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Stability and Aromaticity of Charged Möbius[4*n*]Annulenes

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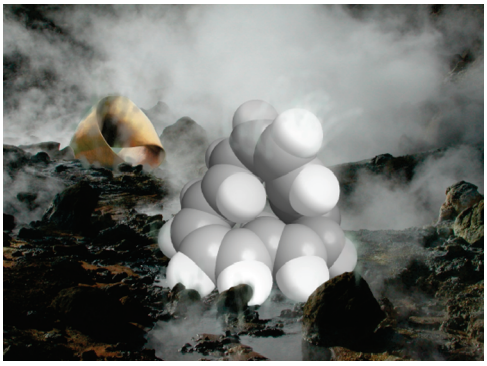

A number of parent aromatic Möbius annulenes that violate the Hückel rule have been proposed theoretically. Unfortunately, these species are thermodynamically and kinetically unstable and probably impossible to synthesize. We therefore systematically screened a large number of annulene anions, dianions, and dications and predict that a Möbius [14]annulene dication is not only the most stable isomer among these monocyclic structures but also the global minimum on the $(CH)_{14}^{2+}$ hypersurface including bicyclic and tricyclic isomers. Thus, under stable ion conditions the Möbius [14]annulene dication should be stable toward *cis*−*trans* isomerizations and electrocyclic reactions which are the most probable pathways limiting the lifetime of Möbius annulenes.

Introduction

Möbius rings are exceptional systems because they are one-sided and nonorientable.[1] The Möbius topology was first introduced into chemistry by Heilbronner 1964.[2] He predicted that Möbius-type annulenes violate the Hückel rule. Annulenes with 4*n* electrons which are antiaromatic in "normal" cyclic conjugated systems are stabilized by the Möbius twist according to simple Hückel calculations. Higher level quantum chemical calculations that were performed later on a number of twisted annulenes confirmed that in fact the Hückel rule is reversed if an odd number of 180° twists is introduced into the cyclic π system of an annulene.[3,4] Möbius annulenes were considered to be exotic and extremely hypothetical systems because the twist should build up considerable strain in the ring and because there was no synthetic strategy for the preparation of such a system. However, Fowler and Rzepa pointed out that a large part of the strain can be projected into writhe if the planar twisted ring would distort into 3D, e.g., a figure 8 shape system.[5] We earlier noted that double-twisted systems are abundant among extended porphyrins.[4b] Latos-Grażyński[6] and Osuka[7] recently prepared and characterized a number of single-twisted extended Möbius porphyrins. The

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first stable and weakly aromatic annulene derivative with Möbius topology was synthesized in 2003.[4a,8] The twist in this Möbius [16]annulene was stabilized by the introduction of a pyramidalized bianthraquinodimethane building block. The parent [16]annulene is almost planar,[9] and the most stable parent Möbius isomer is predicted to be more than 4 kcal mol^{-1} higher in energy[3,4a,8] (and never was observed experimentally). In contrast, the most stable bianthraquinodimethane-modified [16]annulene Möbius structure is >5 kcal mol^{-1} more stable than the most stable Hückel isomer.[4a,8] Theoretical calculations predict that in neutral unsubstituted [*n*]annulenes (n = 12, 16, and 20) the Hückel (untwisted) isomers are always more stable than their Möbius pendants.[3a,10] Obviously, any stabilization by Möbius aromaticity is more than outmatched by the ring strain induced by the twist. Thus, the synthesis of an unsubstituted Möbius annulene is still one of the most challenging targets in "non-natural product chemistry". Unfortunately, [*n*]annulenes are extremely flexible structures. They undergo facile *cis*−*trans*-isomerization and bond shifting.[11] The Möbius isomers are not only thermodynamically but also kinetically unstable. Thus, even low-temperature isolation or trapping of a Möbius intermediate should be extremely difficult. On the route to the synthesis of a stable, parent Möbius annulene we therefore screened the charged annulenes (cations, dications, anions, and dianions). Mauksch et al. previously suggested that charged Möbius annulene anions and cations[12] are diatropic and more stable than their nonaromatic counterparts.[13]

