963, 881, 838, 819, 804, 783, 751, 727, 710, 615 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 1.57$ (d, $J = 8.5$ Hz, 1H, H$_a$15), 1.78 (d, $J = 8.5$ Hz, 1H, H$_b$15), 2.72 (s, 1H, H5), 2.76 (s, 1H, H2), 2.96 (s, 1H, H7), 3.28 (s, 1H, H10), 5.50 (dd, $J = 5.7$, 2.2 Hz, 1H, H3), 5.54 [dd, $J = 5.7$, 2.2 Hz, 1H, H4), 5.67–5.75 [m, 4H, H11(12,13,14)], 6.01 [s, 2H, H8(9)]; ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 45.9$ (−, C15), 46.6 (+, C5), 49.7 (+, C2), 58.4 (+, C7), 61.8 (+, C10), 68.9 (C$_{quat}$, C6), 79.5 (C$_{quat}$, C1), 132.0, 132.7, 133.5, 134.2, 134.8, 135.5, 135.6, 135.7 [+, C3(4,8,9,11,12,13,14)]; MS (EI, 70 eV), *m*/*z* (%): 195/194 (6/31) [*M*$^+$], 179 (10), 165 (7), 128 (100) [*M*$^+$ − C$_5$H$_6$], 102 (8); anal. calcd for $C_{15}H_{14}$: 194.1095 (correct MS).

3:4,15:16-Dibenzopentacyclo[5.5.2.2^{2,5}.0^{1,6}.0^{6,10}]hexadeca-3,8,11,13,15-pentaene (16): A solution of water (2.0 g, 111 mmol) in THF (20 mL) was added with a syringe pump within 20 h to a stirred suspension of **10a** (1.12 g, 4.75 mmol) and anthracene (5.4 g, 30 mmol) in benzene (50 mL). The mixture was filtered, the layers separated and the solvent of the organic layer evaporated in vacuo. The remaining residue was treated with dichloromethane (10 mL). Undissolved components were removed by filtration, and the filtrate was concentrated in vacuo to give a crude oil. Purification by column chromatography (10 g of silica gel, 0 % →1 % diethyl ether in *n*-pentane) yielded dimer **14** (115 mg, 18 %) and **16** (222 mg, 15 %) as a colourless solid, which was recrystallized from *n*-pentane. M.p. 179 °C; $R_f = 0.19$ (1 % diethyl ether in *n*-pentane); IR (KBr): $\tilde{\nu} = 3045$, 2922, 2881, 1464, 1436, 1340, 1295, 1227, 1170, 1058, 1022, 963, 835, 820, 759, 721, 712, 684, 636, 492 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 3.12$ [bs, 2H, H7(10)], 4.02 (s, 1H, H2), 4.21 (s, 1H, H5), 5.20 [dd, $^3J = 5.6$, $^4J = 1.5$ Hz, 2H, H12(13)], 5.38 [dd, $^3J = 5.6$, $^3J = 2.3$ Hz, 2H, H11(14)], 5.53 [s, 2H, H8(9)], 6.92–7.19 (m, 8H, aryl-H); ^{13}C NMR (125.7 MHz, CDCl$_3$, DEPT): $\delta = 51.2$ (+, C2), 52.6 (+, C5), 60.9 [+, C7(10)], 66.8 (C$_{quat}$, C6), 79.9 (C$_{quat}$, C1), 124.8 (+, aryl-C), 125.1 (+, aryl-C), 125.3 (+, aryl-C), 125.6 (+, aryl-C), 132.5 [+, C8(9)], 134.2 [+, C12(13)], 135.2 [+, C11(14)], 140.7 (C$_{quat}$, aryl-C), 143.1 (C$_{quat}$, aryl-C); MS (EI, 70 eV), *m*/*z* (%): 307/306 (5/17) [*M*$^+$], 179 (15), 178 (100) [anthracene$^+$], 128 (3) [*M*$^+$ − anthracene]; anal. calcd for $C_{24}H_{18}$: 306.1408 (correct MS).

