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Annulenes

Is the [9]Annulene Cation a Möbius Annulene?[**]

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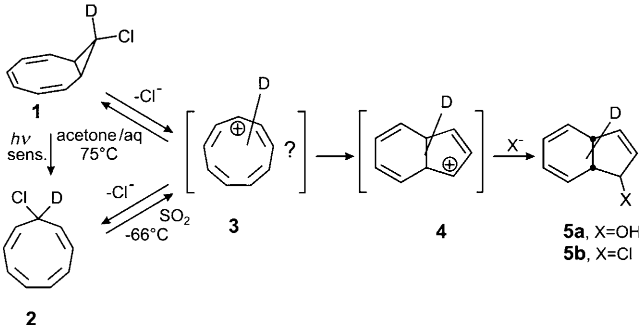
Möbius annulenes[1] are highly unusual compounds because they break the Hückel rule. This violation of one of the most pivotal laws in chemistry was first theoretically predicted in 1964 by Heilbronner, who stated that introducing a 180° twist in an antiaromatic $4n$ π electron annulene would make it stable; that is, the Möbius twist would reverse the Hückel rule.[2] As a restriction, Heilbronner argued that the reduced p orbital overlap induced by the twist would lower the stability, and only very large rings (> [20]annulenes) would be isolable. However, Heilbronner's concerns are only valid for planar Möbius rings. In three dimensions, the twist can be projected into writhe, (that is, the twisted ring adopts a figure-of-eight shape), which alleviates the overlap problem and most of the strain.[3] Therefore, smaller Möbius rings could also be stable. Indeed, the first Möbius annulene that was synthesized (39 years after Heilbronner's theoretical prediction) was a [16]annulene.[4] Meanwhile, a number of extended Möbius porphyrins were prepared and characterized.[5]

The first evidence for a Möbius annulene as a short-lived intermediate was obtained a few years after Heilbronner's seminal work. In 1971, Schleyer et al. observed that upon solvolysis, 9′-chloro-9-deuterobicyclo[6.1.0]nona-2,4,6-triene **1** yields dihydroindenol (**5a**) in which the deuterium was stochastically distributed over all nine carbon centers.[6] Anastassiou and Yakali observed a similar scrambling process upon solvolysis of deuterated 9-chlorocyclononatetraene **2** (Scheme 1).[7]

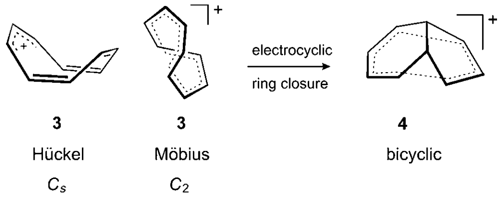


Scheme 1. Generation of the [9]annulene cation **3** as a short-lived intermediate by solvolysis of two different precursors (**1** and **2**). If **1** and **2** are deuterated at the 9-position, the deuterium is equally scrambled over all the carbon centers in **5**.

The ease of solvolysis is remarkable, and Yakali speculated that the otherwise instable and antiaromatic [9]annulene cation **3** could be stabilized by Möbius aromaticity.[8] However, direct spectroscopic observation by NMR spectroscopy at $-80\,^{\circ}\mathrm{C}$ and trapping reactions to show the intermediacy of the [9]annulene cation were unsuccessful. The formation of a transannular bond by electrocyclic ring closure at (symmetry or time averaged symmetry) equivalent positions is clearly very fast and leads to the dihydroindene cation **4**, which explains the deuterium scrambling.

In 1998, Schleyer et al. presented evidence, based on theoretical calculations, that the [9]annulene cation is indeed a strongly aromatic Möbius annulene (NICS: -13.4).[9] The structure has one *trans* bond and a three-dimensional figure-of-eight structure with C_2 symmetry. According to DFT calculations (B3LYP/6-311+G**), there is another (*all-cis*)-isomer, which is not twisted and only 0.9 kcal mol^{-1} higher in energy. (Scheme 2.) Frequency calculations revealed that this structure is a transition state. CCSD(T)/DZP single-point calculations confirmed the energy difference in favor of the Möbius isomer. ($\Delta E = 1.1$ kcal mol^{-1})

Meanwhile, it has become evident that DFT methods suffer from the self-interaction error that leads to the overestimation of the stability of delocalized states.[10]



Scheme 2. Hückel and Möbius isomers of the [9]annulene cation and the homoaromatic product of the electrocyclic ring closure reaction.

