[10] 4: Monoclinic, space group $P2_1/c$, $Z=2$, $a=982.8(1)$, $b=1186.6(1)$, $c=1222.0(1)$ pm, $\beta=121.92(1)°$, $V=1.209 \times 10^9$ pm³, $\rho_{calc}=1.142$ g/cm³; $3° < 2\theta < 40°$ (Mo$_{K\alpha}$, $\lambda=71.07$ pm), 1052 independent reflections, Lorentz and polarization corrections, molecule at crystallographic inversion center, position of the hydrogen atoms calculated according to ideal geometry and optimized, anisotropic refinement of the carbon atoms, $R=0.070$, $R_w=0.048$ for 1048 structure factors ($|F|_0 > 0$). 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-51911, the names of the authors, and the full citation of the journal.

[11] M. C. Böhm, R. Gleiter, Theor. Chim. Acta 59 (1981) 127; calculated singlet-electron transitions of 4: λ_{max}(oscillator strength) = 525 (0.15), 380 (0.02), 320 (0.36), 299 (0.75), 273 (0.07), 269 (0.27), 264 nm (0.30).

[12] T. Nakajima, T. Saijo, H. Yamaguchi, Tetrahedron 20 (1964) 2119.

[13] Deuteration experiments show that 4 is protonated in the 2-position and the resulting cation then rapidly rearranges to 12.

9b-Methyl-9bH-benzo[cd]azulene—
A Novel Antiaromatic 12π-Electron System**

By Klaus Hafner* and Volker Kühn

Dedicated to Professor Edgar Heilbronner on the occasion of his 65th birthday

Of the hitherto reported cyclic conjugated 12π-electron systems, only 1,7-methano-[12]annulene[1] allows conclusions to be drawn about the expected antiaromaticity of the planar 12π perimeter, since [12]annulene[2] and 1,6-methano-[12]annulene[3] are conformationally mobile and the π-perimeters deviate considerably from the planar geometry. In cycl[3.3.3]azine (9b-azaphenalene) and cycl[4.3.2]azine[4] the properties of the perimeters are influenced by electronic interactions with the central nitrogen atom. Contrary to singly bridged annulenes multiple bridging of the perimeter should result in an increased planarity due to less transannular interactions and therefore allow a substantial delocalization of the peripheral π-electron system. In the case of the 10π-perimeter this expectation was confirmed by Rees et al.[5] with the synthesis of 7b-methyl-


1   2   3
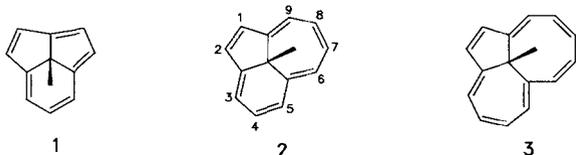
7bH-cyclopenta[cd]indene 1. An unexpected reaction of 4-alkylideneazulenide salts 4 with electrophiles recently opened up a simple access to 9b-methyl-9bH-benzo[cd]-azulene 2, the first tricyclic [12]annulene,[6] which proves to be an antiaromatic [12]annulene par excellence among the 12π-electron systems. At the same time, 2 fills the gap between the tricyclic annulenes 1 and 3.[7]

Whereas reaction of the resonance-stabilized lithium 4-methyleneazulenide 4[8] with primary alkyl halides in diethyl ether affords exclusively the 4-alkylazulenes 5, reactions with sec- and tert-alkyl halides as well as with dimethyl sulfate or methyl trifluoromethanesulfonate (TFA-Me)

[*] Prof. Dr. K. Hafner, Dipl.-Ing. V. Kühn
Institut für Organische Chemie der Technischen Hochschule
Petersenstrasse 22, D-6100 Darmstadt (FRG)

lead chiefly to 3a-alkyl-3a,4-dihydro-4-methyleneazulenes 6 and small amounts of 5, with removal of the azulenoid 10π-electron system.[9] The different regiochemical course of these reactions could be due to competing substitution mechanisms (S_N, SET).[10]