7-Bromo-3:4,15:16-dibenzopentacyclo[5.5.2.2^{2,5}.0^{1,6}.0^{6,10}]hexadeca-3,8,11,13,15-pentaene (19): To a suspension of **16** (16 mg, 52 μmol) and *N*-bromosuccinimide (NBS) (15 mg, 84 μmol) in CCl$_4$ (0.5 mL) and C$_6$D$_6$ (0.1 mL) in an NMR tube was added a small amount of dibenzoylperoxide. The lower end of the tube was heated to 80 °C, while the upper end was cooled with ice. After 1 h the characteristic NMR signals of **16** could no longer be observed. In addition to **19** the solution contained small amounts of dissolved succinimide and benzoic acid as impurities. ^{1}H NMR (250 MHz, C$_6$D$_6$): $\delta = 3.12$ (s, 1H, H10), 4.01 (s, 1H, H2), 4.46 (s, 1H, H5), 4.95 (dd, $J = 5.7$, 2.3 Hz, 1H, H12), 5.06 (dd, $J = 5.8$, 1.1 Hz, 1H, H13), 5.36 (dd, $J = 5.6$, 2.4 Hz, 1H, H11), 5.43 (d, $J = 5.7$ Hz, 1H, H14), 5.48 (d, $J = 5.6$ Hz, 1H, H9), 5.68 (dd, $J = 5.7$, 1.4 Hz, 1H, H8), 6.88–7.44 (m, 8H, aryl-H); signals at $\delta = 2.21$ (s), 7.98 (dd) were assigned to the impurities; ^{13}C NMR (62.9 MHz, C$_6$D$_6$, DEPT): $\delta = 51.9$ (+), 53.6 (+), 61.0 (+), 70.6 (C$_{quat}$), 76.3 (C$_{quat}$), 77.4 (C$_{quat}$), 124.2 (+), 125.3 (+), 125.4 (+), 125.7 (+), 125.9 (+), 125.9 (+), 128.9 (+), 130.6 (+), 131.4 (+), 133.6 (+), 133.9 (+), 134.6 (+), 136.3 (+), 137.4 (+), 140.2 (C$_{quat}$), 141.1 (C$_{quat}$), 143.3 (C$_{quat}$), 144.1 (C$_{quat}$); signals at $\delta = 28.4$, 85.9, 126.5, 130.1, 133.7 were assigned to the impurities; MS (EI, 70 eV), *m*/*z* (%): 385/383 (40/32) [*M*$^+$ − H], 322 (60), 305 (23) [*M*$^+$ − Br], 178 (100) [anthracene$^+$], 127 (13).

7-Hydroxy-3:4,15:16-dibenzopentacyclo[5.5.2.2^{2,5}.0^{1,6}.0^{6,10}]hexadeca-3,8,11,13,15-pentaene (20): The attempt to purify **19** (52 μmol) by column chromatography (1 g of silica gel, 33 % diethyl ether in *n*-pentane) yielded **20** (7 mg, 22 μmol, 42 %). IR (KBr): $\tilde{\nu} = 3548$, 1653, 1456, 1105, 1078, 1055, 1027, 791, 750, 728 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 1.72$ (s, 1H, OH), 3.28 (m$_c$, 1H, H10), 4.32 (s, 1H, H2), 4.48 (s, 1H, H5), 5.16 (dd, $J = 5.6$, 2.4 Hz, 1H, H12), 5.32 (dd, $J = 5.4$, 1.4 Hz, 1H, H13), 5.46 (d, $J = 5.6$ Hz, 1H, H11), 5.63–5.76 [m$_c$, 3H, H8(9,14)], 7.05–7.38 (m, 8H, aryl-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 49.1$ (+), 51.7 (+), 61.4 (+), 64.2 (C$_{quat}$), 68.7 (C$_{quat}$), 75.7 (C$_{quat}$), 96.5 (+), 124.8 (+), 125.2 (+), 125.3 (+), 125.5 (+), 125.8 (+), 126.3 (+), 126.4 (+), 133.2 (+), 133.3 (+), 133.4 (+), 134.3 (+), 136.2 (+), 137.0 (+), 141.9 (C$_{quat}$), 142.8 (C$_{quat}$), 143.2 (C$_{quat}$), 143.9 (C$_{quat}$); MS (EI, 70 eV), *m*/*z* (%): 322 (16) [*M*$^+$], 208 (13), 178 (100) [anthracene$^+$], 122 (25), 105 (52), 43 (25); anal. calcd for $C_{24}H_{18}O$: 322.1357 (correct MS).

