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Neutral Möbius Aromatics: Derivatives of the Pyrrole Congener Aza[11]annulene as Promising Synthetic Targets

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Dedicated to the memory of Professor Edgar Heilbronner

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Amino- and methyl-disubstituted derivatives of an aromatic 12π electron pyrrole homologue Möbius 1H-aza[11]annulene are predicted computationally at the B3LYP/6-31G* level of theory to be distinctly aromatic and a neutral ground state on its potential surface. The parent annulene has a nonaromatic conformation, which is 6.0 kcal mol^{-1} lower in energy at the CCSD(T)/D95*//B3LYP/6-31G* level of theory than a structurally very similar Möbius conformation. After derivatization, however, geometry optimizations of the two lowest-energy – Möbius and non-Möbius – heteroannulene conformations both converged two a single Möbius minimum, whereas two (Möbius and non-Möbius) distinct difluoro-substituted species could be located 1.8 kcal mol^{-1} apart in energy at the B3LYP level. The Möbius minimum is 7.5 kcal mol^{-1} lower in energy at the coupled cluster level than a "Hückel topology" form derived from a known bridged 1H-[4,9]methano[11]annulene. Several possible reactive modes are investigated in order to assess the relative stability of the Möbius parent annulene. In addition, we report formal novel examples for charged and neutral Möbius triplet aromatic annulenic and heteroannulenic systems, some of which also exhibit distinct aromatic properties. Further fundamental insights into the phenomenon of "Möbius aromaticity" are suggested. The aromaticity of Möbius annulenes is for the first time linked to wavefunction boundary conditions.

Introduction

A Möbius strip is a one-sided, single-edged manifold. The paper representation of such a Möbius strip can be constructed by giving one end of a strip of paper a half turn of 180° and gluing the ends together. Edgar Heilbronner predicted in 1964 in his seminal paper based on Hückel molecular orbital (HMO) theory that Möbius twisted 4*n* electron annulenes resulting from a single orbital phase inversion in a string of contiguous, "laticyclically" overlapping *p*-orbitals are possible as closed-shell singlets without apparent loss in π energy.[1] The presence of this unusual stabilizing effect in [4*n*]annulenes, solely employing molecular orbital topology, was unexpectedly discovered computationally only about a decade ago.[2,3] This finding was accompanied by the belated recognition of Möbius aromaticity in the mono-*trans* helical conformation of the cyclononatetraenyl cation.[2,3] The latter report in particular motivated other researchers to further investigate chemical structures that exhibit the Möbius topology and fuelled the resurgence of a general interest in Möbius strip topology, and some of the more recent developments are summarized in two important reviews.[4,5]

In 2003, Herges and coworkers succeeded spectacularly in synthesizing the first stable, weakly Möbius aromatic compound, a [16]annulene derivative, by employing the mono-*trans* carbon–carbon bond motif, and built into a rigid molecular framework to prevent its wriggling back into more-stable nonaromatic conformations.[6,7] Following the recent discovery of a porphyrin-based Möbius–Hückel aromaticity switch,[8] it was reported that expanded porphyrins, employed as ligands in metal complexes, even spontaneously adopt the Möbius topology and possess distinct aromaticity.[9]

After the successful identification of the first ground-state molecule possessing Heilbronner–Möbius aromaticity,[2,3,10,11] neutral Möbius annulenes were also sought by several researchers, as they are usually regarded as being more accessible synthetically than ionic forms and also because neutral annulenes are already more thoroughly studied.[12–14] The first examples, Möbius[12]- and Möbius[16]annulenes and dehydroannulenes, were computationally proposed in 1999,[2] but until now, nonaromatic conformations of neutral parent annulenes have always

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been found to be lower in energy than Möbius forms, which proved to be elusive.[5,15]

In contrast, charged $4n\pi$ electron Möbius[$4n$–1]annulene anions and Möbius[$4n$+1]annulene cations were proposed as being diatropic and more stable than their nonaromatic conformations.[2] Hence, it appeared to us a good strategy to obtain neutral variants of these ions by replacing either isoelectronically a CH^- unit by NH or, alternatively, by replacing CH^+ by BH. Karney, Rzepa, and coworkers investigated Möbius aromatic forms of 8π electron heteropines computationally, among them fluoro-substituted azepine-like systems, but they found that nonaromatic geometries were always significantly preferred energetically.[16] To the best of our knowledge, 1H-aza[$4n$–1]- or 1H-aza[$4n$+1]-heteroannulenes have not been considered before as potential Möbius aromatic species.

Such systems are not unknown experimentally though, and a nearly planar [4,9]methano-bridged aza[11]annulene (a pyrrole or 1H-azepine homologue) and an aza[15]annulene annelated with furan rings have been reported.[17,18] At the time of their characterization, the observed paratropicity of the 12 and 16π electron conjugated molecules was not unexpected.[12,13] However, herein we report the surprising computational finding that Möbius conformations of neutral aza[11]annulenes are aromatic and that the parent Möbius aza[11]annulenes are pronouncedly more stable than a nonaromatic conformation derived from the experimentally known molecule (Figure 1a). As shown in the following, the Möbius system could easily be derivatized to obtain a ground-state neutral and distinctly aromatic annulene. Hence, we propose this Möbius aromatic molecule to be a very promising synthetic target, which could become the smallest neutral Möbius aromatic molecule that could possibly be synthesized and the first stable Möbius heteroannulene.