4

5   6
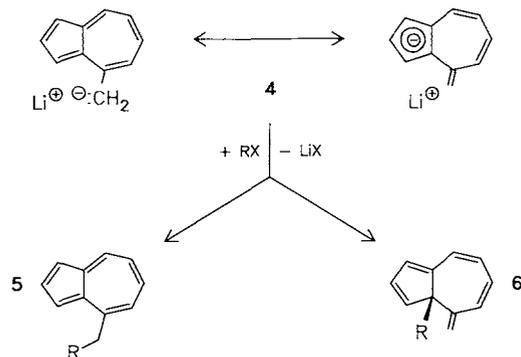
Also 4,5-dihydro-3H-benz[cd]azulene 7,[11] after deprotonation with lithium diisopropylamide (LDA), reacts, like 4, with dimethyl sulfate or TFA-Me to give the tricyclic pentaene 8 (yellow oil, yield 52%).[12] Bromination of 8

7   8
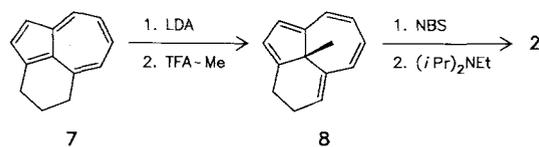
with N-bromosuccinimide (NBS) in CCl_4 at 0°C yields an unstable bromo-derivative (yellow, oil), which is dehydrobrominated to 2 with diisopropylethylamine in tetrahydrofuran at room temperature without further purification. Thereby, the blue hydrocarbon 2 is obtained in ca. 30% yield; 2 is stable in solution up to 80°C. Solid 2 rapidly transforms into yellow high molecular products, even at −30°C.

Table 1. Spectral data of 2, 8, and 9.

2A: 300-MHz ¹H-NMR ([D₆]DMSO): $\delta=3.88$ (d, $J=7.1$ Hz; 1 H, 6-H), 3.98 (d, $J=5.8$ Hz; 1 H, 3-H), 4.01 (d, $J=9.5$ Hz; 1 H, 5-H), 4.18 (d, $J=6.7$ Hz; 1 H, 9-H), 4.27–4.41 (m: $\delta=4.30$ (7-H), 4.37 (8-H), 4.39 (4-H)), 4.67, 4.69 (AB system, $J=5.8$ Hz; 2 H, 1,2-H), 4.75 (s; 3 H, Me), UV (n-hexane) (qualitative): $\lambda_{max}=262$, 286, 351, 368, 387 sh, 491 sh, 559 sh, 567 nm

8: 300-MHz ¹H-NMR (CDCl₃): $\delta=0.76$ (s; 3 H, Me), 2.42–2.56 (m; 2 H, 3-H), 2.81–2.93 (m; 2 H, 4-H), 5.86–6.05 (m; 4 H, 6-H or 9-H and 5,7,8-H), 6.18 (dd, $J=1.7$ Hz, $J=2.0$ Hz; 1 H, 2-H), 6.43 (d, $J=1.7$ Hz; 1 H, 1-H), 6.66 (d, $J=10.7$ Hz; 1 H, 6-H or 9-H); UV (n-hexane): λ_{max}(lgε) = 262 (4.25), 266 (4.25), 289 sh (3.23), 304 sh (3.04), 350 sh (3.39), 370 sh (3.53), 384 (3.59), 402 sh (3.45) nm

9: 300-MHz ¹H-NMR ([D₆]DMSO): $\delta=1.07$ (s; 3 H, Me), 5.87 (d, $J=10.4$ Hz; 1 H, 9-H), 6.15 (dd, $J=6.5$ Hz, $J=10.4$ Hz; 1 H, 8-H), 6.44 (dd, $J=6.5$ Hz, $J=11.5$ Hz; 1 H, 7-H), 6.71 (d, $J=5.5$ Hz; 1 H, 1-H), 6.79 (d, $J=5.5$ Hz; 1 H, 2-H), 7.03 (d, $J=11.5$ Hz; 1 H, 6-H), 7.20 (dd, $J=1.1$ Hz, $J=7.7$ Hz; 1 H, 3-H or 5-H), 7.28 (dd, $J=7.1$ Hz, $J=7.7$ Hz; 1 H, 4-H), 7.44 (dd, $J=1.1$ Hz, $J=7.1$ Hz; 1 H, 3-H or 5-H); UV (n-hexane): λ_{max}(lgε) = 211 (4.12), 257 (4.34), 265 (4.38), 375 (3.61) nm