The [9]annulene cation is probably the smallest annulene that conceivably could accommodate a twist in its π system. The Möbius [9]annulene cation was predicted to be a short-lived intermediate in the solvolysis of 9-chloro[6.1.0]bicyclononatriene.[14] However, according to recent calculations and flash photolysis experiments, the intermediate is most probably a nontwisted [9]annulene cation.[15] The cation cannot be isolated or even trapped because it undergoes a very fast electrocyclic ring closure to a more stable bicyclic system. Hence, the Möbius [9]annulene cation is neither thermodynamically nor kinetically stable. The next higher homologues are the [13]-, [17]-, and [21]annulene cations. Recent calculations predict that the most stable isomer of the [13]annulene cation is a Möbius structure and that electrocyclic ring closure (which is the most probable reaction for destruction of the cation in an inert solvent and with a non-nucleophilic counterion) is endothermic with a high barrier of activation. Concerning the [17]- and [21]annulene cation, the case is less clear-cut.[16] Unfortunately, a suitable precursor for the [13]annulene cation is difficult to synthesize.

To find an easier accessible synthetic target for a parent Möbius annulene we theoretically investigated the homologue series of annulene anions ([11], [15], and [19]), dications ([10], [14], and [18]) and dianions ([10], [14], and [18]). We analyzed the potential energy hypersurface (PES) of each of the $(CH)_n^{m+}$ or $(CH)_n^{m-}$ annulene systems by generating a very large number of isomers using a Monte Carlo force field method.[17] The isomers were ranked by relative energy, aromaticity and topology. The most promising Möbius targets were investigated concerning their susceptibility toward electrocyclic ring-closure reactions.

Computational Details

Isomers of each annulene series were generated using a Monto Carlo force field method.[17] Redundant structures were automatically removed and energy cut-offs were set to reduce computational cost. The remaining structures were subjected to semi-empirical PM3[18] calculations and the structures passing a second and lower energy cutoff were optimized[19] at KMLYP/6-31G*.[20] The 20 most stable isomers were also calculated at KMLYP, BH&HLYP,[21] and B3LYP[22] functional using the 6-311+G** basis set. Unfortunately, DFT methods are known to suffer from a number of deficiencies such as self-interaction error, severe underestimation of dispersion energies, and other medium-correlation energy problems.[23] The errors are cumulative, so that the DFT methods will exhibit larger errors for larger structures. There are mainly two popular approaches to reduce these deficiencies in DFT: (a) including a larger amount of Fock exchange or (b) including parts of conventional wave function methods (e.g., B2PLYP). To get an idea of the accuracy and reliability of our results we used a number of different DFT approaches (B3PW91/6-311+G**,[24] MPWB1K/6-311+G**[25] and B2PLYP/6-311+G**[26]) for structure optimizations. Unfortunately, also post SCF ab initio

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methods such as MP2 exhibit systematic errors such as overestimation of aromaticity. Therefore, we performed calculations at the SCS-MP2,[27] a spin-component scaled MP2 method, using the Ahlrich basis set def2-TZVP.[28]

Coupled cluster calculations at the CCSD(T) level including a flexible basis set are considered to be the gold standard in ab initio theory. However, optimizations at this level are prohibitive for large systems. According to our experience with the [9]annulene cation hypersurface CCSD(T), single-point calculations on SCS-MP2 optimized geometries are very close to the gold standard CCSD(T)/CBS.[29] Unfortunately, only the smaller systems ([10]annulene dication, [10]annulene dianion, [14]annulene dication, and the [11]annulene anion) could be treated at this level. CASSCF/cc-pVTZ and CASPT2/cc-pVTZ[30] single-point calculations based on UB3PW91/6-311+G**-optimized geometries were performed[31] for the most stable Hückel and the most stable Möbius isomer of the [14]annulene dication to assess their diradical character. The active space for the CASSCF calculations is formed by 12 electrons in 14 orbitals (all electrons and orbitals in the conjugated π system). For the quantification of aromaticity, the HOMA method[32] and the nucleus-independent chemical shift (NICS(0))[33] at the BH&HLYP/6-311+G**//BH&HLYP/6-311+G** level of theory was used. For the [14]-annulene dication, the density of delocalized electrons and the current density of the ring current was calculated using the ACID program.[34] When the global minimum of an annulene hypersurface was identified as an isomer with Möbius topology, we also investigated its kinetic stability and calculated all conceivable electrocyclic ring-closure pathways at the BH&HLYP/6-311+G** and B3PW91/6-311+G** level of theory.

