carbon catenation products. The $Cd(CF_3)_2$ was selectively dissolved in cold methylene chloride and transferred from the reactor into a chilled glass container (−45 °C) with a NMR tube attached to the bottom. The methylene chloride was vacuum-distilled from the container (−45 °C), leaving behind $Cd(CF_3)_2$ which was subsequently dissolved in CD_2Cl_2 (NMR solvent). The compound, which begins to decompose slowly at 0 °C, is obtained with a purity exceeding 99% (based on ^{19}F NMR). ^{19}F NMR (84.87 MHz, CD_2Cl_2) δ 38.5 (s, $J(Cd^{113/111}-F)$ = 543/508 Hz).

In a separate experiment, glyme was condensed onto the cold finger following the reaction and prior to warming the cold finger. Upon warming, the $Cd(CF_3)_2$ complexed with the glyme, giving $(CF_3)_2Cd$·glyme. The compound was isolated by first pumping the volatiles from the reactor followed by extraction of the nonvolatile residue with diethyl ether in an inert atmosphere. The complex was obtained in 11% yield (66 mg) based on metal vaporized and gave an IR and ^{19}F NMR identical with that obtained for an authentic sample prepared by a method described by Morrison.[9]

Discussion

Although the yields obtained were generally low, the merits of the metal vapor/plasma technique should be evident. Very unstable compounds such as $Cd(CF_3)_2$ and $Zn(CF_3)_2$ can be prepared, isolated, and studied with use of this technique. Equally important, complexes such as $Cd(SiF_3)_2$·glyme and $Zn(SiF_3)_2$·2pyridine can be uniquely prepared by using a metal vapor reactor. Although many other trifluorosilyl–metal complexes will eventually be made by using this technique, the cadmium and zinc complexes will probably provide an alternate route to these complexes by serving as trifluorosilyl transfer reagents in much the same way as $Cd(CF_3)_2$·glyme and $Hg(CF_3)_2$ have been used to prepare trifluoromethyl-substituted compounds.[9,10]

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Registry No. Cd, 7440-43-9; Zn, 7440-66-6; C_2F_6, 76-16-4; Si_2F_6, 13830-68-7; $Cd(SiF_3)_2$, 101834-99-5; $(SiF_3)_2Zn$·2pyridine, 101835-02-3; $(SiF_3)_2Cd$·glyme, 101835-01-2; $Zn(SiF_3)_2$, 101835-00-1; $Zn(CF_3)_2$, 70331-87-2; $Zn(CF_3)_2$·2pyridine, 71672-49-6; $Cd(CF_3)_2$, 33327-66-1; $(CF_3)_2Cd$·glyme, 76256-47-8.

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Reductive Alkylation of Aceheptylene—A Simple Route to a Series of Novel π-Perimeters

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Abstract: ^1H and ^{13}C NMR spectroscopic studies point out that the dianion of aceheptylene (**9**), in accordance with theoretical predictions, tends to localize the greatest portion of the excess charge at the inner angular carbon C-10b. The kinetically controlled addition of an electrophile allows one to attack this quaternary center. Thus, methylation readily affords the quench products **10**, **11**, **12a**, and **12b** in good yields. Deprotonation of **12a** and **12b** gives rise to strongly diatropic monocyclic ions, **13a** and **13b**, respectively, the first 14π-homologues of the cyclopentadienide ion. The monoanion **13a** can be submitted to a hydroxymethylation reaction followed by a solvolytic ring enlargement of the corresponding tosylate to yield the new annulene **15**. The dimethyl adducts **10** and **11**, which constitute linear 12π-systems, undergo a remarkable 12 + 2 cycloaddition with dimethyl acetylenedicarboxylate. The resulting diesters **19a** and **20a** transform into the ethanediylidene[14]annulenes **7** and **14**. Easily accessible quench products thus allow for a most straightforward synthesis of the novel perimeter systems **7**, **13**, **14**, and **15**. The spectroscopic characterization of these compounds sheds light on the subtle interdependence of steric and electronic effects in π-perimeters.

Toward an understanding of cyclic π-conjugation the annulenes have served as useful model compounds. Their structural elucidation however is severely complicated by the occurrence of configurational and conformational interconversions[1,2] as well as by steric interactions of hydrogens inside the ring.[3,4] A logical extension therefore was the construction of bridged annulenes[5-7] since they give rise to essentially planar rigid perimeters with well-defined ring configurations. A fascinating example is the family of [14]annulenes which comprises, e.g., Sondheimer's parent compound **1**,[8] Schröder[9] and Staab's[10] derivatives of **1**, Vogel's acene perimeters **2** and **3**,[11-17] Boekelheide and Mitchell's pyrene

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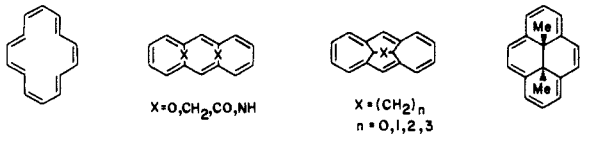
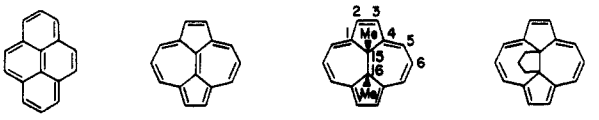
perimeter **4**[18-22] as well as Nakagawa's bisdehydroannulenes.[23] Although these compounds laid the basis for a rich annulene chemistry and also stimulated extensive theoretical and spectroscopic studies, the electronic and steric effects of the bridging units are not fully understood.[24-35]

The need for further reference compounds with different molecular architecture and the lengthy synthesis of **1**–**4** encouraged us to search for a completely new synthetic approach to annulenes. Toward that end we investigated the possibility of directly transforming pyrene (**5**) or its isomer dicyclopenta[ef,kl]heptalene