Results and Discussion

We began our survey by looking at some of the Möbius annulene ions from the literature.[2] The cycloundecapentadienyl anion (**1**; Figure 1a), to the best of our knowledge first studied computationally in ref.[2], is strongly delocalized at the B3LYP/6-31G* level of theory with near C–C bond length equalization (ΔR_{cc} = 0.03 Å, Table 1) and contains a single "*trans*" HCCH configuration[19] where the "Möbius twist" in the geometry is located with a remarkable NICS value of –12.5. It should be noted that the localization of the geometric twist − here on the C_2 axis − is not the consequence of the enforced Möbius topology, but rather the effect of strain − a mathematical realization of a Möbius strip has an evenly distributed twist.[20,21] The CH

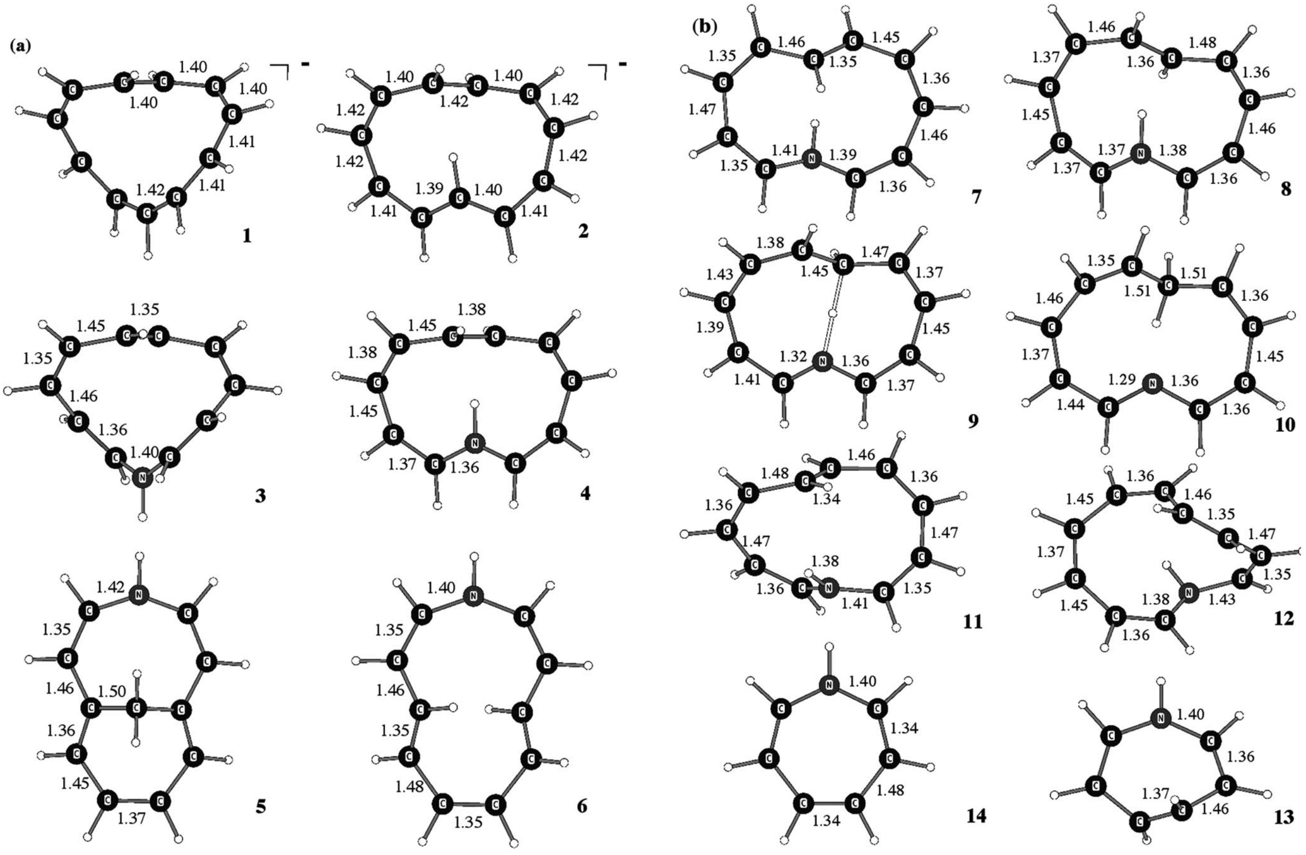

Figure 1. Möbius [11]annulene and -heteroannulene minima **1**–**4** (a) and **13** (b) and related Hückel topology species, as discussed in the text, computed at the B3LYP/6-31G* level. Transition-state structures **8**, **9**, and **11** (b), pertaining to reactive modes of the Möbius ground state **4** are depicted.

bond opposite to the "*trans*" bond in **1** points outwards (Figure 1a). The pseudo-C_2 (i.e., C_1) form, in which the CH bond is made to turn inwards, **2**, is lower in energy by about 1.8 kcal mol^{-1},[22] which is significantly more aromatic (according to the NICS aromaticity index,[23] which is –19.2 here) and even slightly better delocalized than that in **1** (Table 1). However, the conformation restrained to C_2 symmetry is not a minimum, but rather a transition state for the "pendulum motion" of the inwards pointing CH bond around the potential maximum, pertaining to C_2 symmetry.[2,24] This finding motivated us to replace a CH$^-$ unit on the C_2 axis by NH to obtain the neutral aza[11]annulene systems **3** and **4** (Figure 1a), which can be regarded as higher, unknown 12π homologues of pyrrole or 1*H*-azepine with the Möbius topology!

Table 1. B3LYP/6-31G* relative energies (ZPE corrected), range of C–C bond lengths (ΔR_{cc}), and NICS aromaticity indices for neutral Möbius and Hückel azaannulenes and -annulene ions.

