[17] A stirred 10% solution of polycarbonate in tetrahydrofuran was treated with 5–10 μmol of 4b. The solution was transferred to a petri dish and the solvent removed by evaporation at 55 °C. The remaining film of residue was irradiated with light of wavelengths $\lambda = 313$ nm and $\lambda = 436$ nm.

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Synthesis and Structure of 2,7-Di-tert-butyldicyclopenta[a,e]cyclooctene**

By *Klaus Hafner,* Georg F. Thiele,* and *Carsten Mink*

Bicyclic conjugated π-electron systems with two odd-numbered rings, such as pentalene, azulene or heptalene,[1] can be viewed as annulenes bridged by a single bond. Even when an even-numbered ring is inserted between the two odd-numbered rings, the bridging bonds in all Kekulé structures remain single bonds. The only tricyclic systems of this kind reported to date are s-indacene 1 and a few of its derivatives, in which the substituents have a remarkable influence on the bonding behavior.[2] Comparable with the 12 π-electron system of s-indacene 1 is the 14π-perimeter of the dicyclopenta[a,e]cyclooctene 2, for which π-SCF calculations indicate that the bond localization is essentially similar to that in s-indacene.[3] We report here on the synthesis and molecular structure of its 2,7-di-tert-butyl derivative 10.

1   2
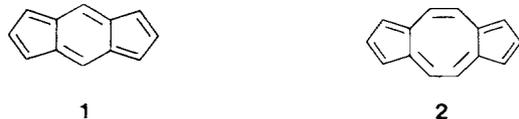
For construction of the tricyclic skeletal framework of 10 we chose the cyclizing condensation of a 1,2-dicyclopentadienylethane with a glyoxal equivalent. The selective attack of the glyoxal equivalent at the position adjacent to the ethano bridge, which is necessary for the cyclization, can be achieved by substitution of the cyclopentadienyl moiety with a sterically bulky tert-butyl group.[4] The corresponding 1,2-bis-(tert-butylcyclopentadienyl)ethane 4[5] can be readily obtained from sodium tert-butylcyclopentadienide 3 and 1,2-dibromoethane (colorless oil, yield 61% (Scheme 1). The alkylation of 3 with 1,2-dibromoethane at low temperatures initially affords the spiro-[4.2]heptadiene 5,[6] whose cyclopropane ring is opened by nucleophilic attack of a second equivalent of 3 to give 6 on heating only in the presence of a crown ether.[7,8]

The cyclization of 4 to the eight-membered ring was accomplished by condensation of its dilithium salt 7 with glyoxal sulfate 8[4,9] (Scheme 2). The bridged pentafulvadiene 9 (red-violet crystals, m.p. 174 °C) is formed as the sole low molecular weight product in 9% yield. Unexpected difficulties were encountered with the introduction

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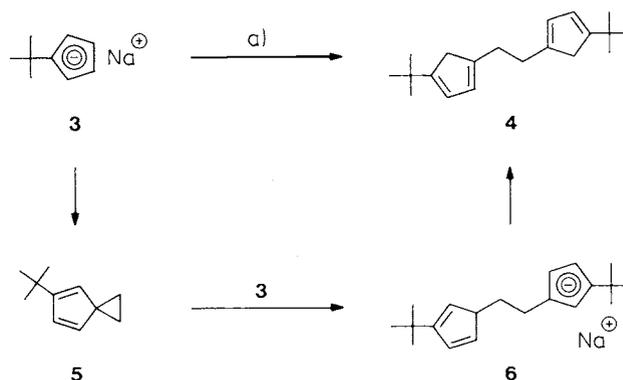
Scheme 1. a) 1,2-Dibromoethane, NaH, dibenzo[18]crown-6, bis(2-methoxyethyl) ether, -30 °C to 160 °C, 5 h; 2. H_2O.