Proof of the structure of 2 is provided, in particular, by its ¹H-NMR spectrum[13] (see Table 1), which, at the same time, provides interesting insights into the bonding structure of this [12]annulene, which according to model considerations has a rigid planar structure. From the spec-

trum, which is temperature-independent up to 80°C, the structure of the π-bond isomer 2A could be deduced on the basis of the coupling constant $J = 5.8$ Hz for the AB system of 1 H and 2 H and the vicinal coupling constants of 3-H, 5-H, 6-H, and 9-H. In comparison to the spectrum of the dihydro derivative 8, in the spectrum of 2 the signals of the central methyl group and of the peripheral ring protons appear in the opposite sequence. The signals of the perimeter protons exhibit a strong upfield shift of about 2 ppm in the range $\delta = 3.88-4.69$, whereas the methyl group singlet experiences a substantial downfield shift of about 4 ppm to $\delta = 4.75$. The extremely high-field resonances of the ring protons of 2 compared to the ^{1}H-NMR shifts of the perimeter protons of [12]annulene ($\delta = 5.91$), 1,7-methano[12]annulene ($\delta = 5.1-5.8$) and 1,6-methano[12]annulene ($\delta = 5.50-6.17$) are consistent with a pronounced paramagnetic ring current in the 12π-perimeter of 2.

The electronic spectrum of 2 (see Table 1), like those of the mono- and bicyclic [12]annulenes and the dehydro[12]annulenes,[14] shows a strong absorption in the region of 260 nm and, in contrast to these, an additional long-wave absorption at 567 nm. The absorption corresponds to the singlet-electron transitions calculated by Lindner[15a] for the localized 12π-electron system 2A.

2A   2B

9
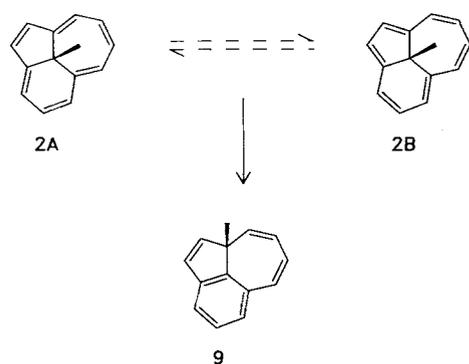
According to π-SCF force field calculations,[15b] the standard enthalpies of formation of 2A and 2B should be about the same, and the activation enthalpies for the π-bond shift should be more than 25 kcal·mol^{-1}. However, contrary to expectations based on these calculations, isomer 2B was not detected. Hence, the equilibrium may lie further to the side of 2A than predicted by the calculations, or a higher barrier between 2A and 2B is involved. At elevated temperatures a, presumably sigmatropic, methyl-group shift takes place in 2 — as is found in the case of 1;[5] the 9a-methyl-9aH-benz[cd]azulene 9 (yellow oil) having a benzenoid partial structure is formed. In contrast to 1, this isomerization already occurs at 80°C (in dimethyl sulfoxide) in case of 2, and proceeds quantitatively within 15 min in boiling xylene.

[1] E. Vogel, H. Königshofen, K. Müllen, J. F. M. Oth, Angew. Chem. 86 (1974) 229; Angew. Chem. Int. Ed. Engl. 13 (1974) 281.
[2] J. F. M. Oth, H. Röttele, G. Schröder, Tetrahedron Lett. 1970, 61; J. F. M. Oth, J.-M. Gilles, G. Schröder, ibid. 1970, 67.
[3] E. Vogel, M. Mann, Y. Sakata, K. Müllen, J. F. M. Oth, Angew. Chem. 86 (1974) 231; Angew. Chem. Int. Ed. Engl. 13 (1974) 283.