Results and Discussion

[*n*]Annulene Dications. Figure 1 presents an overview of the most stable Möbius and Hückel structure in each series of the [10]-, [14]-, and [18]annulene dications. We used the B3PW91 functional for an initial comparison of the different species because this functional proved to provide reliable relative energies in the [9]annulene cation and [13]annulene cation series and because the more reliable ab initio methods such as CCSD(T) are too expensive to be applied to the large [18]annulene dications.

The most stable isomer of the [10]annulene dication is the aromatic C_2 mono *trans* Möbius species **1a** at all levels of theory

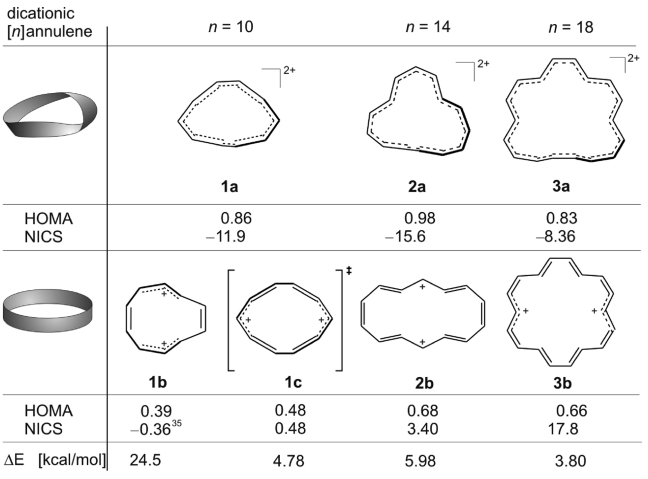

FIGURE 1. Relative energies of the most stable Hückel and Möbius isomer of [10]-, [14]-, and [18]annulene dications at the B3PW91/6-311+G** level of theory. The structures are two-dimensional representations of the optimized geometries (B3PW91/6-311+G**) of the most stable isomer of both topologies in each series of annulenes. Hydrogen atoms are omitted for clarity. The positive charge is almost equally delocalized in the aromatic Möbius annulenes but more or less localized in an allyl or pentadienyl unit in the antiaromatic Hückel systems. The HOMA and NICS values are determined at BH&HLYP/6-311+G**/BH&HLYP/6-311+G**. According to frequency calculations, **1c** is the transition state of the racemization of **1a**.

(NICS = −11.9; HOMA = 0.86) (see Table 1, Figure 1). The most stable Hückel isomer **1b** is at least 18.2 kcal mol^{-1} higher in energy (see Table 1).[36]

The structure of **1a** resembles the Möbius structure of the [9]annulene cation.[14,15] Both annulenes include one *trans* bond, exhibit C_2 symmetry, and are chiral. the transition state of the racemization of **1a** is a D_2 symmetric structure **1c**. The barrier, however, is quite low with 4.46 kcal mol^{-1} at the MPWB1K, 3.92 kcal mol^{-1} at the B3LYP, 4.78 kcal mol^{-1} at the B3PW91, 6.06 kcal mol^{-1} at the B2PLYP, and 8.18 kcal mol^{-1} at the SCS-MP2 level of theory. A CCSD(T)/cc-pVTZ calculation at the SCS-MP2/def2-TZVP-optimized geometry confirmes that the Möbius isomer is the global minimum within ab initio theory. The transition state (**1c**) of the racemization of the Möbius structure **1a** is 4.75 kcal mol^{-1}. To check the kinetic stability of **1a**, we investigated a number of conceivable ring-closure pathways. The Möbius isomer **1a** undergoes a disrotatory ring closure with an activation barrier of 7.71 kcal mol^{-1} at the B3PW91/6-311+G** level of theory and leads to the formation of the bicylic homoaromatic product **4** (see Scheme 1). This reaction is exothermic with −19.2 kcal mol^{-1}. Thus, the Möbius [10]annulene dication **1a** is neither thermodynamically nor kinetically stable, difficult to detect, and probably impossible to isolate.