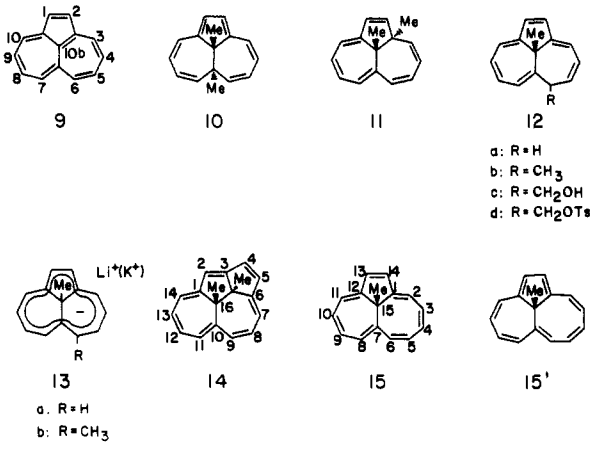
1 2 3 4

(**6**)[37] into the dialkyl dihydro derivatives **4** and **7**, respectively. Indeed, the reductive methylation of **6** afforded the bridged [14]annulene **7** in 71% yield.[36] This simple one-step annulene synthesis took advantage of a starting compound which had recently been made readily available by Hafner.[38] The transformation **6** → **7** which implied the kinetically controlled addition of an electrophile to the dianion salt $6^{2-}/2Li^{+}$ proved to be extremely versatile. Thus, the reaction did not only allow for the introduction of hydrogen and various alkyl groups but also afforded, via a slight modification of the quenching procedure, the cis-bridged analogue **8**.[39]



5 6 7 8

It was along this line that we investigated the reductive alkylation of the tricyclic 14π-system aceheptylene (**9**).[40,41] The NMR spectroscopic characterization of the corresponding dianion salt which we could prepare via reduction with alkali metals suggested that 9^{2-} might accept an electrophile in the inner angular



9 10 11 12 13 14 15 15'

position C-10b.[42] The realization of this concept which is reported here led us to the synthesis of the primary alkyl derivatives **10**, **11**, **12a**, and **12b**; making use of these easily accessible quench products we obtained an independent synthesis of **7** and the preparation of the novel [14]annulenes **14** and **15**. While **7** and **14** possess an ethane bridge and are thus related to **3** and **4**, compound **15** constitutes a yet unprecedented 14π-perimeter with one methine bridge. This compound deserves particular attention since it is homologous to the [10]annulene **16** and the [12]annulene **17** which have recently been made accessible by the elegant work of Rees[43] and Hafner,[44] respectively.

16 17

Results and Discussion

One learns from a simple π-MO model that the LUMO of **9** has the highest AO-coefficient at the inner angular center C-10b. Consequently, the corresponding radical anion and dianion should build up the highest spin or charge density at this quaternary carbon. Being aware that the individual ^{13}C resonances adequately

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reflect the local π-charge densities of a carbanion, ^{13}C NMR spectroscopy can be used to test this prediction. Indeed, upon going from **9** to the dianion $9^{2-}/2Li^+$, the signal of C-10b is shifted upfield by 61 ppm.[42] This shift is much larger than that observed for the peripheral centers. Rabinovitz and Hafner have suggested that 9^{2-} exists as a diatropic 13-center 14π-perimeter with one charge residing in the periphery and one being localized at the bridge.[45]

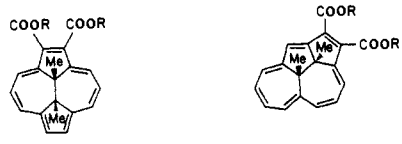
The reaction of $9^{2-}/2Li^+$ with alkylating agents provides convincing chemical support for this view. The three dimethyl adducts which we obtained from the reaction between $9^{2-}/2Li^+$ and dimethyl sulfate (tetrahydrofuran [THF], −20 °C), **10**, **11**, and **12b**, have in common that a methyl group has entered at the inner angular position. One concludes that the quenching reaction proceeds as a kinetically controlled attack of the electrophilic agent at the position of the highest π-charge. Naturally, this mechanistic view can only describe the regioselective addition of the first electrophile to the dianion, the potential regioselectivity of the second alkylation step should then be controlled by the charge distribution within the intermediate monoanion. It was important therefore that the monoalkyl monoanion **13a** could be obtained separately (see below) and characterized via NMR spectroscopy. Indeed, the δ_c-values of **13a** indicate a relatively uniform charge distribution within the 13-center periphery thus not allowing for a regioselective quenching reaction.

The three dimethyl dihydroaceheptylenes **10**, **11**, and **12b** could be separated via chromatography and were obtained in 27, 20, and 20% yield, respectively. The structure of **10** with C_s-symmetry and of **11** with C_1-symmetry followed from the observation of two singlet ^1H NMR signals for the methyl protons and from the number of ^{13}C NMR signals of quaternary and proton-bearing carbons.

The relative configuration of the methyl groups in **10** and **11** could not be inferred from spectroscopic evidence. That indeed both groups are trans to each other will be deduced from the transformation of **10** into **7** and of **11** into **14** (see below).[46]

Characteristic for the third dimethyl adduct **12b** was the doublet signal of one methyl group. The introduction of the methyl group at carbon C-6 of the periphery was proven via a detailed analysis of its ^1H NMR spectrum. Independent chemical evidence for the structure of **12b** came from its deprotonation with potassium hydride in THF which yielded the monoanion **13b**. In **13b** the protons of one methyl group are significantly shielded, and those of the ring protons, in spite of the increasing charge, are deshielded. This finding indicates a strong diatropic character which can be explained by the formation of a monoanionic 14π-perimeter system with one methyl group being attached to the inner angular carbon. The anion **13b** and its related system **13a** (see below) constitute the first 14π-homologues of the cyclopentadienide ion.[47]