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Hybrid density functionals including HF exchange attenuate the problem; however, there are a number of examples in which B3LYP favors aromatic over non-aromatic structures by several kcal mol^{-1}, especially for annulenes.[11] Recently, two reviews were published that address the severe problems of the B3LYP functional.[12] Therefore, it was to be expected that the very small energy preference of the aromatic Möbius structure over the non-aromatic Hückel isomer could eventually be reversed if adequate theoretical methods would be applied.

Herein we present theoretical and experimental evidence that the [9]annulene cation is probably not an aromatic twisted Möbius structure, but rather a weakly antiaromatic or non-aromatic Hückel annulene (NICS: −0.9). However, based on our calculations and LFP experiments, we cannot exclude that the Möbius species could be present in small concentrations in a fast equilibrium with the Hückel isomer.

To make sure that we would not overlook a stable isomer of the [9]annulene cation **3**, we generated a large number of structures using a Monte Carlo algorithm, checked for redundancy,[13] and optimized the remaining structures at various DFT levels (see computational details). In agreement with Schleyer et al.[9] the Möbius (C_2 symmetry) and the Hückel structure (C_s symmetry) were found to be the most stable stationary points of the [9]annulene cation. To compare the relative energies of the [9]annulene cation isomers, we applied the density functionals KMLYP and BH&HLYP[11b] including a large amount of Fock exchange (50 % vs. 20 % in B3LYP). As expected, the relative stability of Hückel and Möbius isomers changed in favor of the non-twisted Hückel structure (Table 1).

Both the Möbius and Hückel structures vary mainly in the dihedral angle θ of a single bond (Figure 1). The Möbius isomer contains one *trans* bond and the Hückel species is *all-cis*. Both structures can be converted into one another by a torsion around this bond.

The potential energy surface (PES) is quite flat in the region of the torsion angle θ between 70–95°. At this section, three stationary points, weakly antiaromatic or non-aromatic Hückel structures of C_s, C_1, and C_2 symmetry (NICS = 0.34, 0.27, −0.13 (KMLYP)), were located. The C_s Hückel isomer, which was previously found to be the transition state of the racemization of the C_2 Möbius species at the B3LYP level,[9] is more stable than its Möbius topology counterpart when using the KMLYP functional (see Table 1). The energy difference between the C_s, C_1, and C_2 Hückel structures is smaller than 1.0 kcal mol^{-1} at all basis sets, the C_s structure being the most stable at KMLYP/aug-cc-pVTZ. Calculations using the BH&HLYP functional agree with those obtained with KMLYP. The C_s, C_1, and C_2 stationary points with Hückel topology were also found at the BH&HLYP level (see the Supporting Information).

Table 1: Relative energies of the Hückel and Möbius isomers using various DFT and ab initio methods.

Level				
Energy		Optimization		$\Delta E_{\text{H-M}}$[a]
		KMLYP	cc-pVTZ	−1.15
		BH&HLYP	cc-pVTZ	–[b]
		B3LYP	cc-pVTZ	1.04
		SCS-MP2	TZVPP[c]	3.45
CCSD(T)/	cc-pVTZ	SCS-MP2	TZVPP	1.23
CCSD(T)/	CBS[d]	SCS-MP2	TZVPP	0.83
CCSD(T)/[e]	CBS[f]	CCSD(T)/[e]	cc-pVTZ	0.62
Corrections:				
Solvent[g]				−0.31
Frozen core		SCS-MP2	cc-pVTZ	−0.12
Thermo[h]		SCS-MP2	TZVPP	−0.27
Final energy including corrections:				
CCSD(T)/	CBS[d]	SCS-MP2	TZVPP	0.13
CCSD(T)/[e]	CBS[f]	CCSD(T)/[e]	cc-pVTZ	0.04

[a] Relative energy of the C_s Hückel structure with respect to the C_2 Möbius isomer in kcal mol^{-1}. [b] The Möbius isomer is not a stationary point. [c] def2-TZVPP basis set.[25] [d] Complete basis set extrapolation applying the Helgaker scheme[15] using SCS-MP2/cc-pVQZ and SCS-MP2/cc-pV5Z calculations and a CCSD(T)/cc-pVTZ correction. [e] All-electron calculation. [f] Complete basis-set extrapolation applying the Helgaker scheme[15] using CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ calculations. [g] COSMO[16] calculations using acetonitrile as solvent at the B3LYP/def2-TZVPP level. [h] Vibrational contributions to the enthalpy at the SCS-MP2/def2-TZVPP level.

