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Monocyclic (CH)$_9^+$—A Heilbronner Möbius Aromatic System Revealed**

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Dedicated to Professor Edgar Heilbronner

In 1964 Heilbronner predicted that singlet [4*n*]annulenes would be aromatic systems in twisted conformations where the p orbitals lie on the surface of a Möbius strip (Figure 1).[1]

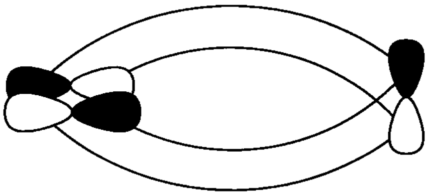

Figure 1. Schematic representation of the Möbius type overlapping p orbitals in (CH)$_9^+$. The C_2 axis lies horizontally; the carbon atom on it (right) is across from the phase inversion (left).

Although the Möbius concept has been employed extensively to interpret reactions and bonding,[2,3] Möbius annulenes conforming to Heilbronner's original idea have still not been reported. Heilbronner pointed out that rings with twenty atoms or more might adopt Möbius geometries "without any apparent angle or steric repulsion strain".[1] However, we have discovered computationally that Möbius aromaticity is possible in a much smaller ring system, namely, the cyclononatetraenyl cation. Moreover, judging from early experimental evidence,[4,5] this species may actually have been encountered more than once almost three decades ago!

A monocyclic (CH)$_9^+$ cation of unspecified nature, but which allowed isotope label scrambling, was first postulated in 1971 as a short-lived intermediate in the solvolysis of *exo*-9-chlorobicyclo[6.1.0]nona-2,4,6-triene in aqueous acetone at 75°C.[4] The reactant containing deuterium at C9 (**1**, Scheme 1) gave a bicyclic product, *cis*-8,9-dihydroindene-1-ol (**3**, X = OH), with uniformly distributed deuterium label.[4] Shortly afterwards Anastassiou and Yakali succeeded in preparing 9-chlorocyclononatetraene (**2**, stereochemistry undetermined).[6] Under ionizing conditions (liquid SO_2 at −66°C), D-labeled **2** gave **3** (X = Cl) by ion-pair return, again with complete statistical distribution of the label (1/9 D per C atom).[5]

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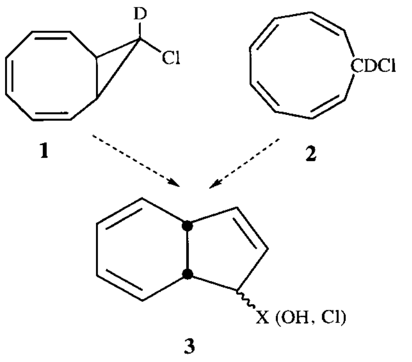

Scheme 1. Reaction of deuterated **1** and **2** to the dihydroindenes **3** with complete statistical distribution of the label.

In view of the expected antiaromaticity of the planar cyclononatetraenyl cation, Anastassiou and Yakali wondered why the ion forms so easily and how the positions could become equivalent.[5a,7] They represented $(CH)_9^+$ in a coiled conformation (**4** in Figure 2, structure on the right),[5b] which was felt to be "incapable of skeletal inversion without experiencing again the adverse effects of antiaromaticity."[5a] We now report computational evidence that the eight-electron monocyclic cation $(CH)_9^+$ actually does prefer this helical C_2-symmetrical structure and is Möbius aromatic rather than nonaromatic.