When considering the potential use of the alkylation products **10**, **11**, and **12b** as synthetic intermediates, we realized that **10** and **11** incorporate linear 12π-systems with C-6/C-7 and C-2/C-3, respectively, as terminal centers. With dimethyl acetylenedicarboxylate (**18**) both species should be prone to undergoing a thermally allowed 12 + 2 cycloaddition. This type of reaction has been extensively applied by Hafner for the construction of polycyclic π-systems.[48] Indeed, when **10** and **11** were treated with **18** in tetralin, we obtained the adducts **19a** and **20a**, respectively. Obviously, a 12 + 2 cycloaddition takes place which is followed by the loss of hydrogen. The low yields (see Experimental Section) must be ascribed to the fact that the above thermolysis also induces other cycloadditions; however, the diesters **19a** and **20a** can easily be isolated via column chromatography.



a: R = CH_3
b: R = H

19

a: R = CH_3
b: R = H

20

The most significant property of **19a** and **20a** is the ^1H NMR absorption of the methyl groups inside the π-systems at extremely high field (**19a** δ_H −3.93, −4.05; **20a** δ −3.50, −4.34). There is thus no doubt that the 12 + 2 cycloaddition has produced 14π-perimeter systems with a strong diatropic character.

The transformation of the diesters into the corresponding hydrocarbons could readily be accomplished via hydrolysis and subsequent decarboxylation of the diacids.

The product thus obtained from **19b** is identical with the compound which can be prepared by reductive methylation of **6** and must be identified as the 15,16-dimethylethanediylidene-[14]annulene **7**. It is known from the crystal structure of **7** that the methyl groups are trans to each other.[36] Consequently, upon methylation of the dianion salt $9^{2-}/2Li^+$ the electrophiles must have entered from different sides of the ring. If, on the other hand, the dimethyl dihydroaceheptylene **10** can be transformed into **19a** and **7**, then it is clear that the methyl groups of **10** also possess a trans configuration. The reductive methylation of **6** and **9** thus differs from that of anthracene which produces the *cis*-9,10-dimethyl-9,10-dihydroanthracene.[49]

The relative positions of the methyl groups in **11** are less clear. However, we know from a comparison of **7** and **8** that the perimeter of the cis-bridged annulene deviates much more from planarity than that of its trans analogue. Related findings have been reported by Boekelheide.[50] Due to its bent perimeter the diatropism of **8** is much less pronounced than that of **7**. The strongly diatropic character of **14** points toward a more or less planar perimeter which finding is only compatible with a trans-configurated bridge. It is then compelling to assign a trans configuration of the methyl groups to the adduct **11**.

The positions of the inner methyl groups relative to the π-perimeters of **4**, **7**, and **14** are slightly different, which inhibits a straightforward application of the relevant ^1H NMR chemical shifts as a measure of the anisotropic ring current effects. Nevertheless, the striking similarity of the $\delta_H(CH_3)$ values [δ_H −4.25 (**4**); −4.56 (**7**); −4.60, −3.98 (**14**)] indicates the close structural analogy of the π-systems. For the case of **14** it is adequate to assign the resonance at highest field (δ_H −4.60) to the methyl group at C-16, i.e., that one being closer to the center of the perimeter. The electron absorption spectra of **7** and **14** exhibit the typical annulene appearance; the compounds show the weak ^1L_b bands at about 600 nm as well as the strong ^1B_a, ^1B_b bands at about 340 nm.[51]

It is significant for the present technique of reductive alkylations that any of the quench products can initiate further chemical transformations. The drawback of the above route is the need for chromatographic separation of the products **10**, **11**, and **12b**, which results from the nonselective alkylation of the intermediate monoanion **13a**. In our attempts of affecting the relative yields of these dimethyl adducts within a spectroscopically designed quenching reaction we considered the ion pair structure of the dianion 9^{2-} and, thus, the role of counterions and solvent. The π-charge distribution of 9^{2-} is not significantly changed when going from the lithium to the sodium salt. We next investigated the role of liquid ammonia as solvent. This is important since we have

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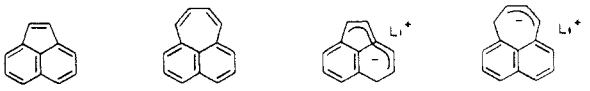
recently shown that dianions of various conjugated hydrocarbons do not resist protonation in liquid ammonia. Typical examples are acenaphthylene (**21**) and pleiadiene (**22**), both species being

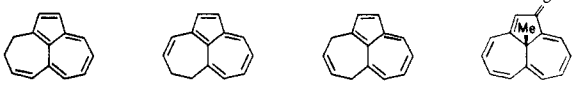


21 22 21-H⁻ 22-H⁻

structurally related to aceheptylene. With lithium in $NH_3(l)$ compounds **21** and **22** regioselectively transform into the monohydroanions **21**-H⁻ and **22**-H⁻ as sole products.[52] It is clear that depending on whether the dianion or the monoanion is quenched by the alkylation reagent, the regioselectivity of the overall process will be different. It turns out however that the aceheptylene dianion salt $9^{2-}/2Li^+$ persists in liquid ammonia so that one will not expect a dramatic change of the quenching in $NH_3(l)$.

Nevertheless, upon methylation of $9^{2-}/2Li^+$ in $NH_3(l)$/THF (2:1) we observed one single product, the monomethyl dihydroaceheptylene **12a**. Convincing evidence for the structure of **12a** came from an exact analysis of its ^1H NMR spectrum. The resulting data are given in the Experimental Section. After careful optimization of the experiment the yield of **12a** was 89%. One concludes from what has been said above that $9^{2-}/2Li^+$ is again methylated at C-10b to yield **13a** as primary product. It is known, on the other hand, that even at low temperatures dimethyl sulfate reacts with ammonia.[53] The resulting ammonium salt can serve as proton source and allows for the ready transformation of **13a** into **12a**. The original blue color of the dianion solution (**9**; Li, 2.3 equiv, $NH_3(l)$/THF, 2:1, −78 °C) changed to yellow after the addition of 1–1.5 equiv of the electrophile. A dimethyl adduct was not observed even when using an excess of dimethyl sulfate. If the amount of lithium was increased or decreased, one also isolated small amounts of hexahydro or dihydro derivatives, respectively.