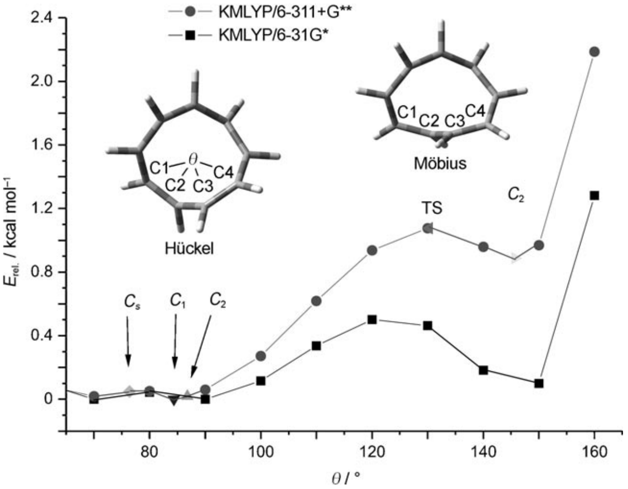

Figure 1. KMLYP calculated minimum energy reaction path of the topological isomerization of Hückel and Möbius [9]annulene cations. Relative energy is given as a function of the dihedral angle θ, TS = transition state.

We also repeated the calculations using the B3LYP functional (see the Supporting Information). In agreement with previous calculations,[9] the Möbius isomer is the global minimum and the C_s structure is a transition state. The C_1 and C_2 Hückel isomer were not found on the potential energy surface. Although B3LYP is known to overestimate delocalization in annulenes, as mentioned above, the energy difference between the C_s Hückel isomer and the C_2 Möbius species decreases from 2.18 to 0.92 kcal mol^{-1} upon increasing the basis set from 6-31G to 6-311++G** and from 1.46 to 0.74 kcal mol^{-1} (cc-pVDZ to aug-cc-pVTZ).

We also applied the SCS-MP2 method[14] in combination with a TZVPP basis set for optimization and performed single-point calculations at the CCSD(T) level of coupled-cluster theory. The complete basis-set limit (CBS) was estimated using the Helgaker extrapolation scheme on the SCS-MP2 level.[15] At this level of theory, the energy difference between the Hückel and Möbius isomer is 0.83 kcal mol^{-1} in favor of the Möbius structure. Solvent effects using the COSMO approach[16] and acetonitrile as the solvent, and consideration of vibrational contributions to the enthalpies, reduce the energy difference to 0.13 kcal mol^{-1} (Table 1). At this level of theory both isomers are almost isoenergetic. Upon optimization of the Hückel and Möbius structures at the CCSD(T) level (which is often called the gold standard of quantum chemistry) and application of the above corrections, the energy difference is further reduced to 0.04 kcal mol^{-1} (Table 1).

The theoretical results suggest that Hückel and Möbius structures are isoenergetic within computational estimated error ($\pm 0.1\ \text{kcal mol}^{-1}$). We performed a laser flash photolysis (LFP) study to compare the theoretical findings with experiments and to finally settle the question whether the [9]annulene cation **3** has a Möbius or a Hückel structure. The LFP setup has been described in detail elsewhere.[17]

Nanosecond LFP ($\lambda_{\text{exc}} = 266$ nm) of a 0.1 mM solution of the non-deuterated precursor **1***H* in acetonitrile, purged with argon, resulted in the observation of two transient species. Transient **A** ($\lambda_{\max} = 346$ and ca. 590 nm, $\tau = 1.5$ μs) was not quenched by oxygen, but reacted with methanol (see the Supporting Information). On the other hand, saturation of the solution with NaN_3 or addition of 20 mM tetra-*n*-butylammonium bromide had no effect on the transient lifetime. As the intensity of transient **A** correlates linearly with the laser energy (see the Supporting Information), it is formed in a monophotonic process. Figure 2 presents a comparison of the experimental transient spectrum of **A** with the TD-DFT-calculated UV/Vis spectrum of the [9]annulene cation **3** in its C_S Hückel geometry. According to our calculations, the long-wavelength absorption of about 570 nm is characteristic for the Hückel isomers of **3**. No other isomer of the [9]annulene cation, including the Möbius structure, exhibits an electronic transition above 370 nm, nor does the product **4** or **5** or the bicyclic precursor **1**. The chemical reactivity and the good agreement between the measured and the calculated UV/Vis spectrum (Figure 2) provide further evidence that transient **A** is identical with the Hückel structure of the [9]annulene cation **3**. The lifetime of the transient **A** ($\tau = 1.5$ μs) is also in qualitative agreement with the calculated barrier ($\Delta H^{\neq} =$ 4.1 kcal mol^{-1} at the CCSD(T)/cc-pVTZ//SCS-MP2/def2TZVPP level of theory) for the electrocyclic ring closure of Hückel C_s **3** to form the bicyclic product **4**.