4,7-Bis(trimethylsilyl)dihydroacepentalene (7c): A suspension of **10a** (226 mg, 1.0 mmol) in *n*-hexane (10 mL) was added at −78 °C to a solution of chlorotrimethylsilane (634 μL, 5 mmol) in *n*-hexane (20 mL). The mixture was stirred at −78 °C for 1 h and then slowly warmed to room temperature, whereupon the colour changed from red to yellow. The reaction mixture was filtered and the solvent evaporated in vacuo. Purification of the crude product by bulb to bulb distillation at 10^{-3} Torr yielded **7c** (242 mg, 89 %) as a colourless oil. IR (film): $\tilde{\nu} = 3020$, 2960, 2840, 1257, 1096, 1022, 800 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 0.15$ [s, 18H, Si(CH$_3$)$_3$], 5.71 [s, 2H, H5(6)], 6.46 [d, $J = 4.5$ Hz, 2H, H3(8)], 6.58

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[d, $J = 4.5$ Hz, 2H, H2(9)]; ^{13}C NMR (100.7 MHz, C_6D_6): $\delta = -0.72$ [$Si(CH_3)_3$], 65.39 [C4(7)], 130.75 [C5(6)], 135.53 [C2(9)], 137.76 [C3(8)], 167.67 (C1), 183.71 (C10); MS (EI, 70 eV), m/z (%): 272 (22) [M^+], 257 (10), 184 (14), 169 (12), 128 (13), 89 (5), 76 (24), 73 (100) [$Si(CH_3)_3^+$]; anal. calcd for $C_{16}H_{24}Si_2$: 272.1416 (correct MS).

4,7-Bis(trimethylstannyl)dihydroacepentalene (**7d**): A solution of trimethylstannyl chloride (2.0 g, 10 mmol) in diethyl ether (20 mL) was added slowly at $-78\,^\circ$C to a stirred suspension of **10a** (1.13 g, 5 mmol) in *n*-hexane (50 mL). The mixture was slowly warmed to room temperature and filtered. The residue was suspended in ether (50 mL) and cooled to $-78\,^\circ$C. The addition of a solution of trimethylstannyl chloride (2.0 g, 10 mmol) in diethyl ether (20 mL) was repeated and the mixture warmed to room temperature. After filtration under argon, the solvent was evaporated from the filtrate in vacuo. Bulb to bulb distillation of the crude brown oil at 50 °C and 10^{-4} Torr yielded **7d** (1.39 g, 61 %) as a colourless oil, which crystallized slowly when stored under argon. M.p. 35 °C; IR (argon matrix): $\tilde{\nu} = 3087, 2992, 2925, 1607, 1450, 1193, 791, 770, 759, 613, 531$ cm^{-1}; UV (*n*-hexane): λ_{max} (lg ε) = 232 nm (4.06), 323 (3.13); ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta = 0.20$ [s, 18H, $Sn(CH_3)_3$], 5.79 [bs, 2H, H5(6)], 6.36 [bs, 2H, H3(8)], 6.42 [bs, 2H, H2(9)]; ^{13}C NMR (100.7 MHz, [D$_8$]THF, DEPT): $\delta = -8.0$ [+, $Sn(CH_3)_3$], 68.8 [C_{quat}, C4(7)], 128.3 [+, C5(6)], 137.8 [+, C3(8)], 144.1 [+, C2(9)], 162.6 (C_{quat}, C1), 191 (C_{quat}, C10); MS (EI, 70 eV), m/z (%): 454 (8) [M^+], 291 (6) [$M^+ - SnMe_3$], 276 (67), 261 (43), 246 (24), 165 (100) [$SnMe_3^+$]. The isotopic pattern of the molecular ion $m/z = 454$ confirmed the molecular formula $C_{16}H_{24}Sn_2$.

