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Synthesis and Properties of the First Möbius Annulenes

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Dedicated to Professor Edgar Heilbronner on the occasion of his 85th birthday

Abstract: Heilbronner in 1964 predicted that annulenes with "… a planar perimeter of $N=4r$ AO's, which would yield an open shell configuration when occupied by $4r$ electrons, can be twisted into a closed shell Möbius strip perimeter without loss in π electron energy". We have been able to synthesize the first [4*n*]annulene with such a Möbius topology and now present further Möbius isomers and the details of their preparation as stable compounds. To address the question whether the twist in the π system has an effect on the properties we systematically investigate energy, geometry and magnetic parameters of a large number isomers of [16]annulenes. The Möbius twisted annulenes are consistently more aromatic than the non-twisted isomers. This is true for the parent as well as our benzoannelated systems. Our results are in contrast to those published recently by C. Castro, W. L. Karney, P. von R. Schleyer et al.

Keywords: annulenes • aromaticity • metathesis • Möbius twist • photochemistry

Introduction

Most surfaces in every day life are two-sided, for example, a round sphere or a strip of paper. There is an inside and outside or back and front that can be stained in two different colors. A Möbius band that can be created by twisting a rectangular strip by 180° before affixing both ends has only one side and one edge. The mathematical properties of Möbius objects were first described and published by Johann Benedict Listing in 1858, two months before August Ferdinand Möbius after whom the two-dimensional one-sided topology is named. A more general property than the "one-sidedness" is the non-orientablity of this topological object. In contrast to the "sidedness", orientability is an intrinsic property and more generally applicable (also in higher dimensions). Consider the structure of L-lactic acid drawn on a (transparent) Möbius band. If you move it around the Möbius band it will return as its mirror image (D-lactic acid) and upside down. The Möbius band therefore is said to be non-orientable. The fascinating properties of the Möbius topology have inspired mathematicians, engineers, and artists. Heilbronner roused the interest in chemistry in 1964 when he predicted that Möbius-like twisted annulenes with $4n$ electrons should be closed-shell species.[1] By replacing the resonance integral β by $\beta\cos(\pi/N)$ ($N=$ number of ring atoms) to account for the twist, he obtained an analytical solution of the secular Hückel equations that contains exclusively degenerate energy eigenvalues (except the highest unoccupied orbital in odd-membered annulenes). Coincidentally, the energy levels of a Möbius annulene correspond to the vertical positions of the N vertices of a regular polygon drawn in such a way that the lowest edge (bond) is horizontal. If the polygon representing the [*n*]annulene is inscribed in a circle with a diameter of 4β and a center at α (Coulomb integral, origin of the energy axis), the vertical positions of the vertices are identical with the Hückel MO energies of the corresponding annulene. A similar procedure is known as the Frost–Musulin mnemonic for determining the MO energies of Hückel annulenes.[2] In this case the polygon has to

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be drawn in such a way that a vertex (atom) is the lowest point in the sphere (Figure 1).

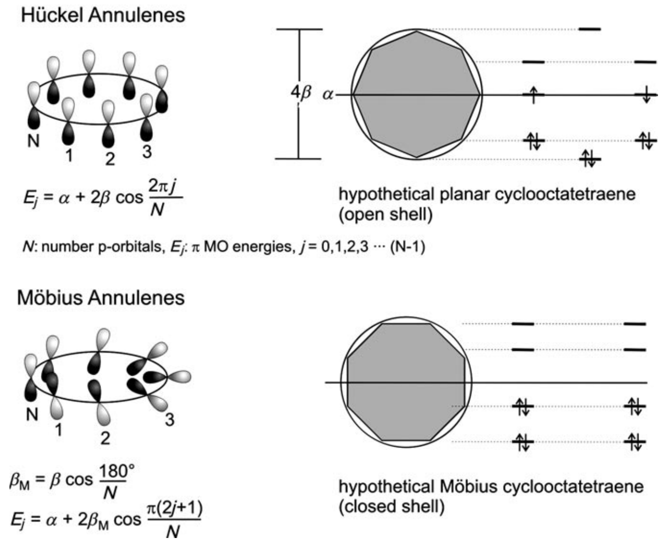
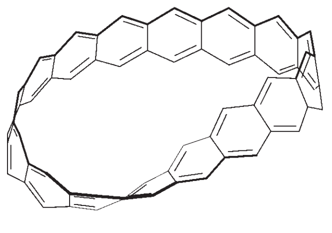
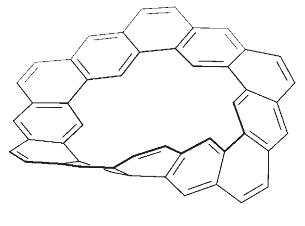


Figure 1. Frost–Musulin mnemonic to determine the MO energies for Hückel and Möbius annulenes.