[4] D. Farquhar, T. T. Gough, D. Leaver, J. Chem. Soc. Perkin Trans. 1 1976, 341, and references cited therein; W. Flitsch, A. Gurke, B. Müter, Chem. Ber. 108 (1975) 2969.
[5] R. McCague, C. J. Moody, C. W. Rees, J. Chem. Soc. Perkin Trans. 1 1984, 165 and following publications.
[6] Attempts to synthesize 9b-Methyl-9bH-phenalene have been reported by M. Moore, A. Amaro, P. D. Noire, K. G. Grohmann, Abstr. 4. Int. Symp. Chem. Novel Aromatic Compounds, Jerusalem 1981.
[7] K. Müllen, Pure Appl. Chem. 58 (1986) 177.
[8] K. Hafner, H. Pelster, H. Patzelt, Justus Liebigs Ann. Chem. 650 (1961) 80; K. Hafner, Pure Appl. Chem. 28 (1971) 153; K. Hafner, K.-P. Meinhardt, W. Richarz, Angew. Chem. 86 (1974) 235; Angew. Chem. Int. Ed. Engl. 13 (1974) 204.
[9] V. Kühn, K. Hafner, unpublished.
[10] N. Kornblum, Angew. Chem. 87 (1975) 797; Angew. Chem. Int. Ed. Engl. 14 (1975) 734.
[11] W. Treibs, H. Froitzheim, Justus Liebigs Ann. Chem. 564 (1949) 43; R. N. McDonald, N. L. Wolfe, H. E. Petty, J. Org. Chem. 38 (1973) 1106; M. Müller, Dissertation, Technische Hochschule Darmstadt 1982.
[12] Correct elemental analyses or mass spectra were obtained for all the compounds described.
[13] We thank Dr. S. Braun for recording and discussing a 2D-^{1}H-NMR spectrum (COSY) of 2.
[14] K. G. Untch, D. C. Wysocki, J. Am. Chem. Soc. 88 (1966) 2608; F. Sondheimer, R. Wolovsky, P. J. Garratt, I. C. Calder, ibid. 88 (1966) 2610.
[15] a) H. J. Lindner: Singlet transitions of 2A calculated according to the π-SCF-CI method: λ_{max}(oscillator strength) = 244 (1.873), 255 (0.941), 297 (0.003), 580 nm (0.005); b) H. J. Lindner, Tetrahedron 30 (1974) 1127; Program PIMM 82, unpublished, Technische Hochschule Darmstadt 1982.

Synthesis and Dynamic Properties of Substituted Cyclohepta[ef]heptalene**

By Klaus Hafner,* Günter L. Knaup, and Hans Jörg Lindner

As in the case of the mono- and bicyclic [4n]-π-electron systems cyclobutadiene,[1a] cyclooctatetraene,[1b] pentalene[1c] and heptalene[1d] which contain localized double bonds in the ground state, a π-bond shift should also be observed in polycyclic non-alternating [4n]-π-electron systems. However, all previously reported peri-annelated tri- and tetracyclic compounds[2] with [4n]-π-electrons contain either benzenoid or azulenoid partial structures, which impede this dynamic process. The still unknown tricycles cy-

1   2
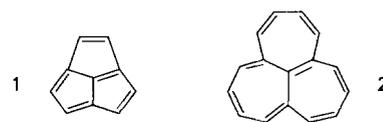
clopenta[cd]pentalene 1 and cyclohepta[ef]heptalene 2,[3,4] on the other hand, do not have any aromatic structural elements. In contrast to the mono- and bicyclic [4n]-π-systems, in the case of 1 and 2 three isodynamic structures with localized double bonds should be in equilibrium with each other. Furthermore, the seven-membered rings of cyclohepta[ef]heptalene (pleiaheptalene) 2 should prefer a boat conformation, so that a ring inversion also could occur as a further dynamic process in this tricycle, as in the case of cyclooctatetraene[1b] and heptalene.[5] With the synthesis of substituted cyclohepta[ef]heptalenes we have now

[*] Prof. Dr. K. Hafner, Dr. G. L. Knaup, Prof. Dr. H. J. Lindner
Institut für Organische Chemie der Technischen Hochschule
Petersenstrasse 22, D-6100 Darmstadt (FRG)