Species (NIMAG)	Topology,[a] point group	Rel. energy[b]	ΔR_{cc} [Å]	NICS[c]
1 (0)	M, C_2	1.8	0.02	–12.5
2 (0)	M, C_1	0.0	0.03	–14.2 (–19.2)[d]
3 (0)	M, C_2	8.8	0.11	–4.6
4 (0)	M, C_2	0.0[e]	0.09	–8.8 (–17.5)[d]
5 (0)	H, C_s	–	0.11, 0.08[f]	+6.3, +7.8[g]
6 (0)	H, C_2	16.4	0.13	+11.8[g]
7 (0)	H, C_1	–1.6	0.12	+3.0[g]
8 (1)	–, C_1	0.9	0.12	–3.0[g]
9 (1)	–, C_1	15.2	0.10	–8.8,[g] –6.2[h]
10 (0)	–, C_1	–1.9	0.11[i]	–4.1[g]
11 (1)	–, C_1	14.0	0.14	–1.26
12 (0)	H, C_1	3.7	0.12	–2.9[g]
13 (0)	M, C_2	34.7	0.10	–6.4
14 (0)	H, C_{2v}	0.0	0.14	+37.2

[a] Topology M = Möbius, H = Hückel. Tracing the π system along one face of the ring, a return to the starting point on the same face indicates Hückel, whereas a return on the opposite face indicates Möbius topology.[25] It should be noted that this assignment is ambiguous, when a (H)CC(H) dihedral angle of or close to 90° is encountered during this passage. [b] With respect to reference compound of the same stoichiometry. [c] With GIAO method at B3LYP/6-31G*.[26] NICS points were set at the center of mass of the heavy atoms. [d] We report here NICS(1) values taken about 1 Å above the projected plane of the ring, NICS(0) values in parenthesis. [e] The HN(CH)$_{10}$ potential surface could exhibit, for example, bicyclic species lower in energy than **4**. [f] Experimental value.[17] [g] We also report off-center values relative to a related reference frame when necessary to avoid getting in the way of bonds or electron lone pairs (see Supporting Information for position of NICS points). [h] In smaller conceived "ring", see Figure 1b and Supporting Information. [i] Distances only between C(sp^2)-C(sp^2) atoms.

Looking for an experimental example, we found the [4,9]methano-bridged variant of **3** (i.e., **5**; Figure 1a and Table 1), which is, however, paratropic (experimentally detected downfield shift of the bridge protons average at 5.0 ppm; at B3LYP/6-31G* this becomes 6.0 ppm with NICS = +6.3) and which contains a nearly planar heteroannulenic ring.

We supposed that the bridging reduces the orbital overlap at the adjacent carbon atoms in the ring and enforces a conformation that would incur tremendous strain when it would incorporate an additional "*trans*" bond opposite to the nitrogen atom in the ring.

To test this hypothesis, we computed the "two-*trans*"[19] Hückel topology annulene system, **6**, which possesses a conformation that is very close to that of the known methano-bridged variant (cf. e.g., the C4–C9 distance: exp. 2.29 Å, theoret. 2.35 Å), and we compared its energy with those of Möbius aza[11]annulene species **3** and **4**.

Surprisingly, Möbius heteroannulene **4** has been found to be a remarkable 16.4 kcal mol^{-1} lower in energy than C_2 form **6** and distinctly aromatic (NICS = –8.8), whereas **3** is at least 7.6 kcal mol^{-1} lower in energy and modestly aromatic (NICS = –4.6) (Table 1)!

To find out whether these low-energy Möbius molecules are also kinetically stable, we were looking into several conceivable reaction modes that could transform **4** into other molecules on its potential energy surface. In this report, we concentrate solely on the immediate vicinity of **4** on the PES. Hückel topology species **7** (Figure 1b) is a position isomer of **6**, which differs from **6** in the placement of the nitrogen atom and found to be even 1.6 kcal mol^{-1} lower in energy than **4** at the computational level employed (Table 1). The two lowest-energy minima Möbius **4** and Hückel **7** could be connected by a minimum energy pathway through a "bond-rotation" transition state. It was by no means easy to find low-lying transition state **8**, which corresponds to the near 90° rotation of the HCCH unit transfixed by the C_2 axis and where also the geometric "Möbius twist" is located. As transition state **8** is low in energy (Table 1), any synthetic attempt to prepare parent Möbius annulene **4** has to take precautions against the possible facile conversion of **4** into slightly more stable **7** (e.g., by appropriate placement of substituents). Most probably, it would be extremely difficult (unless matrix isolation techniques would be used) or even impossible to observe "pure" Möbius **4**, as transition structure **8** is a mere 0.9 kcal mol^{-1} higher in energy than **4**. Such a finding is not unprecedented. At most one might hope for the existence of a potentially solvent-dependent equilibrium, similar to that reported in ref.[7], provided that the relatively small energy difference prevails at a higher level of computation or in an experiment.