of a further double bond into the eight-membered ring of 9, since all attempts to directly dehydrogenate 9 or to functionalize the methylene groups met with no success. It was possible, however, to carry out an acid-catalyzed tautomerization of 9, which on reaction with trifluoroacetic acid at -20 °C affords a tautomeric mixture (orange-yellow oil) in up to 40% yield. According to the ^{1}H-NMR spectrum the mixture contains predominantly the 3,4-dihydro isomer 11. The driving force behind this reaction may be the decrease of the ring strain in the eight-membered ring, which, according to inspection of models, has an almost strain-free pseudo boat conformation in 11. In contrast to 9, compound 11 and its tautomers can be deprotonated to the dianion 12 with lithium tetramethylpiperidide. Oxidation of 12 with molecular oxygen furnishes the completely conjugated hydrocarbon 10 in 53% yield as air-stable, reddish-brown crystals (m.p. 199 °C).
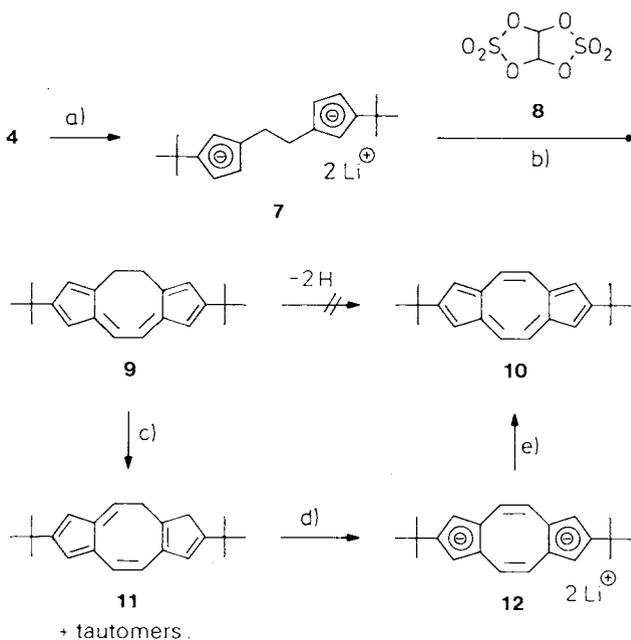
Scheme 2. a) nBuLi, TMEDA, n-hexane; b) THF, -70 °C to 20 °C; c) 1. CF_3COOH, CH_2Cl_2, -25 °C, 30 min; 2. Et_3N; d) lithium tetramethylpiperidide, THF, -70 °C to 20 °C; e) O_2, THF, -70 °C.

The ^{1}H-NMR spectrum of 10 shows a significant downfield shift of all signals compared to those of the dihydro compound 9, thus indicating a noticeable diatropism. The

presence of only three signals in the ^{1}H-NMR spectrum and of six signals in the ^{13}C-NMR spectrum (Table 1) is consistent with a molecular structure with D_{2h} symmetry

Table 1. Spectroscopic data of 4, 9, and 10. ^{1}H-NMR (CDCl$_3$, 300 MHz), ^{13}C-NMR (CDCl$_3$, 75.47 MHz), UV (n-hexane).

4: ^{1}H-NMR: $\delta=1.14$–1.28 (m, 18 H, tBu), 2.48–3.02 (m, 8 H, CH$_2$), 5.75–6.26 (m, 4 H, olefin-H); UV: λ_{max}(lgε)= 253 nm (3.83)

9: ^{1}H-NMR: $\delta=1.16$ (s, 18 H, tBu), 2.39, 2.86 (2 br. s, 4 H, CH$_2$), 5.65 (d, $J=2.2$ Hz, 2 H, 1/8-H), 6.15 (s, 2 H, 3/6-H), 6.52 (s, 2 H, 9/10-H); UV: λ_{max}(lgε)= 228 (3.88) sh, 262 (3.47) sh, 327 (4.17) sh, 344 (4.40) sh, 358 (4.52), 376 (4.40), 458 nm (2.78)