The detection of one single adduct does not necessarily point toward a regioselective protonation of **13a**. One might rather assume that the hydromethyl adducts isomerize under proton migration to yield **12a**.[54] It is interesting to note that quench products with a hydrogen atom at the inner center C-10b do not persist. When reducing **9** in $NH_3(l)$/THF with lithium, thereby using alcohol as proton source, we indeed obtained a mixture of products which according to GC–MS analysis (*m/e* 180) were identified as three dihydro derivatives. Their blue color and the ^1H NMR absorptions at rather low field ($\delta > 8$) pointed toward the formation of dihydro species with an azulene moiety such as **23a**, **23b**, or **23c**. These products underwent rapid decomposition when submitted to chromatographic separation.



23a 23b 23c 24

According to the original concept the readily available alkylation product **12a** carries a methyl group in the angular position and can be used for the preparation of further perimeter systems.

Another preparative application of the quench product **12a** is its oxidation to a [13]annulenone. Surprisingly enough, when **12a** was allowed to react with the pyridine complex of chromium oxide, we obtained the ketone **24** whose structural assignment followed from the exact analysis of the ^1H NMR spectrum recorded at 300 MHz (see Experimental Section). Compound **24** constitutes an example of a [4*n* + 1]annulenone.[55]

As expected from the behavior of **12b**/**13b** the parent compound **12a** undergoes deprotonation to yield the monoanion **13a**. It was tempting to submit **13a** to a hydroxymethylation by reacting it with monomeric formaldehyde. Thereby, **13a** could be prepared in two ways: via deprotonation of **12a** or, more directly, via reaction of 9^{2-} with 1 equiv of the methylating agent, and both routes have actually been taken by us. The hydroxymethyl derivative **12c** shows spectroscopic properties quite similar to those of **12b**. The corresponding tosylate **12d**, when submitted to a solvolysis in glacial acetic acid, underwent a ring enlargement and transformed into the novel [14]annulene **15**. The low yield of 16.5% (with respect to the alcohol) can be explained by the ready occurrence of side reactions. While a large amount of polymeric material was formed, the elimination product with an exocyclic double bond could not be isolated.

The diatropic character of **15** is witnessed by the strong shielding of the methyl protons inside the π-cloud of the perimeter. Care must be exercised when deducing the magnitude of ring current effects simply from chemical shifts since geometric effects such as the projected ring area and the orientation of the C–H bond with respect to the periphery cannot be ignored. Nevertheless, the down field (high field) absorption of the methyl (ring) protons relative to those of, e.g., **7** points toward a partial quench of the ring current effect due to an increasing π-bond fixation in **15**. This can be ascribed to two factors. In a naive view, the tendency toward π-bond delocalization decreases with an increasing energy difference of the two Kekulé structures **15** and **15'**. Furthermore, the eight-membered moiety of **15** is expected to deviate appreciably from planarity and thus to induce π-bond alternation. The relatively large flexibility of the perimeter of **15** is obvious from its failure to exhibit a fine structure in its $B_{a,b}$- and L_a-absorption bands at −196 °C. This finding clearly differs from that obtained for the rigid perimeters **4**, **7**, and **14**. When comparing **15** with its lower homologue, the [10]annulene **16**,[43] the diatropism of the former appears to be somewhat smaller in spite of its larger ring.

When interpreting the UV and PE spectra of the [14]annulenes **4**, **7**, **14**, and **15**[24-31] as well as the ESR spectra[33-35] of their corresponding radical anions and cations, one has to deal with the energetic sequence of the pair of HOMO's and the pair of LUMO's of the cyclic π-systems. Homoconjugative interactions between the bridgehead π-orbitals as well as the inductive and hyperconjugative effects of the bridging groups have been invoked in this context. The π-bonding of **15**, for which homoconjugation should be unimportant, is governed by the nonplanarity of the perimeter. On the other hand, the ESR spectra of the radical anions $4^{\bullet-}$ and $7^{\bullet-}$, i.e., the relative energies of their LUMO's, can only be rationalized when assuming the hyperconjugation between the bridge and the π-perimeter as dominant effect. The π-orbitals accepting the unpaired electron in $4^{\bullet-}$ and $7^{\bullet-}$ possess high AO coefficients at the centers C-3 (C-10) and C-6 (C-13), respectively. When considering the relative importance of the "bridging" effects, an inclusion of the annulene **14** should be meaningful since for reasons of symmetry the above-mentioned hyperconjugation is not significant. Unfortunately, an assignment of the ESR hyperfine coupling constants of $14^{\bullet-}$ and a determination of the energetically favored LUMO is difficult. However, we have carefully analyzed the electron absorption spectra of the title compounds **4**, **7**, **14**, and **15**. This study, which considers the electronic effects of the bridging groups as well as of the ring configuration and ring conformation, will be published in due course.[51]

Conclusion

Characteristic for the present approach toward the synthesis of bridged annulenes is the combination of simple bond theoretical, spectroscopic, and preparative evidence. The crucial step is the investigation of the charge distribution in delocalized carbanions such as 6^{2-} and 9^{2-} (alkali metal salts) which allows for the design of regioselective quench reactions with electrophiles. Reductive alkylations thus afford a whole family of novel perimeter π-systems

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in a most simple and straightforward way.