The most stable isomer of the [14]annulene cation is predicted to be the aromatic (NICS = −15.6, HOMA = 0.98) penta-*trans* Möbius species **2a** with C_2 symmetry (see Figure 2). Another penta-*trans* Möbius structure with C_1 symmetry was found to be 2.14 kcal mol^{-1} higher in energy at B3PW91/6-311+G**. The most stable Hückel isomer **2b** was identified as an almost planar (C_{2h} symmetrical), octa-*trans* species with weak antiaromatic properties (NICS = 3.4, HOMA = 0.68). Anisotropy of the induced current density (ACID) calculations[34] indicate that both **2a** and **2b** exhibit a cyclic system

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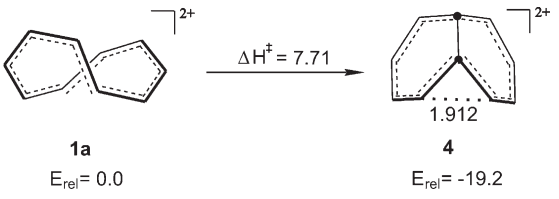
(36) A Hückel structure **1d** could be located with 0.59 kcal/mol higher energy relative to the Möbius twist **1a** at BH&HLYP/6-311+G**, but no other level of theory could be found in the C_{2h} structure **1d** as a stationary point (for more information see the Supporting Information).

TABLE 1. Energies of the Most Stable Möbius Structure and the Most Stable Hückel Isomers of the Charged [*n*]Annulenes (Energies Are Relative to the Most Stable Möbius Structure)

				E_{rel}[d]				E_{rel}[e]		E_{rel}[f]
[*n*][a]	c[b]	s	T[c]	BH&HLYP/ 6-311+G**	MPWB1K/ 6-311+G**	B3LYP/ 6-311+G**	B3PW91 6-311+G**	B2PLYP/ 6-311+G**[h]	SCS-MP2/ def2-TZVP	CCSD(T) cc-pVTZ
10	2+	**1a**	M	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	2+	**1b**	H	+23.70	+24.80	+24.80	+24.50	+26.40	+18.20	+21.10
10	2+	**1c**	H	+1.42[g]	+4.46[g]	+3.92[g]	+4.78[g]	+6.06[g]	+8.18[g]	+4.75
14		**2a**	M	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14	2+	**2b**	H	+2.74	+4.69	+6.02	+5.98	+7.84	+10.80	+5.74
18[f]	2+	**3a**	M	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18[f]	2+	**3b**	H	−0.98	+1.80	+2.84	+3.80	+6.62		
10	2−	**15a**	M	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	2−	**15b**	H	−0.27	−0.96	+1.67	+1.42	+1.06	+5.24	+2.23
14	2−	**16a**	M	0.00	0.00	0.00	0.00	0.00	0.00	
14	2−	**16b**	H	−3.17	+0.34	−0.01	−0.76	+2.42	+7.28	
18[f]	2−	**17a**	M	0.00	0.00	0.00	0.00	0.00	0.00	
18[f]	2−	**17b**	H	−11.90	−8.74	−7.20	−6.15	−0.06		
11	1−	**18a**	M	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	1−	**18b**	H	−2.94	−1.95	−0.02	+0.27	+0.76	+1.06	−1.51
15	1−	**19a**	M	0.00	0.00	0.00	0.00	0.00	0.00	
15	1−	**19b**	H	−3.65	−0.86	−0.30	+0.53	+2.50	+4.50	
19	1−	**20a**	M	0.00	0.00	0.00	0.00	0.00		
19	1−	**20b**	H	−4.12	−1.99	−0.56	+0.15	+3.43		
19[f]	1−	**20c**	H	−4.53	−2.41	−0.55	+0.09	+3.76		

[a][*n*] indicates the number of carbon atoms in the annulene ring. [b]c is the charge of the structure. [c]T: M = Möbius topology, H = Hückel topology. [d]E_{rel} (kcal mol^{-1}) is the relative energy with respect to the energetically most stable Möbius structure after ZPE corrections at the same level of theory. [e]E_{rel} (kcal mol^{-1}) is the relative energy with respect to the energetically most stable Möbius structure (including ZPE corrections at the B3LYP/6-311+G** level of theory). [f]E_{rel} (kcal mol^{-1}) is the relative energy at CCSD(T)/cc-pVTZ//scs-mp2/def2-TZVP level of theory relative to the most stable Möbius isomer (including ZPE corrections at the B3LYP/6-311+G** level of theory). [g]Transition state according to frequency calculation. [h]The basis set 6-31G* was used for the B2PLYP level of theory (including ZPE corrections at the B3LYP/6-311+G** level of theory).