The hybrid B3LYP "general purpose" density functional is extremely popular in computational chemistry, but its capability to give correct predictions of relative energies has been recently criticized.[27] Schleyer and coworkers stated, referring to earlier work, that both MP2 and B3LYP methods overestimate "electron delocalization".[27b] Employing transition-state-optimized[28] BHLYP[29] and KMLYP[30] functionals, which include a much higher ratio of exact (HF) exchange around 50% with respect to B3LYP (with its ca. 20% exact exchange), Schleyer and coworkers were able to achieve a remarkable accordance to their coupled cluster level results on [18]annulene conformations.[27b,28,31] However, Boese and Martin evaluated several density functionals and found that B3LYP gives reliable geometries and superior vibrational frequencies and thermochemical properties, but has inferior performance for activation barriers, where KMLYP and BH&HLYP (synonymous to BHLYP) perform better, because of their more balanced treatment of nondynamical (long range) contribution to electron correlation (i.e., the Coulomb hole).[28] These ongoing discussions motivated us to seek some validation of our results, and we computed the relative energy of **4** vs. that of **7** at different computational levels, including at the CCSD(T)/D95*//B3LYP/6-31G* level of theory with the Huzinaga–Dunning double-zeta quality D95* basis set (Table 2).[32] As a result, **7** was found to be between 0.2 (MP2 full optimization) and 8.4 kcal mol^{-1} (at CCSD/D95 level) lower in energy than **4** (Table 2). We conclude that it is very unlikely that parent annulene conformation **4** will be lower in energy than **7** at any computational level. The most reliable results for this type of system and with respect to the energy spacings appear to be the CCSD(T) calculation data (Table 2), both on the basis of CCSD and the B3LYP geometries. However, discussing the B3LYP potential energy surface appears also justified, as long as the focus is on reactive modes and the nature of stationary points. In contrast, CCSD(T) potential surfaces, due to the lack of analytical second derivatives, have not been reported yet.

Table 2. Comparison of relative energies of Möbius conformation **4** vs. non-Möbius conformation **7** at different levels of approximate density functional and ab initio levels of theory.

Method	E_{rel} **4** vs. **7** [kcal mol^{-1}]
CCSD(T)/D95*//CCSD/D95	5.6
CCSD(T)/D95*//B3LYP/6-31G*	6.0
CCSD/D95*//B3LYP/6-31G*	8.4
CCSD/D95	0.3
B3LYP/6-311+G**//B3LYP/6-31G*	2.5
MP2/6-31G*//B3LYP/6-31G*	2.6
MP2/6-31G*	0.2
B3PW91/6-31G*	1.2

Because of the surprisingly large difference between the B3LYP/6-311+G**//B3LYP/6-31G* and the coupled cluster results (6 kcal mol^{-1}) we computed also the relative energy of **6** with respect to that of **4** at the coupled cluster level (cf. 16.4 kcal mol^{-1} at B3LYP/6-31G*, see Table 1). As a result, non-Möbius conformation **6** is (at CCSD/D95* level) a significant 7.5 kcal mol^{-1} higher in energy than Möbius **4** (Table 2).

However, the above-mentioned strategy, namely to stabilize **4** with respect to the structurally very similar **7** selectively by placement of certain substituents at appropriate positions on the annulene ring, can be easily validated by contemplating, for example, the 6,7-difluoro- (**4a**), 6,7-dimethyl- (**4b**), and 6,7-diamino-substituted (**4c**) heteroannulene **4** (Table 3 and Figure 2). We have chosen these three substituents because of their diverse steric and electronic properties. The position of the substituents is somewhat arbitrary, but we assumed that the substituents' pronounced "*trans* configuration" in the 6- and 7-positions in Möbius **4** might help to avoid direct interaction with each other and neighboring CH bonds, and hence, would give the respective derivative of **4** an edge over the corresponding form of **7**, where some repulsive through-space interaction of the substituents with the CH bonds or the NH bond of the core annulene appears inevitable. Indeed, despite several attempts (even with different methods), we were unable to locate these disubstituted derivatives of **7**, corresponding to **4b** and **4c**! Instead, the input geometries evolved invariably during optimization at B3LYP/6-31G* into the respective variants of Möbius **4**, with the exception of the 6,7-difluoro derivative **7a**, which is even 1.8 kcal mol^{-1} (1.5 kcal mol^{-1} when ZPE corrections are taken into account) lower in energy than **4a** (Table 3). Notably, species **7a** and **4a** differ mostly by changes in the dihedral angles, which are given in Figure 2.

Table 3. B3LYP/6-31G* absolute energies, vibrational zero-point energy values, range of C–C bond lengths, and NICS values (at the B3LYP/6-31G* and the B3PW91/6-31G* level of theory) for 6,7-(R,R′)-disubstituted parent annulenes **4** and **7**.

Species[a]	Abs. energy [hartree]	ZPE [kcal mol^{-1}]	ΔR_{cc} [Å]	NICS[b]	NICS[c]
4a, C_2	–640.79497	105.9	0.08	–8.0	–8.0
R,R′ = F				(–7.4)	(–7.5)
4b, C_2	–553.04602	137.7	0.08	–8.9	–8.9
R,R′ = NH_2				(–10.0)	(–9.8)
4c, C_2	–520.96918	151.1	0.10	–6.9	–7.0
R,R′ = CH_3				(–8.1)	(–8.3)
7a, C_1	–640.79796[d]	106.2	0.12	–1.5	–1.7
R,R′ = F				(–1.3,+3.9)	(–1.4,+3.8)

[a] All species are minima at the computational level employed. [b] B3LYP/6-31G*. The values in parenthesis are off-center values. [c] B3PW91/6-31G*. [d] Relative energy of **4a** vs. **7a**: 1.8 kcal mol^{-1}.