Experimental Section

Aceheptylene (**9**) was prepared from 4-methylazulene as previously described. The product was purified prior to reduction by recrystallization (mp 82 °C).[40,41]

Reduction of Aceheptylene (9) in THF-d_8. Fifteen mg of **9** was placed at the bottom of a 5-mm NMR tube, and 0.5 mL of dry THF-d_8 was distilled in under vacuum. The solution was degassed by repeated freeze–pump cycles. Lithium wires were inserted into the evacuated tube by means of a press. The highly active metal was kept in the upper part of the tube by a constriction in the glass. The tube was sealed, and the solution was brought into contact with the metal at −20 °C. The dianion formation was complete after ca. 2 days when the color of the solution was deep blue and well-resolved NMR spectra could be recorded: ^{1}H NMR (60 MHz, −20 °C) δ 7.23 (d, 2 H, H-6, H-7), 6.65 (s, 2 H, H-1, H-2), 6.47 (t, 2 H, H-4, H-9), 6.18 (d, 2 H, H-3, H-10), 5.35 (t, 2 H, H-5, H-8); ^{13}C NMR (75 MHz, −20 °C) δ 122.1 (C-2a, C-10a), 117.5 (C-6a), 91.0 (C-10b), 124.0, 116.6, 115.2, 99.2, 91.3 (C-1–C-10).

***trans*-6a,10b-Dimethyl-6a,10b-dihydroaceheptylene (10), *trans*-2a,10b-Dimethyl-2a,10b-dihydroaceheptylene (11), and 6,10b-Dimethyl-6,10b-dihydroaceheptylene (12b) via Quenching of $9^{2-}/2Li^+$ with Dimethyl Sulfate.** A solution of 1 g (5.6 mmol) of aceheptylene (**9**) in 60 mL of dry degassed THF was contacted with lithium wires in a sealed glass ampoule at −20 °C. The ampoule contained two separate compartments. This allowed one to separate the dianion solution from the metal and to perform the quenching reaction. When the color of the solution had turned deep blue, the ampoule was opened at a sidearm under argon, and 1.5 mL (15.8 mmol) of freshly distilled dimethyl sulfate was added to the magnetically stirred dianion solution. Thereby the color of the solution turned to deep red. The solvent was evaporated, and the residue was filtered through alox (neutral, II–III) with pentane as solvent. Subsequent chromatography on silica gel using pentane as solvent gave one red, two yellow, and one green fraction. The first fraction was clean *trans*-6a,10b-dimethyl-6a,10b-dihydroaceheptylene (**10**) which after evaporation of the solvent could be obtained as a red oil in 27% yield (= 240 mg, with respect to reacted **9**). The yellow fractions were submitted to preparative GC (column SE 30, 160–170 °C, He flow rate 50 mL/min) and gave 180 mg (20%) of *trans*-2a,10b-dimethyl-2a,10b-dihydroaceheptylene (**11**) and 180 mg (20%) of 6,10b-dimethyl-6,10b-dihydroaceheptylene (**12b**) as yellow oils. The green fraction contained 230 mg of aceheptylene (**9**).

Spectroscopic Characterization of 10, 11, and 12b. **10**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.05–5.20 (m, 10 H), 2.20 (s, 3 H, CH_3), 1.88 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3 (C-2a, C-10a), 139.3, 133.3, 128.3, 123.5, 123.1 (C-1–C-10), 58.3, 47.3 (C-6a, C-10b), 25.6, 22.4 (CH_3); UV (*n*-hexane) 232 (8560), 290 (8286), 300 (7467), 475 nm (2049); MS (70 eV), *m/e* (rel intensity) 208 (M^+, 32), 193 ($M^+ - CH_3$, 100), 178 ($M^+ - 2\ CH_3$, 100).

11: ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.50–5.75 (m, 10 H), 1.20 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3); UV (*n*-hexane) 234 (16424), 272.5 (14321), 282.5 (15422), 425–450 nm (2043); MS (70 eV), *m/e* (rel intensity) 208 (M^+, 15), 193 ($M^+ - CH_3$, 94), 178 ($M^+ - 2\ CH_3$, 100).

12b: ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.20–5.55 (m, 9 H), 3.08 (quint., 1 H), 1.53 (s, 3 H, CH_3), 1.51 (d, 3 H, CH_3); UV (*n*-hexane) 247 (12418), 255 (12919), 276 (14621), 420 nm (2363); MS (70 eV), *m/e* (rel intensity) 208 (M^+, 12), 193 ($M^+ - CH_3$, 82), 178 ($M^+ - 2\ CH_3$, 100); exact mass calcd for $C_{16}H_{16}$ 208.1252, found 208.1254.