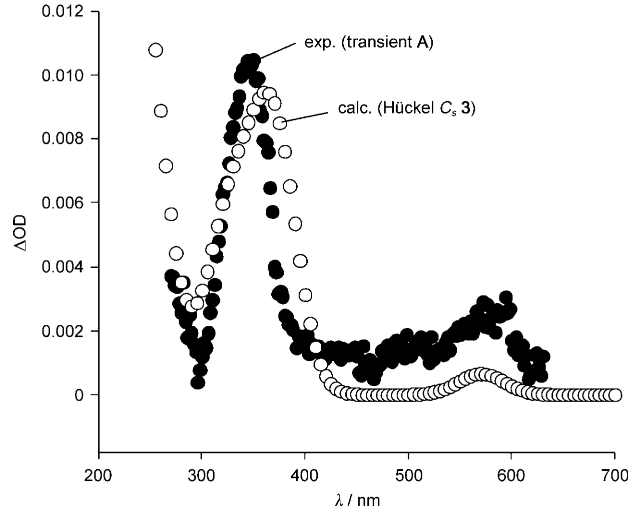

Figure 2. ●: Transient **A**, experimental transient difference spectrum observed after LFP of **1***H* in acetonitrile under an argon atmosphere (530 ns after LFP of **1***H* minus 7.5 μs after LFP). ○: Calculated UV/Vis spectrum (TD-B3LYP/6-31G*//BH&HLYP/aug-cc-pVTZ) of the C_S-symmetric Hückel isomer **3** (for calculation at other levels, see the Supporting Information).

The second transient **B** has a lifetime $\tau = 60$ μs, with $\lambda_{\max} =$ 268 nm and circa 330 nm. It is not quenched by oxygen, and the addition of 1% MeOH or addition of tetra-*n*-butylammonium bromide up to 20 mM does not reduce its lifetime. The transient UV/Vis spectrum of **B** is in qualitative agreement with the calculated UV/Vis spectrum of *all-cis*-9-chlorocyclononatetraene, **2***H*,[18] which is known to be formed from **1** in a photochemical reaction.[7a] Chlorocyclononatetraene **2** solvolyzes very rapidly in liquid SO_2,[7b] which is in agreement with the observed short lifetime in our LFP experiment.

In conclusion, high-level coupled-cluster calculations, including corrections for solvent and vibrational contributions, predict that the Hückel and the Möbius isomer of the [9]annulene cation are very close in energy. UV/Vis spectra measured in LFP experiments clearly are in favor of a "normal" Hückel structure being the most stable isomer of the [9]annulene cation. The aromatic 4*n* electron Möbius structure might be in equilibrium with the Hückel structure under the experimental conditions albeit in small concentrations below the detection limit. Thus, even though a number of Möbius extended porphyrins have been found within the last few years, an example for a stable charged or uncharged parent Möbius annulene is still elusive.

Experimental Section

Computational details: A large set of 524 configurations and conformations of $(CH)_9^+$ were generated using a Monte Carlo algorithm and automatically checked for redundancy.[13] The energies of the remaining 220 structures were computed with the semi-empirical method PM3.[19] All structures less stable than 65 kcal mol^{-1} with respect to the most stable structure were discarded, and the remaining 196 candidates were optimized at different levels of DFT. Four different structures, which were more stable than 25 kcal mol^{-1} with respect to the most stable isomer, could be localized. All DFT, TD-DFT, and ab initio calculations were performed using the Gaussian 03 program,[20] Turbomole 6.0,[21] and Molpro 2006.[22] Geometry optimizations and single-point energy calculations at the frozen core and all-electron CCSD(T)/cc-pVTZ and cc-pVQZ level of theory have been carried out with the parallel version of the CFour program package.[23]

Experimental details: *anti*-9-Chlorobicyclo[6.1.0]nona-2,4,6-triene and *anti*-9-chloro-9'-deutero-bicyclo[6.1.0]nona-2,4,6-triene **1** were prepared from cyclooctatetraene following a literature procedure.[24] The mixture of *syn* and *anti* isomers were separated by distillation and subsequent column chromatography (silica gel, pentane). The LFP experiments were performed as described previously.[17] Spectroscopic-grade acetonitrile was used for all experiments.

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