Even if **4b** and **4c** are stable twisted ground states of a twisted 1-H-azepine congener derivative, are they also aromatic? Because the LYP functional has also been suspected lately to deliver unreliable response (e.g., magnetic) properties,[27b,33] we have computed NICS values with both the B3PW91 and the B3LYP density functional for derivatized **4** and **7** (Table 3), but we found almost no difference in the results. Geometry may also severely affect the validity of magnetic shielding calculations, as, for example, shown by Schleyer.[23b] Hence, we recalculated NICS values for parent species **4** and **7** for the geometries obtained at the CCSD/D95 level, which gave ΔR_{cc} values of 0.13 Å for both molecules, less bond-equalized than at the DFT level (Table 1). The results of the shielding calculation, although yielding somewhat reduced values for **4**, they hardly differed from the results obtained for the B3LYP geometries: **4** has NICS(0) = –10.8 [NICS(1) = –4.0] and –11.0 (–4.2) at B3PW91 level, respectively, whereas **7** yielded +3.3 (B3LYP) and +3.2 (B3PW91). The values obtained for the derivatized annulenes appear, therefore, to be reliable and show very clearly that **4b** and **4c** are neutral distinctly Möbius aromatic ground-state annulene systems, and their aromaticity is not reduced with respect to the parent annulene (Table 1). In contrast to the rather rigid Möbius[16]annulene core in the Herges system,[4] **4b** and related derivatives

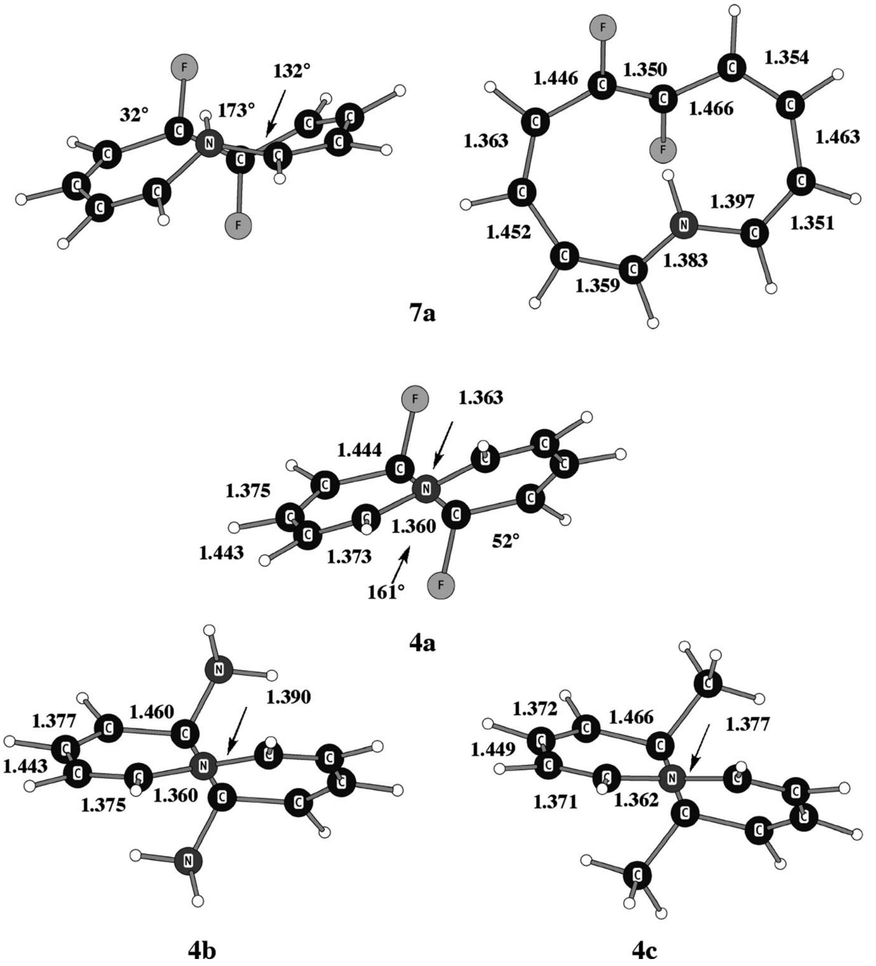

Figure 2. Depiction of derivatized Möbius conformation **4** and non-Möbius conformation **7**. Among the three hypothetically possible species, only the 6,7-difluoro derivative of **7** (i.e., **7a**) could be located on the B3LYP/6-31G* potential surface, which is shown in two different views. The display on the left shows the structural similarity of **7a** with Möbius **4a**. The 6,7-difluoro- (**4a**), 6,7-diamino- (**4b**), and 6,7-dimethyl-substituted (**4c**) Möbius aza[11]annulenes are all helically twisted C_2 molecules.

are proposed to be flexible molecules that could assume the Möbius aromatic conformation spontaneously!

In contrast, difluoro derivative **7a** appears to be a special case. Fluorine is known to withdraw σ electron density. This might lead to stabilization of the twisted form under the assumption that the bond-strain energy originates mostly from the σ framework. On the other hand, both **4a** and **7a** should profit from this effect. As the FCCF dihedral angle in **7a** is larger than that in **4a** (Figure 2), a principally conceivable "*gauche* effect",[34] explicable by hyperconjugation, can also not be the reason for the greater stability of **7a** vs. **4a**. The problem might be reformulated: although **7a** is even somewhat lower in energy than **4a**, one may wonder why hypothetical non-Möbius molecules **7b** and **7c** apparently do not exist on the B3LYP potential surface. We assume that the more sterically demanding NH_2 and CH_3 groups are repelled more strongly by the inwards pointing NH bond of the pyrrole nitrogen. We reasoned, therefore, that the "out" isomer variants of "Möbius" **4b** (with **3** as core annulene) and hypothetical **7b** (a conformation we have not explicitly considered here) might both coexist on the potential surface, albeit with higher energy. Indeed, 6,7-diamino-substituted **3** with Möbius topology (not shown here) is found about 15 kcal mol^{-1} higher in energy than "in" isomer **4b**, but we were, somewhat unexpectedly, not even able to find a viable structure on this very flat potential surface and that corresponds to a respective non-Möbius conformation. We conclude that the two stationary points on the PES, corresponding to species **4** and **7**, coalesce upon derivatization, as described above, into a single minimum pertaining to a Möbius aromatic molecule.