10b-Methyl-6,10b-dihydroaceheptylene (12a). A threenecked round-bottomed 2-L flask equipped with a gas inlet tube, a dry ice condenser, a KOH drying tube, and magnetic stirring was flushed with argon and dried with a flame. It was then cooled with an acetone–dry ice bath, and 1.1 L of ammonia was distilled in from a storage vessel which contained a Li/NH_3 solution. Aceheptylene (9) (5.34 g, 30 mmol) was dissolved in 550 mL of dry degassed THF, cooled to −78 °C, and rapidly poured into the reaction vessel containing the liquid ammonia. Lithium (625 mg, 90 mol) was added as freshly pressed wire, and the solution was allowed to stir for 20 min. Dry degassed dimethyl sulfate (4.6 mL, 48 mmol) was injected with a syringe in small portions. The quenching reaction caused the color of the solution to turn from blue to yellow. The reaction mixture was stirred for another 5 min, 5 mL of H_2O was added, and the cooling bath was removed. While a weak flow of argon was bubbling through the solution the ammonia was allowed to evaporate. The remaining solution was evaporated under reduced pressure and the residue chromatographed over silica gel (*n*-hexane) to yield 5.15 g (89%) of 10b-methyl-6,10b-dihydroaceheptylene (**12a**) as orange oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.22, 6.08 (2 H, H-1, H-2), 5.66 (H-3), 6.11 (H-4), 6.07 (H-5), 5.65 (H-7), 5.75 (H-8), 6.01 (H-9), 5.88 (H-10), 3.79, 2.81 (2 H, H-6, H-6′), 1.41 (s, 3 H, CH_3); $J_{1,2}$ = 5.4 Hz, $J_{3,4}$ = 5.2, $J_{4,5}$ = 10.7, $J_{5,6}$ = 4.0, $J_{5,6'}$ = 7.5, $J_{4,6}$ = 1.8, $J_{4,6'}$ = 1.0, $J_{6,6'}$ = −13.5, $J_{6,7}$ = 1.8, $J_{7,8}$ = 7.2, $J_{8,9}$ = 11.0, $J_{9,10}$ = 6.8; ^{13}C NMR (75 MHz $CDCl_3$) δ 161.0, 150.7, 144.9 (C-2a, C-6a, C-10a), 137.6, 134.6, 129.5, 127.9, 127.7, 127.1, 120.6, 118.0, 117.9 (C-1–C-5, C-7–C-10), 52.6 (C-10b), 39.9 (C-6), 20.0 (CH_3); UV (*n*-hexane) 245 (17010), 253 (18900), 270 (20081), 413 nm (3119); MS (70 eV), *m/e* (rel intensity) (M^+, 17), 179 ($M^+ - CH_3$, 100), 178 ($M^+ - CH_3 - H$, 47); exact mass calcd for $C_{15}H_{14}$ 194.1095, found 194.1087.

Potassium 10b-Methylaceheptylenide (13a). A 5-mm NMR tube which was separated into two compartments by fritted glass was flushed with dry N_2 and dried with a flame. A solution of 25 mg (0.13 mmol) of 10b-methyl-6,10b-dihydroaceheptylene (**12a**) in 0.5 mL of chloroform was inserted from the top and transferred to the bottom of the tube by cooling. The solvent was removed under vacuum, and the tube was again flushed with N_2. An excess of potassium hydride was added and deposited on the fritted glass. THF-d_8 (0.5 mL) was distilled under vacuum, and the solution at the bottom of the tube was carefully degassed. The sealed tube was then turned around, and the solution was brought into contact with the base which immediately caused the color to change from orange-yellow to deep green. The resulting potassium 10b-methylaceheptylenide was characterized by NMR spectroscopy.

Potassium 6,10b-dimethylaceheptylenide (**13b**) was prepared in the same fashion.

13a: ^{1}H NMR (60 MHz, THF-d_8) δ 8.23–7.90 (m, 4 H, H-3, H-6, H-7, H-10), 7.63 (s, 2 H, H-1, H-2), 7.25–6.70 (m, 4 H, H-4, H-5, H-8, H-9), −3.75 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, THF-d_8) δ 144.2, 120.2, 119.2, 118.9, 111.7, 110.9, 108.6 (C-1–C-10, C-2a, C-6a, C-10a), 43.4 (C-10b), 20.5 (CH_3).

13b: ^{1}H NMR (90 MHz, THF-d_8) δ 8.10–6.80 (m, 9 H, H-1–H-5, H-7–H-10), 3.15 (s, 3 H, CH_3), −3.90 (s, 3 H, CH_3).

Attempted Synthesis of 6,10b-Dihydroaceheptylene. Aceheptylene (**9**) (320 mg, 1.8 mmol) was dissolved in 50 mL of dry degassed THF and injected with a syringe into 80 mL of liquid ammonia under an argon atmosphere. Freshly pressed lithium (37.3 mg, 5.3 mol) was added, and the solution was stirred magnetically for 20 min, followed by the addition of 4 mL of methanol. The cooling bath was removed; during the evaporation of the ammonia (under strict exclusion of air) the color of the solution turned from dark red to deep blue. The residual solution was concentrated and chromatographed on alox (neutral II) using *n*-hexane. Two blue fractions were eluted. The first one, after evaporation of the solvent under reduced pressure, gave 30 mg (9.3%) of a blue-green oil which according to a GC–MS analysis contained two isomeric dihydroaceheptylene species with *m/e* 180 (M^+). From the second fraction one isolated 40 mg (12.3%) of another dihydro isomer. All three compounds were air sensitive and partially decomposed upon attempted column chromatography. the ^{1}H NMR spectra of the freshly eluted blue materials gave rise to ^{1}H NMR absorptions at δ > 8 indicating the formation of dihydroaceheptylene species with azulene units.

6-(Hydroxymethyl)-10b-methyl-6,10b-dihydroaceheptylene (12c). Aceheptylene (**9**) (1.0 g, 5.6 mmol) in 60 mL of THF was reduced into the corresponding dianion with lithium at −78 °C under an argon atmosphere. Dimethyl sulfate (0.5 mL, 5.2 mmol) was added in small portions to the vigorously stirred solution. Upon quenching the color of the solution changed from blue to green. The reaction mixture was rapidly poured into a solution of 2 g of monomeric formaldehyde (prepared by thermal depolymerization of *p*-formaldehyde at 180–200 °C) in 20 mL of dry degassed THF. The solvent was removed under reduced pressure, the residue was extracted with *n*-hexane/ethyl acetate (1:1), and the organic material was washed with water. The orange solution was dried with $CaCl_2$, filtered, and concentrated. Column chromatography over silica gel with *n*-hexane/ethyl acetate (4:1) gave an orange-yellow fraction (10 mg of **12a**), a green fraction (200 mg of **9**), and an orange fraction which was 6-(hydroxymethyl)-10b-methyl-6,10b-dihydroaceheptylene (330 mg, 33%, with respect to transformed **9**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.22–5.63 (m, 9 H), 3.97 (m, 1 H, CH_2), 3.82 (m, 1 H, CH_2), 3.21 (m, 1 H, CH), 1.78 (m, 1 H, OH), 1.55 (s, 3 H, CH_3); MS (70 eV), *m/e* (rel intensity) 224 (M^+, 17), 209 ($M^+ - CH_3$, 46), 178 ($M^+ - CH_3 - CH_2OH$, 100); IR (film) 3500–3200 (OH), 3030, 2971, 2930, 2894, 2867 (C–H), 1032 cm^{-1} (C–O); UV (CH_2Cl_2) 249 (13518), 257 (13853), 277 (15864), 422 nm (3016).