SCHEME 1. Kinetically Most Favorable Electrocyclization of the Most Stable [10]Annulene Dication (B3PW91/ 6-311+G + ZPE)[a]**



[a]The homoaromatic bond distance is given in Å, and E_{rel} and $\Delta H^{\ddagger}$ are given in kcal mol^{-1}.

of delocalized electrons (Figure 2). However, the current density vectors plotted on top of the ACID isosurface reveal that the Möbius structure **2a** contains a strong diatropic ring current indicating aromaticity, whereas in the Hückel isomer **2b** the ring current circulates in reverse direction (paratropic current) indicating antiaromaticity. All DFT and ab initio levels of theory agree in that the Möbius isomer **2a** is the global minimum (see Table 1).

Calculations at the coupled cluster level of theory (CCSD(T)/cc-pVTZ) revealed that the Möbius species **2a** is 5.74 kcal mol^{-1} more stable than its Hückel counterpart **2b**. Karney et al. recently found that several transition states of bond-shifting isomerization of the neutral [14]annulene exhibit a strong singlet diradical character.[11b] To assess the degree of open shell character in **2a** and **2b**, we performed unrestricted B3PW91/6-311+G** optimizations and CASSCF/cc-pVTZ and CASPT2/cc-pVTZ single-point calculations. The unrestricted DFT wave functions converged to the previously calculated restricted wave functions. The analysis of the CASSCF wave functions revealed that the main determinant contributes 73% and 76% to the total wave function (3% and 1% of the second most important determinant) for **2a** and **2b**. The diradical character of both species obviously is rather low, and DFT and particularly CCSD(T) calculations should fully account for the correlation energy due to singlet open shell character. A similar conclusion can be derived from CASPT2 calculations. The singlet diradical character is expected to be more important for the antiaromatic Hückel compound **2b**. Thus, a more adequate treatment of the correlation problem should rather lower the energy of **2b** with respect to **2a**. The energy difference ($\Delta E = E_{2b} - E_{2a}$) computed with CASPT2 (7.99 kcal mol^{-1}), however, is even larger than ΔE calculated with CCSD(T) (5.74 kcal mol^{-1}) or B3PW91 (5.98 kcal mol^{-1}).

To evaluate the feasibility of isolation or trapping, we investigated its kinetic stability. Several electrocyclic ring closure reactions were calculated, and the thermodynamically most favorable reaction is shown in Scheme 2.

According to our computations (B3PW91/6-311+G**) the most favorable intramolecular reaction of the Möbius dication **2a** involves an isomerization to **2c**, which is followed by an endothermic conrotatory electrocyclization to the bicyclic structure **5** with a barrier as large as 26.3 kcal mol^{-1}. The second exothermic ring closure proceeds with a barrier of only 2.54 kcal mol^{-1} to the tricyclic dication **6**. Among 51 tricyclic $(CH)_{14}^{2+}$ structures, the [9.3.0^{4,8}] system **6** is lowest in energy but, however, still 4.81 kcal mol^{-1} higher in energy than Möbius [14]annulene **2a**. Thus, Möbius annulene **2a** is the most stable isomer on the $(CH)_{14}^{2+}$ hypersurface, and there is a good chance that it can be generated by ionization of a suitable bicyclic or tricyclic precursor. A set of potential tricyclic dications is given in Figure 3.

Calculations on the PES of the [18]annulene dication predict that the most stable monocyclic isomer Möbius