1-Acetoxy-4,7-bis(trimethylsilyl)triquinacene (**22a**): A solution of acetic acid (0.05 mL, 0.88 mmol) in *n*-hexane (5 mL) was added to a solution of **7c** (99 mg, 0.36 mmol) in *n*-hexane (20 mL) and isopropyl alcohol (2 mL). The solution was stirred for 45 h at room temperature. The reaction mixture was extracted with saturated $NaHCO_3$ solution (2 × 5 mL), dried ($MgSO_4$), and the solvent evaporated in vacuo. Purification by column chromatography (11 g of silica gel, 33 % diethyl ether in *n*-pentane) yielded **22a** (91 mg, 0.27 mmol, 75 %) as a colourless solid. M.p. 77 °C; $R_f = 0.79$; IR (KBr): $\tilde{\nu} =$ 2955, 1735 (C=O), 1258 (C–Si), 1221, 1044, 972, 868, 842, 791, 752, 731, 712 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.03$ [s, 18H, $Si(CH_3)_3$], 2.00 (s, 3H, CH_3), 3.36 (s, 1H, H10), 5.45 [s, 2H, H5(6)], 5.72 [d, $^3J = 5.6$ Hz, 2H, H3(8)], 6.12 [d, $^3J = 5.6$ Hz, 2H, H2(9)]; ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = -3.2$ [+, $Si(CH_3)_3$], 21.7 (+, CH_3), 57.2 [C_{quat}, C4(7)], 60.3 (+, C10), 108.0 (C_{quat}, C1), 129.5 [+, C5(6)], 131.2 [+, C2(9)], 139.2 [+, C3(8)], 170.6 (C_{quat}, C=O); MS (EI, 70 eV): m/z (%): 332 (< 1) [M^+], 317 (1) [$M^+ - CH_3$], 200 (100) [$M^+ - OAc - Si(CH_3)_3$], 185 (42) [$M^+ - OAc - Si(CH_3)_3 - CH_3$], 169 (3), 127 (5) [$M^+ - OAc - 2Si(CH_3)_3$], 73 (30) [$(Si(CH_3)_3)^+$]; anal. calcd for $C_{18}H_{28}O_2Si_2$ (332.6): C 65.00, H 8.49; found C 64.76, H 8.55.

1-Benzoyloxy-4,7-bis(trimethylsilyl)triquinacene (**22b**): A solution of benzoic acid (264 mg, 2.16 mmol) in isopropyl alcohol (4.5 mL) was added to a solution of **7c** (120 mg, 0.44 mmol) in *n*-hexane (7.5 mL). The solution was stirred for 3 h at room temperature. The reaction mixture was extracted with a saturated $NaHCO_3$ solution (5 mL), dried ($MgSO_4$) and the solvent evaporated in vacuo. Purification by column chromatography (11 g of silica gel, 33 % dichloromethane in *n*-pentane) yielded **22b** (74 mg, 0.19 mmol, 43 %) as a colourless solid. M.p. 86 °C; $R_f = 0.42$; IR (KBr): $\tilde{\nu} = 2954$, 1713 (C=O), 1453, 1317, 1295, 1249 (C–Si), 1230, 1178, 1120, 1043, 1027, 955, 937, 842, 791, 731, 718, 706 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.08$ [s, 18H, $Si(CH_3)_3$], 3.57 (s, 1H, H10), 5.48 [s, 2H, H5(6)], 5.79 [d, $^3J = 5.6$ Hz, 2H, H3(8)], 6.28 [d, $^3J = 5.6$ Hz, 2H, H2(9)], 7.43 (m, 2H, H3′), 7.54 (m, 1H, H4′), 8.03 (m, 2H, H2′); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = -3.1$ [+, $Si(CH_3)_3$], 57.3 [C_{quat}, C4(7)], 60.4 (+, C10), 108.7 (C_{quat}, C1), 128.3 (+, C3′), 129.4 [+, C5(6)], 129.6 (+, C2′), 131.2 [+, C2(9)], 131.4 (C_{quat}, C1′), 132.5 (+, C4′), 139.5 [+, C3(8)], 166.0 (C_{quat}, C=O); MS (EI, 70 eV), m/z (%): 394 (11) [M^+], 379 (42) [$M^+ - CH_3$], 273 (83) [$M^+ - OBz$], 257 (100), 200 (100) [$M^+ - OBz - Si(CH_3)_3$], 185 (40) [$M^+ - OBz - Si(CH_3)_3 - CH_3$], 127 (7) [$M^+ - OBz - 2Si(CH_3)_3$], 105 (8), 73 (31) [$(Si(CH_3)_3)^+$]; anal. calcd for $C_{23}H_{30}O_2Si_2$ (394.7): C 70.00, H 7.66; found C 69.32, H 7.68.