15-Methyltricyclo[6.5.2^{13,14}.0^{7,15}]pentadeca-1,3,5,7,9,11,13-heptene (15). To 230 mg (1 mmol) of the alcohol **12c** in 10 mL of dry pyridine at −20 °C was added 230 mg (1.2 mmol) of tosyl chloride under argon atmosphere. The solution was maintained at this temperature for 16 h, and another 230 mg (1.2 mmol) of tosyl chloride was added. The reaction, which was monitored by DC chromatography (silica gel, *n*-hexane/ethyl acetate 5:1, R_f (tosylate) 0.45, R_f (alcohol) 0.24), was complete after ca. 48 h. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (*n*-hexane, saturated with argon). Fraction 1 was the rearrangement product **15** (30 mg, 14% with respect to transformed alcohol), and fraction 2 was ca. 150 mg of re-

covered tosyl chloride. *n*-Hexane/CH_2Cl_2 (5:1) eluted 10b-methyl-6-O-tosyl-6,10b-dihydroaceheptylene (**12d**) (80 mg, 20%) as an orange oil. Compound **12d** [MS (70 eV), *m/e* (rel intensity) 378 (M^+, 2), 363 ($M^+ - CH_3$, 9), 192 ($M^+ - CH_3$ - O-Tos, 100)] was air sensitive and, therefore, submitted to solvolysis without further purification.

A mixture of 80 mg (0.21 mmol) of the tosylate **12d** and 66.7 mg (0.42 mmol) of $NaH_2PO_4 \cdot 2H_2O$ in 25 mL of glacial acetic acid was stirred at 85 °C for 24 h under an argon atmosphere. The reaction mixture was brought to 0 °C, neutralized with $NaOH/H_2O$ (1 N), and extracted with ether. The organic layer was separated and dried over Na_2SO_4. Chromatography on silica gel with *n*-hexane gave an orange-yellow fraction which was 5.3 mg (12%) of **15**.

The compound, an orange oil, is stable in solution at low temperatures; in pure form it slowly polymerizes: ^1H NMR (300 MHz, acetone-d_8) δ 7.26–6.53 (m, 11 H), –0.68 (s, 3 H, CH_3); UV (CH_2Cl_2) 307 (28 912), 380 nm (4899); MS (70 eV), *m/e* (ref intensity) 206 (M^+, 26), 191 ($M^+ - CH_3$, 100); exact mass calcd for $C_{16}H_{14}$ 206.1095, found 206.1110.

10b-Methylaceheptylen-2-one (24). A mixture of 2 mL (25.6 mmol) of dry pyridine and 25 mL of dry CH_2Cl_2 was saturated with argon and cooled to 0 °C. Dry, finely powdered CrO_3 (1.25 g, 12.5 mmol) was added under vigorous stirring; the mixture was stirred at this temperature for 5 min and then allowed to warm to room temperature. To the resulting $CrO_3 \cdot (pyridine)_2$ complex was added 160 mg (0.82 mmol) of 10b-methyl-6,10b-dihydroaceheptylene (**12a**) in 3 mL of dry CH_2Cl_2, and the mixture was stirred for 4 h at room temperature. The solution was decanted, and the residue was washed with CH_2Cl_2. The combined organic extracts were washed pyridine free with HCl solution (2 N), dried over $CaCl_2$, and filtered. After evaporation of the solvent under reduced pressure, the residue was chromatographed over silica gel with *n*-hexane/ether (2:1). One eluted 20 mg (11.7%) of the ketone **24** as a red-brown oil: ^1H NMR (300 MHz, CD_2Cl_2) (the data were obtained from an exact analysis of the spectra by means of the computer program Panic 85 Bruker) δ 5.86 (H-1), 6.58 (H-3), 6.12 (H-4), 6.20 (H-5), 5.64 (H-6), 5.86 (H-7), 5.50 (H-8), 5.75 (H-9), 6.13 (H-10), 2.25 (s, 3 H, CH_3); $J_{3,4}$ = 6.3, $J_{4,5}$ = 11.1, $J_{5,6}$ = 7.7, $J_{7,8}$ = 12.4, $J_{8,9}$ = 7.1, $J_{9,10}$ = 11.2 Hz; UV (CH_2Cl_2) 260 (sh) (22 781), 269 (26 990), 343 (2971), 475 nm (1373); IR (film) 3027, 2969, 2927, 2866 (C–H), 1686 cm^{-1} (C=O); MS (70 eV, *m/e* (rel intensity) 208 (M^+, 17), 193 ($M^+ - CH_3$, 83), 165 ($M^+ - CH_3 - CO$, 100); exact mass calcd for $C_{15}H_{12}O$ 208.0888, found 208.0890.