To counter a possible further objection regarding the orientation of the nitrogen lone pair on the amino groups in **4b** (restricted to C_2 symmetry during the geometry optimization) and in light of the more-or-less unhindered rotation around the C–NH_2 single bond, we also tried to locate a nonaromatic "Hückel topology" variant of **4b,** in which the lone pairs point outwards; again, the final structure (2.4 kcal mol^{-1} higher in energy than **4b** at the B3LYP/6-31G* level) possessed "Möbius" topology. Nonetheless, some traces of uncertainty remain: could an experiment or a coupled cluster geometry optimization possibly reveal that derivatized non-Möbius forms of aza[11]annulene are more stable than Möbius conformations like **4b** and **4c** after all? Even if this might be the case in certain situations, we are convinced that more involved substitution strategies could easily be envisaged that could yield a substantial predelection for the Möbius system without giving up the additional prerequisites of aromaticity and structural flexibility.

Another, but less facile, reaction mode of parent annulene **4** occurs through peculiar [1,6]-hydrogen shift transition-state structure **9** (Figure 1b), which is a remarkable 15.2 kcal mol^{-1} higher in energy than **4** and leads over to minimum **10**, which contains an sp^3 carbon atom that is higher in energy than **4**, probably because of the apparent diminishing of the aromatic stabilization in **10**. However, species **10** shows some traces of residual aromatic delocalization, even when the NICS points are placed in off-center positions (see Table 1 and Supporting Information). Heterocyclic examples of neutral homoaromatics have been recently reported,[35] and the "homo"-distance in **10** is a mere 2.44 Å. At this point, however, we do not claim that **10** is another representative of this elusive class of molecules. Minimum **4** could conceptually be divided by moving the trajectory of the hydrogen into two fused rings (see the structure of **9** in Figure 1b). The distinctly negative NICS values in the center of masses of both rings indicates that the reaction might be pericyclic (i.e., with eight electrons and antarafacial), rather than, for example, pseudopericyclic.[36] In principle, the transition state could be expected to be aromatic when there is orbital overlap between the nitrogen lone pair (which has 79.7% *p* orbital contribution in comparison to almost 100% *p* orbital lone pair in **4** and 73.9% *p* orbital contribution in **10**, according to the NBO analysis) and the *p* orbital of the carbon terminus of the migrating hydrogen (with strict orthogonality of the orbital array at the terminal C and N atoms, the net overlap would be zero and the transition state could, in principle, not be aromatic).[36b]

A third reactive mode, starting from **4**, seems to proceed via transition state **11**, which is 14.0 kcal mol^{-1} higher in energy and has a localized 12π electron system but still attains the Möbius topology. Whereas the "Möbius" topology, that is, the helically twisted topology, even in fully conjugated 4*n* electron systems is of course not necessarily related to aromatic stabilization,[20] the cyclic delocalization in **11** is effectively "switched off" because the C6(H)–N(H) bond angle is 83.8°, that is, close to 90° (see Figure 1b). We found, by inspecting the transition vector, that is, the atomic displacements at the "hilltop", that this transition state is connected on the other end of the minimum energy pathway on the potential surface to the nonsymmetric and nonaromatic minimum structure **12**, which very much resembles the conformation of a "D_2" form of [12]annulene.[2,15]

Another reaction that could potentially be conceived of, starting from Möbius **4**, is a 6π or 8π electrocyclic ring closure similar to that which produces a bicyclic dihydroindene cation species from the Möbius cyclononatetraenyl cation,[3] but the geometry of **4** does not appear to be very favorable for such a reactive mode. In addition, a transition-state structure for ring closure and that involves the nitrogen atom as a terminus, is probably very high in energy as a charge separated species with an ammonium cation might result as a product. This adverse effect could be alleviated though, in principle, by an immediate [1,2] H-shift from the nitrogen atom to the adjacent C10 carbon atom to give a more stable bicyclic product. We will report on these follow-up reactions in another report in the near future, only to reveal here that the respective bicyclic adduct is 12.4 kcal mol^{-1} more stable than **4**, but it is obtained only through a high activation barrier of about 46.1 kcal mol^{-1}! We conclude that Möbius heteroannulene **4** might indeed be a very promising synthetic target, provided that the facial reaction via TS **8** could be somehow hampered, for example, by introducing substituents, as discussed above.

The smallest Möbius annulene species, known since 1996, is Möbius benzene, which exists as a shallow minimum about 100 kcal mol^{-1} above the C_6H_6 ground state (107.9 kcal mol^{-1} at the computational level employed here).[37] The idea of replacing CH$^-$ by NH in 4*n*–1 annulenes, though, can be applied at least to a neutral seven-membered ring system: Möbius C_6H_6NH (**13**; Figure 1b), which has eight π electrons and a NICS value of –6.4 (Table 1). Whereas the C–N bond length is considerably extended to 1.40 Å, the range of C–C bond lengths (ΔR_{cc} = 1.36–1.46 Å) is hardly characteristic of a strongly delocalized molecule. The non-Möbius C_{2v} form, **14**, though, is strongly antiaromatic (NICS = +37.2), but 34.7 kcal mol^{-1} more stable! This result again illustrates the dominant role of strain energy introduced by the Möbius twist, despite a stabilizing trade-off from aromaticity in **13**.