10: ^{1}H-NMR: $\delta=1.33$ (s, 18 H, tBu), 6.84 (s, 4 H, 1/3/6/8-H), 7.27 (s, 4 H, 4/5/9/10-H); ^{13}C-NMR: $\delta=30.22$ (q, C(CH$_3$)$_3$), 32.85 (s, C(CH$_3$)$_3$), 124.90 (d, C-1/3/6/8), 126.15 (d, C-4/5/9/10), 139.30 (s, C-3a/5a/8a/10a), 160.87 (s, C-2/7); UV: λ_{max}(lgε)= 217 (4.19), 324 (4.88) sh, 335 (5.02), 413 (3.51) sh, 425 (3.54) sh, 435 (3.59), 460 (3.53), 923 (1.99), 1015 (1.93) sh, 1064 (1.91) sh, 1375 nm (1.64) sh

and delocalized π-electron system. This is confirmed by the X-ray structure analysis,[10] which reveals a planar ring system with inversion center for 10 (Fig. 1). The maximum distance of the ring-C atoms from the mean plane is ±1.5 pm. The perimeter of the molecule, with CC bond lengths of about 140 pm, exhibits substantial bond equivalency, whereas the two bridges are noticeably longer (149 pm). Thus, the bridging bonds have predominantly single-bond character, as in azulene.[11]
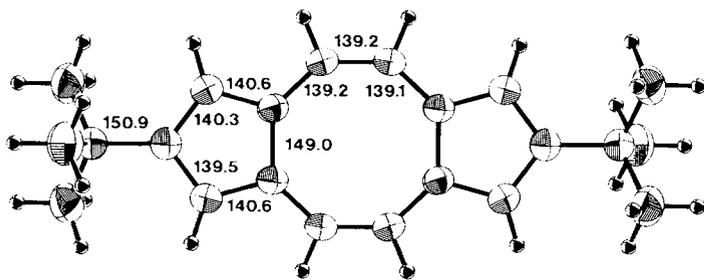
Fig. 1. Crystal structure of 10 (ORTEP, vibration ellipsoids at the 50% probability level) at room temperature with selected bond lengths [pm].

The analogy to azulene also extends to the electronic spectrum of 10, which like that of azulene consists of three structural band systems whose extinctions decrease with increasing wavelength. Their positions compared to those of the bands of azulene, however, are strongly bathochromically shifted, so that the longest wavelength absorptions already lie in the near IR.

10 not only belongs to the few hydrocarbons with a planar eight-membered ring,[1, 12] but, in addition, it is also a completely planar 14 π-electron system which has no further cyclic conjugated subunits apart from the 14 π perimeter. The molecular structure and spectroscopic properties justify the classification of 10 as a non-benzenoid aromatic hydrocarbon.

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[8] The unsubstituted 1,2-dicyclopentadienylethane can also be obtained from sodium cyclopentadienide using this method (colorless crystals, m.p. 10°C, yield 41%).
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[10] Crystal data for 10: triclinic, $P\bar{1}$, $Z=1$, $a=955.2(4)$, $b=866.4(4)$, $c=621.2(3)$ pm, $\alpha=105.39(1)°$, $\beta=95.82(1)°$, $\gamma=115.21(1)°$. Mo$_{K\alpha}$ radiation, 1991 independent reflections, 1741 observed ($I>2\sigma(I)$), 141 parameters refined, $R=0.062$, $R_w=0.053$. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD-53 098, the names of the authors, and the journal citation. We thank Prof. Dr. H. J. Lindner and Dr. H. Paulus for the X-ray structure analysis.
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Centrohexaindan, The First Hydrocarbon with Topologically Non-Planar Molecular Structure**

By Dietmar Kuck* and Andreas Schuster

Herein we report on the synthesis of centrohexaindan 1 (hexabenzohexacyclo[5.5.2.2^{4,10}.1^{1,7}.0^{4,17}.0^{10,17}]heptadecane) and some properties of this unique hydrocarbon.
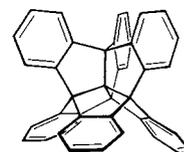
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Like dodecahedrane 2[1,2] among the spherically annelated polyquinanes, the "C$_{17}$-hexaquinane"[3] 3 is the most fascinating member of the centrally annelated so-called centropolyquinanes.[4] In contrast to 1, however, centrohexacyclic hydrocarbons like the centrohexaquinane 3 and the corresponding hexaene 4 have not yet been synthesized, even though they are of considerable interest regarding their special ring coupling.[4-7]
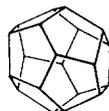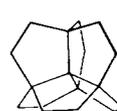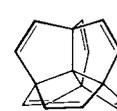
2   3   4   5

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