Dimethyl *trans*-15,16-Dimethyl-1,4;8,11-ethanediylidene[14]annulene-2,3-dicarboxylate (19a). A mixture of 150 mg (0.72 mmol) of 6a,10b-dimethyl-6a,10b-dihydroaceheptylene (**10**) and 90 μL (0.73 mmol) of dimethyl acetylenedicarboxylate in 3 mL of freshly distilled tetralin was stirred for 1 h under reflux. The reaction was controlled via DC chromatography (SiO_2, CH_2Cl_2) whereby the cycloaddition product **19a** could easily be detected by its fluorescence at 350 nm. Another 90 μL of dimethyl acetylenedicarboxylate was added, and stirring was continued for 30 min. The residue obtained after evaporation of the solvent was filtered over alox. With *n*-hexane one eluted 10 mg of starting material, and with ether/*n*-hexane (3:2) one eluted a yellow and a green fraction. Column chromatography over silica gel with CH_2Cl_2 gave a green solution from which one isolated, after recrystallization from pentane, 30 mg (12%) of **19a** as red-brown needles: mp 111–112 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 9.30, 8.68 (m, 4 H, H-5, H-7, H-12, H-14), 8.80 (s, 2 H, H-9, H-10), 8.17 (m, 2 H, H-6, H-13), 4.20 (s, 6 H, OCH_3), –3.93 (s, 3 H, CH_3), –4.05 (s, 3 H, CH_3); UV (CH_2Cl_2) 360 (90 672), 408 (6321), 430 (6194), 453 (4789), 518 (294), 562 (1047), 582 (511), 620 nm (1252); IR (CsJ) 3011, 2972, 2931, 2870 (C–H), 1724 cm^{-1} (C=O); MS (70 eV), *m/e* (rel intensity) 348 (M^+, 95), 333 ($M^+ - CH_3$, 21), 318 ($M^+ - 2\ CH_3$, 21); exact mass calcd for $C_{22}H_{20}O_4$ 348.1358, found 348.1362.

***trans*-15,16-Dimethyl-1,4;8,11-ethanediylidene-2,3-dicarboxylic Acid (19b).** **19a** (43.5 mg, 0.125 mmol) in 3 mL of methanolic KOH (2 N) was heated to reflux for 2 h. After having been cooled to 0 °C, 3 mL of water and 0.7 mL of HCl (concentrated) were added. The reaction mixture was extracted with ether, and the organic layer was separated, dried over $CaCl_2$, and evaporated. One obtained 39.2 mg (98%) of **19b** as a green powder which was used for subsequent decarboxylation without further purification: mp 221 °C; ^1H NMR (60 MHz, CD_3OD) δ 9.30, 8.78 (m, 4 H, H-5, H-7, H-12, H-14), 8.89 (s, 2 H, H-9, H-10), 8.20 (m, 2 H, H-6, H-13), –4.25 (s, 3 H, CH_3), –4.35 (s, 3 H, CH_3); IR (CsJ) 3200–2500 (O–H), 1687 cm^{-1} (C=O); MS (70 eV) *m/e*, (rel intensity) 320 (M^+, 10) 202 ($C_{16}H_{10}^+$, 22).

***trans*-15,16-Dimethyl-1,4;8,11-ethanediylidene[14]annulene (7).** **19b** (35 mg, 0.11 mmol) was dissolved in 4 mL of freshly distilled quinoline, 20 mg of Cu–bronze was added, and the mixture was heated to reflux for 1 h. After having been cooled to room temperature, the solution was filtered and mixed with 40 mL of ether. The quinoline was removed by shaking 3 times with 40 mL of HCl/H_2O (2 N), and the organic layer was dried over $CaCl_2$, and evaporated. The residue was filtered over silica gel with *n*-hexane to yield, after recrystallization from *n*-hexane, 19 mg (75%) of **7** as red needles: mp 186 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 8.78 (d, 4 H, H-5, H-7, H-12, H-14), 8.74 (s, 4 H, H-2, H-3, H-9, H-10), 8.05 (dd, 2 H, H-6, H-13), –4.56 (s, 6 H, CH_3). The further structure proof was performed by comparison with an authentic sample.[36]

Dimethyl *trans*-15,16-Dimethyl-1,10;3,6-ethanediylidene[14]annulene-4,5-dicarboxylate (20a) and *trans*-15,16-Dimethyl-1,10;3,6-ethanediylidene[14]annulene (14). *trans*-2a,10b-Dimethyl-2a,10b-dihydroaceheptylene (**11**) 120 mg (0.57 mmol) was submitted to the cycloaddition with dimethyl acetylenedicarboxylate in the same fashion as described above for compound **10**. Chromatography over alox (basic, II–III) with ether/*n*-hexane gave the green solution of a mixture which was chromatographed over silica gel with CH_2Cl_2. From the green fraction one obtained, after recrystallization from *n*-pentane, 30 mg (15.1%) of the light green diester **20a**: mp 110–111 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 9.01–8.61, 8.34–7.90 (m, 8 H), 4.29 (s, 3 H, OCH_3), 4.25 (s, 3 H, OCH_3), –3.50 (s, 3 H, CH_3), –4.34 (s, 3H, CH_3); MS (70 eV), *m/e* (rel intensity) 348 (M^+, 8), 333 ($M^+ - CH_3$, 35), 318 ($M^+ - 2\ CH_3$, 13).

Hydrolysis of 40 mg of the diester **20a** gave 35 mg (99%) of the raw dicarboxylic acid **20b** (mp 110 °C) which was used for the decarboxylation without further purification. The decarboxylation was accomplished as described above for the preparation of **7**. Filtration over silica gel (*n*-hexane) and recrystallization from *n*-pentane afforded 13.5 mg (53%) of the [14]annulene **14** as red needles: mp 73 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 9.15–8.41, 8.24–7.58 (m, 10 H), –3.98 (s, 3 H, CH_3), –4.60 (s, 3 H, CH_3); UV (CH_2Cl_2) 335 (74 330), 356 (43 356), 390 (7095), 418 (sh) (2928), 440 (sh) (2252), 505 (180), 544 (417), 570 (428), 599 nm (901); MS (70 eV), *m/e* (rel intensity) 232 (M^+, 11), 217 ($M^+ - CH_3$, 25), 202 ($M^+ - 2\ CH_3$, 100); exact mass calcd for $C_{18}H_{16}$ 232.1235, found 232.1252.

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