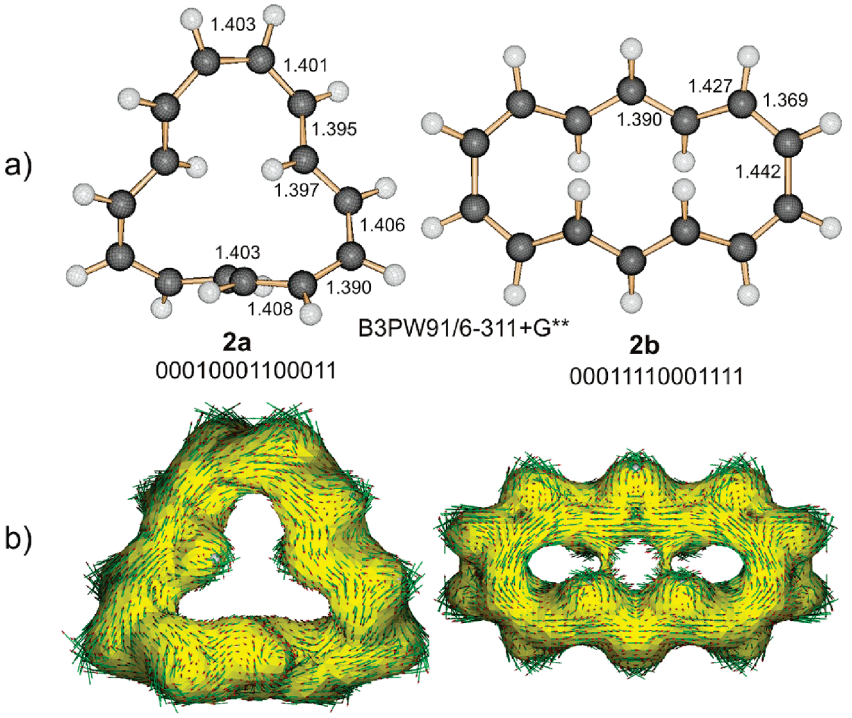
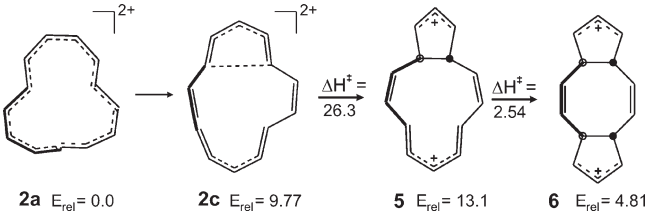


FIGURE 2. (a) Geometries of the most stable Möbius structure **2a** (C_2) and the most stable Hückel isomer **2b** (C_{2h}) of the [14]annulene dications at B3PW91/6-311+G**. C−C bond lengths are given in Å for different levels of theory. The binary numbers indicate the cis (0), trans (1) configuration of each bond in each structure. (b) ACID isosurface plots (isosurface value 0.05) of the Möbius isomer **2a** and the Hückel structure **2b**. Current density vectors are plotted onto the isosurface. A clockwise ring current indicates a diatropic (aromatic) ring current (**2a**), and anti clockwise currents are paratropic (antiaromatic) (**2b**). The magnetic field is oriented parallel to the principal axis of inertia and pointing toward the viewer.

SCHEME 2. Kinetically Most Favorable Electrocyclization Reactions of the Most Stable Isomer 3a (All Energies in kcal mol^{-1} Calculated Relative to 3a at B3PW91/6-311+G + ZPE)**



(**3a**) is somewhat more stable than the most stable Hückel structure (**3b**) (see Figure 1). However, at the B3PW91/6-311+G** level of DFT the energy difference is only 3.80 kcal mol^{-1} (Table 1) Thus, the [18]annulene dication is not one of the most promising candidates for experimental realization.

[*n*]Annulene Dianions. The most stable Hückel and Möbius isomers of the [10]-, [14]-, and [18]annulene dianion series are presented in Figure 4. Obviously, the untwisted Hückel structures are favored with increasing ring size within the [*n*]annulene dianion series.

The exploration of the most stable isomers of both topologies of the [10]annulene dianion revealed that an aromatic mono-*trans* Möbius structure **15a** with C_2 symmetry (NICS = −11.7, HOMA = 0.88) is the global minimum. The most stable Hückel structure is the C_{2h} tetra-*trans* Hückel species **15b** with weakly anti- or nonaromatic properties (NICS = −3.72, HOMA = 0.52)[35b,37] (see Figure 4). According to a CCSD(T) energy calculation based on a SCS-MP2 geometry, the energy difference is as low as 2.23 kcal mol^{-1}, and thus, **15a** is probably not long-lived enough for isolation in an experiment.

In the case of the [14]annulene dianion, the energy difference between the most stable Möbius and Hückel structures is even smaller as compared to the [10]annulene dianion. DFT and ab initio methods disagree as to which topology would be preferred (Table 1). Among the [18]annulene isomers, a Hückel isomer is probably the most stable species. At the B3PW91/6-311+G** level, the Hückel structure **17b** is 6.15 kcal mol^{-1} lower in energy than the Möbius pendant **17a**.