1-Methoxy-4,7-bis(trimethylsilyl)triquinacene (**22c**): To a solution of **7c** (135 mg, 495 μmol) in methanol (20 mL) was added hydrochloric acid (1 mL, 0.1 M). The solution was stirred for 12 h at room temperature. The reaction mixture was extracted with a saturated $NaHCO_3$ solution (3 × 30 mL), dried ($MgSO_4$) and the solvent evaporated in vacuo. Purification by column chromatography (10 g of silica gel, 1 % diethyl ether in *n*-pentane) yielded **22c** (75 mg, 246 μmol, 50 %) as a colourless solid. M.p. 39 °C; $R_f = 0.06$; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.09$ [s, 18H, $Si(CH_3)_3$], 3.23 (s, 3H, OCH_3), 3.38 (s, 1H, H10), 5.37 [s, 2H, H5(6)], 5.61 [d, $^3J = 5.6$ Hz, 2H, H3(8)], 5.71 [d, $^3J = 5.6$ Hz, 2H, H2(9)]; ^{13}C NMR (126.5 MHz, C_6D_6, DEPT): $\delta = -2.7$ [+, $Si(CH_3)_3$], 52.0 (+, OCH_3), 57.9 (+, C10), 58.4 [C_{quat}, C4(7)], 107.1 (C_{quat}, C1), 130.9 [+, C3(8)], 131.3 [+, C5(6)], 137.5 [+, C2(9)].

1-Hydroxy-4,7-bis(trimethylsilyl)triquinacene (**22d**): To a solution of **7c** (790 mg, 2.90 mmol) in *n*-hexane (25 mL) was added hydrochloric acid (4 mL, 0.1 M) within 1 h. The solution was stirred for 10 h at room temperature. The reaction mixture was extracted with a saturated $NaHCO_3$ solution (3 × 30 mL), dried ($MgSO_4$), and the solvent evaporated in vacuo. Purification by column chromatography (10 g of silica gel, 10 % diethyl ether in *n*-pentane) yielded **22d** (190 mg, 0.65 mmol, 22 %) as a colourless solid. M.p. 58 °C; $R_f = 0.05$; ^{1}H NMR (250 MHz, C_6D_6): $\delta = 0.08$ [s, 18H, $Si(CH_3)_3$], 1.80 (s, 1H, OH), 3.14 (s, 1H, H10), 5.32 [s, 2H, H5(6)], 5.52 [d, $^3J = 5.5$ Hz, 2H, H3(8)], 5.58 [d, $^3J = 5.5$ Hz, 2H, H2(9)]; ^{13}C NMR (62.9 MHz, C_6D_6, DEPT): $\delta = -3.0$ [+, $Si(CH_3)_3$], 58.7 [C_{quat}, C4(7)], 63.1 (+, C10), 101.3 (C_{quat}, C1), 131.4 [+, C5(6)], 133.2 [+, C2(9)], 136.8 [+, C3(8)].