Whereas there are already numerous papers that discuss examples of potentially Möbius aromatic systems, very little can be found in the literature on the physical reasons for their very existence. Is there a physical rationale for Möbius aromaticity? Aromaticity itself might be seen in principle − strongly simplifying − as a result of a certain pattern in the eigenvalue spectrum of the Hamiltonian, which, in HMO theory, can be derived from the adjacency graph with signed edges connecting the vertices of the graph (every vertex representing a ring atom). If one (or an odd number) of edges has a negative weight, the lowest π orbital becomes degenerate, also illustrated by the well-known Frost–Musulin mnemnonics.[38] Hückel's rule could, in principle, then be derived from the eigenvalue spectrum in a circular potential well with the angular momentum quantum numbers forming the series m = 0, 1, –1, 2, –2, etc. Filling these orbits pairwise up from below with electrons results in a total of 4*n*+2 electrons needed for a "closed" shell. In contrast, Möbius systems (in a hypothetical, idealized picture) have an eigenvalue spectrum where the smallest eigenvalue is degenerate (in HMO theory) and, hence, 4*n* electrons would be necessary to arrive at a closed shell. However, such a degenerate ground state is unphysical, because it would be always possible to create a linear combination that contains a node from the two degenerate orbital functions − in contradiction to the fundamental physical stipulation that the lowest quantum energy level should be nodeless.[39] At a higher, that is, correlated, level of theory (like, e.g., the DFT method applied here) this unphysical degeneracy is lifted.

Indeed, it has been shown generally[40] that the nature of the lowest eigenvalue of the Hamiltonian that includes at least an exchange correlation potential and in one dimension (which might be seen as an appropriate model for an annulene) could be categorized by the electron count and the total spin of antiferromagnetically coupled electrons in dependence of the boundary conditions. Hence, the respective Hilbert space with an odd/odd combination of spin-up/spin-down π electrons (as, for example, in benzene), and a total number of $4n+2$ electrons, corresponds to a closed-shell singlet only for periodic boundary conditions (like those in benzene), whereas in the respective Hilbert subspace with an even/even combination of spins and for a total of $4n$ electrons, that situation is encountered only with antiperiodic (i.e., Möbius) boundary conditions.[40] It should be noted that topology (i.e., geometric properties) did not enter these quantum-mechanical considerations at all. It seems that despite the wealth of examples for odd-parity (i.e., with an odd number of paired π electrons)[41] Hückel aromatic molecules (with periodic boundary conditions) compared to the apparent rarity of even-parity Möbius aromatics (with antiperiodic boundary conditions), the existence of Möbius aromaticity reflects fundamental physical laws. That Möbius aromatics nonetheless still play rather a maverick role in laboratory chemistry – if at all – could be due to the adverse effect of the strain energy that accompanies the geometric twist.

Heilbronner also suggested that – formally – Hückel topology $4n$ electron triplet annulenes could be twisted to become singlet aromatics with the Möbius topology,[1] but it also follows from Hückel triplet $4n$ electron aromaticity[42] in conjunction with Möbius singlet $4n$ electron aromaticity, as a corollary, that Möbius triplets would be aromatic in the triplet electronic state with $4n+2$ electrons! Imaginatively, the concept of Möbius triplet $4n+2$ electron annulenes can therefore be derived from reversing Heilbronner's idea: "Hückel $4n+2$ electron singlets", twisted to assume the Möbius strip topology, become "Möbius triplet aromatics".[2,43] Such species could conceivably play a role in organic photochemistry.[44] and are subject to the same theoretical treatment as singlet Möbius systems – taking into account the higher spin multiplicity.[40] A paradigm example is the cyclononatetraenyl anion (**15**; with 10π electrons) in its triplet state and which exhibits perfect C–C bond length equalization (ΔR_{cc} 0.01 Å, Table 4 and Figure 3) and a NICS value of –12.0 (–10.8 at RHF/6-31+G*).[2]

The $(CH)_{11}^+$ triplet potential surface[2,45] has only recently been studied again, and very thoroughly.[45] Warner, also employing B3LYP/6-31G*, and, additionally, CCSD(T)/6-31G*//B3LYP/6-31G* computations, validated many of the first authors earlier results.[2,45] Most remarkably, the coupled cluster single-point energies deviated mostly only about 10% from the B3LYP results for minima and transition states, which we see as an additional corroboration for the validity of the computational level we employ in this paper.[45]

Table 4. B3LYP/6-31G* relative energies (ZPE corrected), range of C–C bond lengths (ΔR_{cc}), and NICS aromaticity indices for neutral and charged Möbius triplet $4n+2$ electron aromatic annulenic species and related reference compounds.

Species (NIMAG), Multiplicity	Topology, point group	Rel. Energy	ΔR_{cc}	NICS[a]
15 (0), 3	M, C_2	–	0.01	–12.0 (–10.8)[b]
16 (0), 3	M, C_2	0.0	0.03	–14.1
17 (0), 3	M, C_2	7.4	0.03	–10.0
18 (0), 3	M, C_2	4.5	0.06	–2.83
19 (0), 3	M, C_2	52.0	0.06	–7.7
20 (0), 1	H, C_{2v}	0.0	0.03	–13.6
21 (0), 3	H, C_s	41.0	0.08	+0.1

[a] With GIAO method at B3LYP/6-31G*. NICS points were set at the center of mass of the heavy atoms. [b] From ref.[2] at RHF/6-31+G* level.