[*n*]Annulene Anions. Figure 5 contains an overview of the most stable Hückel and most stable Möbius structures of the [11]-, [15]-, and [19]annulene anions. Theoretical studies on the stability and properties of the [11]- and [15]annulene anion isomers were previously published by Mauksch.[13]

In agreement with previous calculations,[13] the most stable isomer of the [11]annulene anion with Möbius topology is a tri-*trans* aromatic C_1 structure **18a** (NICS = −18.3, HOMA = 0.89), and the most stable Hückel isomer is the weakly antiaromatic tetra-*trans* structure **18b** with C_2 symmetry (NICS = 0.57, HOMA = 0.45). Calculations of Mauksch et al. at the B3LYP/6-31G* level of theory predicted that the Möbius structure **11a** would be the global minimum.[13] Both structures **18a** and **18b** differ in just one dihedral angle (see Figure 4). According to our DFT calculations, the energy difference between **18a** and **18b** is very small; some of the functionals are in favor of the Hückel species, and some

(37) Strong local effects are responsible for the positive NICS value; the neighboring hydrogen atoms are very close to the ghost atom (1.170 Å).

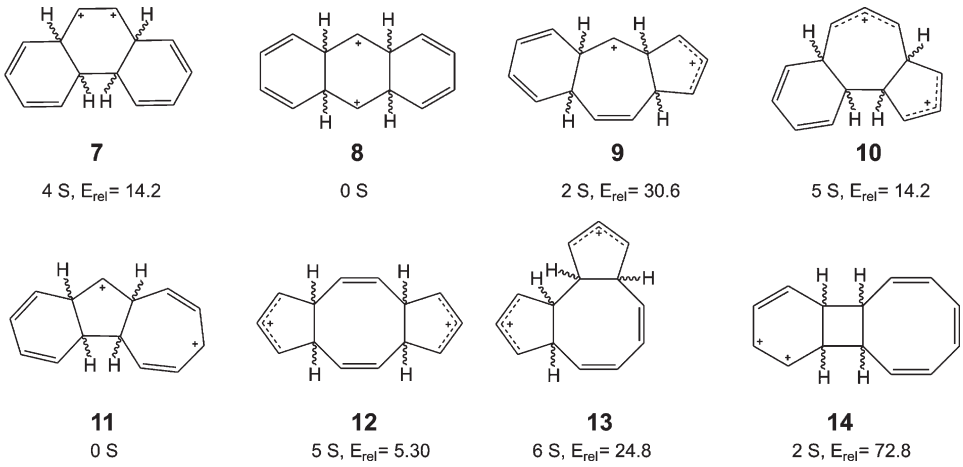


FIGURE 3. Structures and relative energies (in kcal mol^{-1} relative to **2a** at B3PW91/6-31G*) of potential tricyclic precursor dications for the generation of the Möbius dication **2a**. A total of 51 tricyclic dications were calculated (including all conceivable stereoisomers). The number of stereoisomers *S* of each structure which were confirmed as minima is given. Compounds **8** and **11** are not minima but undergo a 1,2 H-shift without activation barrier.

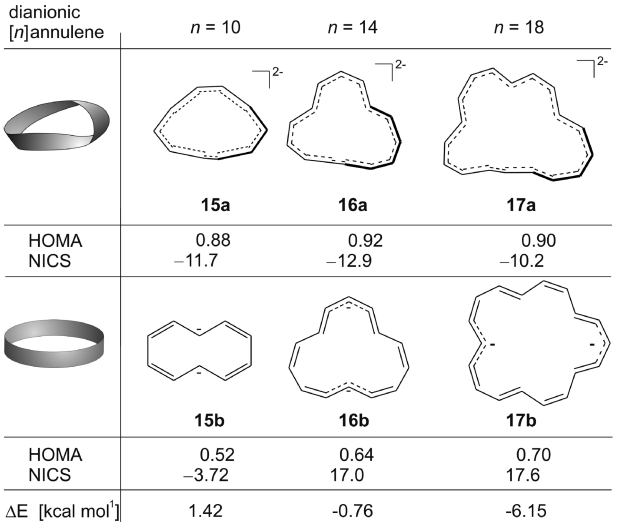


FIGURE 4. Relative energies of the most stable Hückel and Möbius isomers of [10]-, [14]-, and [18]annulene dianions at the B3PW91/6-311+G** level of theory. The structures are two-dimensional representations of the optimized geometries (B3PW91/6-311+G**) of the most stable isomer of both topologies in each series of annulenes. The hydrogen atoms are omitted for clarity. The negative charge is almost equally delocalized in the aromatic Möbius annulenes but more or less localized in an allyl or pentadienyl unit in the antiaromatic Hückel systems. The HOMA and NICS values are performed at BH&HLYP/6-311+G**/BH&HLYP/6-311+G**.