Dilithium acepentalenediide (**10b**): A freshly prepared solution of salt-free methyllithium (1.5 mmol, 0.50 M) in DME (3 mL) was added to a solution of 4,7-bis(trimethylstannyl)dihydroacepentalene (**7d**, 227 mg, 0.50 mmol) in DME (5 mL) at $-78\,^\circ$C. The mixture was allowed to warm to 0 °C within 3 h and filtered under argon through a P4 sinter glass. The orange solution was concentrated in vacuo to a volume of about 1 mL and stored in a freezer at $-30\,^\circ$C for three days. Removal of the supernatant solution yielded dilithium acepentalenediide (DME complex) **10b** (125 mg, 78 %) as colourless crystals. M.p. > 350 °C; ^{1}H NMR (500 MHz, [D$_8$]THF, $-60\,^\circ$C): $\delta = 6.16$ (s, 6H); signals at $\delta = 3.18$ and 3.26 were assigned to complexed DME; ^{13}C NMR (126.5 MHz, [D$_8$]THF, $-60\,^\circ$C, DEPT): $\delta =$ 108.5 [+, *C*2(3,5,6,8,9)], 116.2 [C_{quat}, C1(4,7)], 151.8 (C_{quat}, C10); signals at $\delta = 58.8$ and 72.2 were assigned to complexed DME; ^{7}Li NMR (194.4 MHz, [D$_8$]THF): $\delta = -8.2$ (bs); MS (EI, 70 eV), m/z (%) = 90 (17) [DME^+], 60 (18), 45 (100).

Details of X-ray crystal structure analyses of 14, 16 and 7d:

Crystal data for ***14***: $C_{20}H_{16}$, $M = 256.35$, space group $P2_1/c$, $a = 970.4(3)$, $b =$ 707.1(2), $c = 1948.7(7)$ pm, $\beta = 103.45(3)^\circ$, $V = 1.3001(8)$ nm^3, $Z = 4$, $\rho_{calcd} =$ 1.309 g cm^{-3}, $T = 130$ K, $\mu = 0.07$ mm^{-1}. Data were collected by the $2\theta/\omega$ method in the range $3^\circ < 2\theta < 50^\circ$. Of a total of 3916 reflections, 2319 were independent and 1942 observed ($F_0 > 4\sigma[F]$), the largest difference peak and hole were 260 and -230 e m^{-3}, respectively; $R(F) = 0.0441$, $R_w =$ 0.0512.

Crystal data for ***16***: $C_{24}H_{18}$, $M = 306.38$, orthorhombic, space group *Pnma*, $a = 1035.45(10)$, $b = 1573.4(2)$, $c = 990.9(1)$ pm, $V = 1.6144(3)$ nm^3, $Z = 4$, $\rho_{calcd} = 1.261$ g cm^{-3}, $F(000) = 648$, $T = 153(2)$ K, $\mu = 0.071$ mm^{-1}. Data were collected by the $2\theta/\omega$ method in the range $3.85^\circ < 2\theta < 25.05^\circ$. Of a total of 5898 reflections, 1482 were independent, the largest difference peak and hole were 232 and -198 e m^{-3}, respectively; $R1 = 0.0362$ [$I > 2\sigma(I)$] and $wR2 = 0.0911$ (all data).

Crystal data for ***7d***: $C_{16}H_{24}Sn_2$, $M = 453.75$, space group $P2_1/n$, $a = 785.3(2)$, $b = 2458.2(7)$, $c = 925.2(3)$ pm, $\beta = 104.56(2)^\circ$, $V = 1.7285(8)$ nm^3, $Z = 4$, $\rho_{calcd} = 1.287$ g cm^{-3}, $T = 125$ K, $\mu = 1.46$ mm^{-1}. Data were collected by the $2\theta/\omega$ method in the range $3^\circ < 2\theta < 60^\circ$. Of a total of 8680 reflections, 5040 were independent, 4699 observed ($F_0 > 4\sigma[F]$), ψ-scan absorption correction, the largest difference peak and hole were 264 and -137 e m^{-3}, respectively; $R(F) = 0.0476$, $R_w = 0.0617$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101 086. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+ 44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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