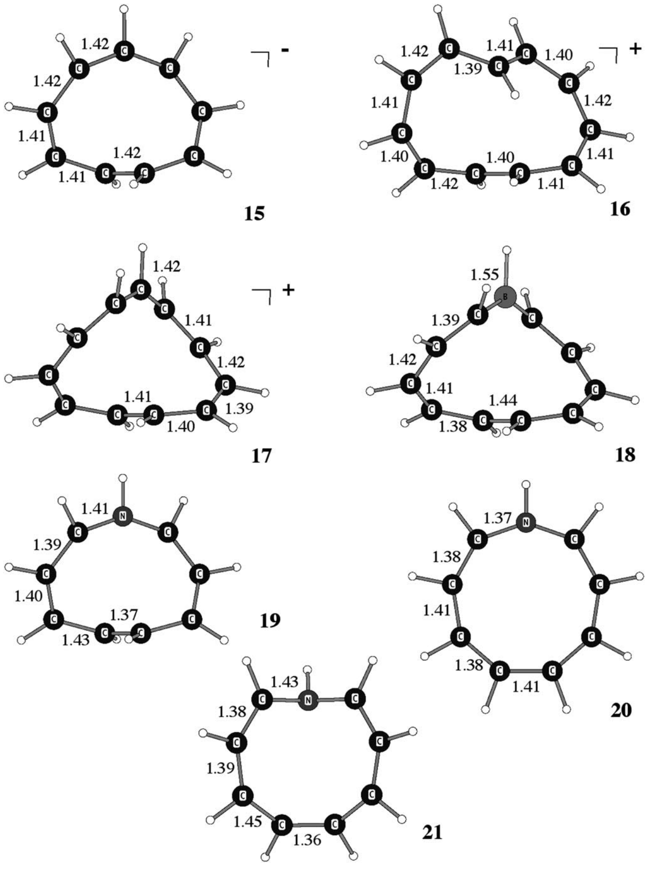

Figure 3. Möbius $4n+2$ electron triplet aromatic species **15**–**19** and Hückel topology reference compounds **20** and **21**.

The "in" isomer **16** (Figure 3) is more stable than the "out" form **17** (not found by Warner) by 7.4 kcal mol^{-1} at UB3LYP/6-31G* (Table 4), which reflects the near-optimal C–C–C bond angles in **16**. The idea of replacing charged methine fragments by neutral XH moieties, and that, for example, led from **2** to **4**, can also be extended to group 13 elements: replacing a CH^+ unit by BH gives the 10-electron neutral species **18**, which is the only Möbius neutral boron-containing heteroannulene we were able to locate in this study, both on the triplet and the singlet potential surfaces.

Boron, with its empty *p* orbital, is already known for its reluctance to take part in aromatic delocalization.[46] Hence, it is not surprising that the NICS value displayed by **18** is very small and hardly indicative of aromaticity (–2.83, Table 2). On the other hand, pyrrole congeners appear to be better suited to exhibit Möbius aromatic properties, and indeed, C_8H_8NH (**19**) assumes a Möbius twisted C_2 conformation with a moderate NICS value (Table 4), but it is 52.0 kcal mol^{-1} higher in energy than the Hückel aromatic (and Hückel topology) singlet **20**, with its NICS value that outsmarts benzene (NICS = –9.6 at this level of theory, also cf. the results in Table 1!). Such planar, nine-membered ring heterocycles like **20** were studied computationally in detail in 2003 by Schleyer and coworkers.[47]

It was surprising for us to find another C_s triplet species, **21** (Figure 3), 11 kcal mol^{-1} lower in energy than **20,** albeit without the Möbius topology and nonaromatic (NICS = +0.1, Table 2). It should be noted that this species could principally not be "Hückel triplet aromatic",[31] because the electron count does not fit. It appears to us that the "Möbius aromaticity" on the singlet or triplet potential surfaces is overall a rather weak effect and that the aromatic stabilization can only rarely overcome other adverse influences.

Conclusions

We have shown that despite recent experimental successes in preparing large Möbius aromatic porphyrin-type molecules that involve coordination to transition metals, it should not be impossible to synthesize much simpler and smaller, neutral heteroannulenic Möbius aromatics by standard laboratory methods. Such molecules could become a competitive synthetic target, which might offer easy access to further investigations of the properties of Möbius aromatic molecules.

However, in contrast to porphyrin systems, annulenes are very flexible and might devolve facially into more stable, nonaromatic conformations. Despite such drawbacks, we are convinced that Möbius heteroannulenes, as those presented here, are, due to their simplicity and low dimensionality, particularly suited for putting hypotheses about the chemical and physical consequences of the Möbius π-type delocalization to a test.

Möbius triplet aromaticity, introduced in 1999, is not yet a widely known concept, at least when ground-state molecules (i.e., potential surface minima) are concerned. That such molecules play an important role on their respective potential surfaces has been, in our opinion, convincingly demonstrated. The concept of Möbius triplet aromaticity completes the set of the four basic types of aromaticity: Hückel, Hückel triplet, Möbius, and Möbius triplet aromaticity.[2,43]

We find that Möbius aromaticity constitutes a fascinating, and, even after 10 years of research, still not fully explored topic in chemistry. An easily accessible synthetic route to singlet Möbius aromatic heteroannulenes remains to be found, as this would facilitate the exploration of their chemical and physical properties. Work to meet this challenge is presently underway in our laboratory.

Experimental Section

Computational Methods: Geometry optimizations were carried out with approximate density functional theory (at RB3LYP/6-31G* and UB3LYP/6-31G* levels) and coupled cluster theory (CCSD/D95 level) by employing the GAUSSIAN 03 program package.[26] Benchmark calculations were performed at the CCSD(T)/D95*//B3LYP/6-31G* level. All species were characterized as either minima or transition-state structures on the B3LYP/6-31G* potential surface by counting the number of imaginary frequencies (NIMAG) by carrying out vibrational frequency calculations with the use of the harmonic approximation and including ZPE corrections. Magnetic shielding calculations were carried out with the gauge-independent GIAO method at the B3LYP/6-31G* and B3PW91/6-31G* levels.

Supporting Information (see footnote on the first page of this article): Cartesian coordinates of the species discussed in the text and the positions of the nucleus-independent chemical shift (NICS) points.

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