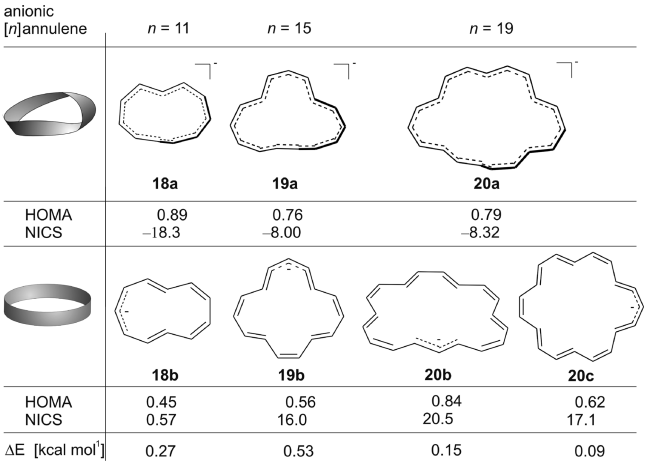


FIGURE 5. Relative energies of the most stable Hückel and Möbius isomer of [11]-, [15]-, and [19]annulene anions at the B3PW91/6-311+G** level of theory. The structures are two-dimensional representations of the optimized geometries (B3PW91/6-311+G**) of the most stable isomer of both topologies in each series of annulenes. The hydrogen atoms are omitted for clarity. The negative charge is almost equally delocalized in the aromatic Möbius annulenes but more or less localized in an allyl or pentadienyl unit in the antiaromatic Hückel systems. The HOMA and NICS values are performed at BH&HLYP/6-311+G**/BH&HLYP/6-311+G**.

prefer the Möbius species. Calculations at the more reliable CCSD(T) level of theory predict the Hückel structure to be more stable by 1.51 kcal mol^{-1}. Similar to the [11]annulene anion, the most stable Hückel and Möbius isomers of the [15]annulene anion are very close in energy.[13a,38] The theoretical results are inconsistent. Unfortunately, the systems are too large to be treated at the coupled cluster level CCSD(T). The number of conceivable isomers increases with increasing ring size. On a combinatorial basis, there are 14310 *cis*−*trans* isomers of the [19]annulene anion. Hence, there are a number of isomers closer in energy than the error bar of simple DFT calculations. Our DFT calculations agree on the most stable Möbius isomer; however, there are two different Hückel structures competing for the most stable species. As in the previous cases, the question remains open whether a Hückel or Möbius structure would be the most stable isomer.

Conclusions

Among the annulenes investigated in this study, the [10]- and particularly the [14]annulene dication are the most promising candidates for the synthesis or at least trapping or spectroscopic detection of unsubstituted Möbius annulenes. Both are global minima among the conceivable monocyclic

(38) Mauksch calculated several isomers of the [15]annulene anion in his thesis; however, different structures are presented here.

isomers. The most favorable intramolecular reaction for the decay of the dications is electrocyclic ring closure. The [10]annulene dication is predicted to cyclize in an exothermic reaction with a low barrier to a more stable dihydronaphthalene dication and thus is kinetically not stable even under stable ion conditions. The [14]annulene dication, however, is thermodynamically and kinetically stable. All bicyclic and even the tricyclic isomers with favorable ring sizes such as 5- and 6-membered rings are higher in energy than the Möbius [14]annulene dication. Provided that the energy barriers are low (which is usually the case in cationic rearrangements), a large number of potential precursors are conceivable for the generation of this interesting species which according to our calculations is strongly aromatic with 12 electrons delocalized in a 14-membered ring, thus violating the Hückel rules for aromaticity.

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Supporting Information Available: Details of computational methods, absolute energies, and Cartesian coordinates; complete ref 19. This material is available free of charge via the Internet at http://pubs.acs.org.