Exploration of the potential energy surface of singlet $(CH)_9^+$ with density functional theory[8] located the Möbius conformation **4** (C_2) besides a second monocyclic minimum **5** (C_s), which is 21.6 kcal mol^{-1} higher in energy (Table 1).[9] As expected for antiaromatic singlet species, both **5** and especially planar C_{2v}-symmetric **6** (a second-order saddle point, 26.3 kcal mol^{-1} less stable than **4**) show strong bond length alternations,[10] positive nucleus-independent chemical shift (NICS) values ($\delta = +8.6$ and $+42.0$, respectively),[11] and average ^{1}H chemical shifts of $\delta = 7.5$ (**5**) and 2.3 (**6**). In contrast, Möbius compound **4** has a small range of C–C bond lengths (maximum difference 0.043 Å, Table 1), the most negative NICS of $\delta = -13.4$ (the value for benzene is -9.7 at the same level![11]), and an average ^{1}H chemical shift of $\delta = 8.5$. The diamagnetic susceptibility of **4**[12] is exalted ($\Lambda = -18.8$ ppm cgs) relative to that of nonaromatic **7** (NICS $= -0.9$), the reference structure (Table 1). In sharp contrast, the antiaromatic conformations **5** and **6** have paramagnetic susceptibility exaltations of $\Lambda = +18.1$ and $+112.5$ ppm cgs (Table 1). The low-lying transition state **7** (0.9 kcal mol^{-1}; confirmed to be 1.1 kcal mol^{-1} at the CCSD(T)/DZP level[13]) permits the facile enantiomerization of **4** (Table 1). Despite the loss of Möbius aromaticity during interconversion of the enantiomers of **4**, the barrier is small since **7** is less strained than the highly twisted **4**.

Möbius conformation **4** also can undergo disrotatory ring closure via the C_1-symmetric transition state **8.** The computed barrier for the rearrangement (8.1 kcal mol^{-1}) of **4** via **8** into bicyclic **9** is in accord with the experimentally estimated half-life of **4** ($t_{1/2} < 10$ min at $-66\,^\circ$C in liquid SO$_2$).[5a,c] Although modest in magnitude, the aromaticity of transition state **8** (NICS $= -6.0$, $\Lambda = -7.0$ ppm cgs; Table 1) is as expected for a pericyclic transition state.[14] The bicyclic C_s-symmetric 1,4-

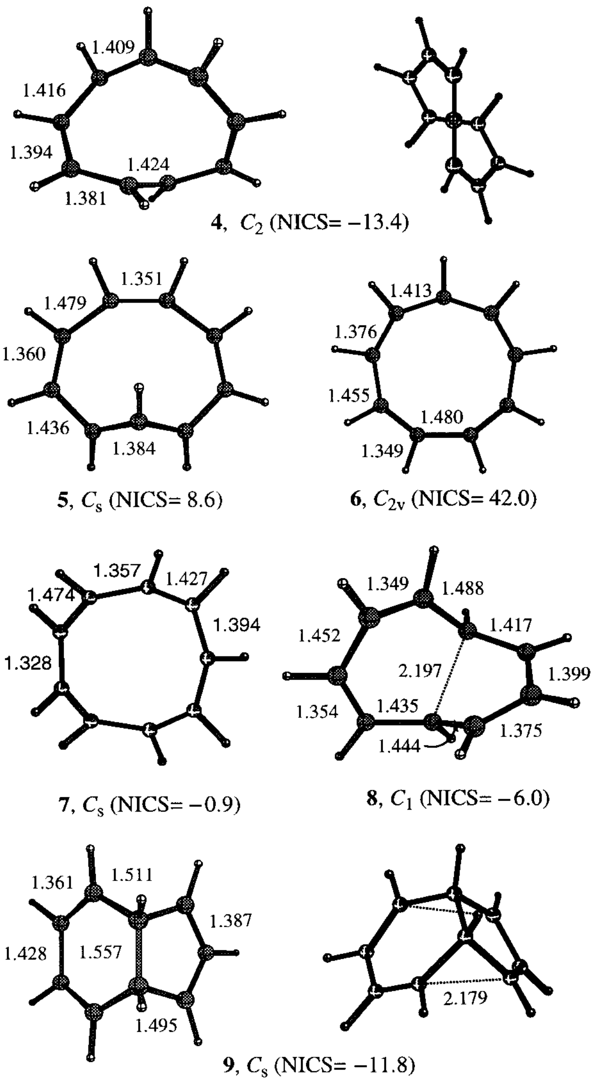

Figure 2. Conformations of $(CH)_9^+$: The Möbius conformation **4** (C_2) and the strongly bond alternating form **5** (C_s); the planar antiaromatic singlet **6** (C_{2v}); **7** and **8** are transition states for enantiomerization and disrotatory ring closure of **4**, respectively. The latter connects to the bicyclic bishomoaromatic **9** (C_s). For further details, see text.

Table 1. Relative energies E_{rel} [kcal mol^{-1}] at the B3LYP/6-311+G** and CCSD(T)/DZP level (including ZPE corrections at the B3LYP/6-31G* level), NICS [ppm], maximum differences in C–C bond lengths ΔR_{C-C} [Å], magnetic susceptibilities χ_{tot}, and diamagnetic susceptibility exaltations Λ [ppm cgs] of singlet $(CH)_9^+$ species.

Species	NIMAG[a]	E_{rel}	ZPE	NICS[b,c]	ΔR_{C-C}	χ_{tot}[d,c]	Λ[e]
4, C_2	0	0.0	94.4	−13.4	0.043	−67.7	−18.8
5, C_s	0	+21.6	94.3	+8.6	0.128	−30.8	+18.1
6, C_{2v}	2	+26.3	93.6	+42.0	0.131	+63.6	+112.2
7, C_s	1	+0.9 +1.1[f]	94.1	−0.9	0.146	−48.9	0.0
8, C_1	1	+8.1	93.9	−6.0	0.139	−55.9	−7.0
9, C_s	0	−16.6	95.9	−11.8	0.067	−67.4	−18.5

[a] Vibrational analysis at the B3LYP/6-31G* level. [b] GIAO method in G94. [c] At the RHF/6-31+G*//B3LYP/6-311+G** level. [d] CSGT method in G94. [e] Relative to **7**. [f] Energy at the CCSD(T)/DZP//B3LYP/6-311+G** level relative to **4** (including ZPE corrections at the B3LYP/6-31G* level)

bishomotropylium cation **9** (16.6 kcal mol^{-1} more stable than **4**), was confirmed to be bishomoaromatic by Cremer based on geometric and magnetic criteria.[15] The NICS at the geometric center of **9** (-11.8) and $\Lambda = -18.5$ ppm cgs (i.e., similar to that of **4**[16]), corroborate this conclusion. This cation reacts to give the observed *cis*-8,9-dihydroindenes **3** (X = OH or Cl).[4,5]

In summary, the geometric and magnetic criteria (NICS and Λ) exhibited by **4** now reveal this species to be the first Möbius aromatic system in the Heilbronner sense, for which there is experimental evidence.[4,5] Without such evidence, the nature of **4** was not recognized originally. Furthermore, early speculations were incorrect: While conformation **6** is avoided, transition state **7** is not high in energy.[5b] The complete scrambling of the deuterium label, observed for **3** even at $-66\,^{\circ}$C, is consistent with the low barrier computed for **7**, permitting rapid interconversion of the helical **4** enantiomers. Ninefold repetition of the enantiomerization results in complete distribution of a deuterium label in **4**. In conclusion, the experimental findings reported nearly three decades ago[4,5] are explained by assuming that the (CH)$_9^+$ intermediates were 4*n*-electron Möbius aromatic systems. Our prediction that **4** is the most stable monocyclic (CH)$_9^+$ cation might be verified by applying modern experimental techniques such as laser flash photolysis, which has been employed to observe short-lived carbocations.[17]

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Cp$_3^*$Al$_5$I$_6$: An Intermediate in Reactions Leading to Elemental Aluminum and Al^{III} Species?[**]

Christoph Üffing, Elke Baum, Ralf Köppe, and Hansgeorg Schnöckel[*]

Dedicated to Professor Heinrich Nöth
on the occasion of his 70th birthday

As we have demonstrated in earlier work, Al^{I} species are reactive both in solid noble gases and under preparative synthetic conditions,[1] and often react to give thermodynamically more stable Al^{III} products and metallic aluminum. [Cp$_2^*$Al]$^+$[Cp*AlCl$_3$]$^-$ is thus formed as the final product from Cp*Al and AlCl$_3$ with simultaneous deposition of aluminum. This isomer of the sesquichloride [Cp$_3^*$Al$_2$Cl$_3$] contains the aluminocenium ion [Cp$_2^*$Al]$^+$ as a structural peculiarity.[2] To understand this reaction mechanism and to find out how Al^{I} species can react in general, we carried out investigations with the aim of capturing intermediate products of the disproportionation.

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