Heilbronner suggested that Möbius twisted [n]annulenes with $n > 20$ should be formed without much strain or sterical hindrance. As this is often the case in natural sciences, the applications of Heilbronner's prediction came from an unexpected field. Only two years later in 1966 Zimmerman[3–5] proposed an alternative version of the Woodward–Hoffman rules based on the Hückel–Möbius aromaticity of transition states. From 1964 to date more than 200 papers were published that predict the properties of hypothetical Möbius annulenes, such as Möbius coronenes and kekulenes,[6,7] Möbius cyclacenes,[8–10] spiroaromatic systems,[11] heteroannulenes,[12] and cyclic allenes.[13]



Möbius [16]cyclacene

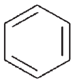
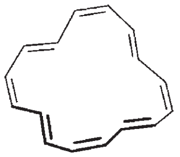
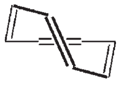
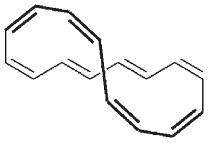


Möbius Kekulene

The first proposal of a cationic Möbius aromatic system was published by E. Yakali in her thesis in 1973.[14] She suggested that the solvolysis of 9-chlorobicyclo[6.1.0]nonatriene[15] would proceed via a Möbius [9]annulene cation $(CH)_9^+$. In 1998 Schleyer et al. presented theoretical calculations providing strong evidence that this short-lived intermediate is indeed Möbius aromatic.[16] The first twisted neutral parent annulene a Möbius [16]annulene was proposed by Rzepa et al.[17] The "trick" to enforce a twist in a cyclic conjugated system is to introduce *trans* double bonds at suitable positions. Unfortunately, however, so far the number of *transoid* bonds and the "suitable positions" have to be found by trial and error. The smallest conceivable system of this kind is *trans* benzene. There are a number of calculations which all agree that this highly strained structure is only a shallow minimum on the energy hypersurface.[18,19] The *trans* benzene structure is about 100 kcal mol^{-1} less stable than D_{6h} benzene, and the dihedral angles of the *trans* double bond with the neighboring *cis* bonds are close to 90°. Therefore it is rather nonaromatic. Similar arguments hold for *trans* cyclooctatetraene.[20] Recently, Castro, Karney, and Schleyer calculated a number of isomers of [n]annulenes and identified several structures as Möbius aromatic.[21]

Although many attempts within the last 40 years have been made,[22] so far no stable aromatic Möbius annulene could be synthesized. So one might ask what the problems are that antagonize the experimental verification. Unfortunately Heilbronner's statement that [n]annulenes of a ring size $n < 20$ should not be strained was not confirmed by density functional theory calculations. In Table 1 the relative energies of the most stable Hückel and the most stable Möbius [n]annulenes for $n = 6$ (benzene),[20] $n = 8$ (cyclooctatetraene),[20] $n = 16$[21] and $n = 20$[21] are listed. In all cases the most stable isomer has Hückel topology. Evidently, the stabilization by Möbius aromaticity cannot overcome the destabilization due to the torsional strain or the reduced overlap of neighboring p orbitals. Even in the [20]annulene system, the most stable Hückel isomer is 6.2 kcal mol^{-1} more stable than the most stable Möbius structure.

Table 1. Relative energy (B3LYP/6-31G*) of the most stable Hückel and the most stable Möbius isomer of several [n]annulenes.

	[n]annulene			
	$n = 6$	$n = 8$	$n = 16$	$n = 20$
most stable Hückel isomer				
most stable Möbius isomer				
energy difference [kcal mol^{-1}]	107.0	21.3	5.1	6.2

In principle, if the Möbius isomers would be kinetically stable there would still be the chance to characterize such a compound as an intermediate. Unfortunately, however, the [n]annulenes with $n = 4r$ ($r = 4, 5, 6$ …) delocalized electrons are extremely "floppy". Barriers to *cis–trans* and bond shift isomerization are very low. For example, [16]annulene[23] in solution is an equilibrium of at least 40 isomers that rapidly interconvert at temperatures as low as −150 °C.[24–28] The larger the annulene, the more isomers exist and the lower the isomerization barriers are. Therefore a parent neutral annulene most probably will never be synthesized.

In a recent communication we reported the synthesis of the first [4*n*]annulene with a Möbius topology[29] and now present further Möbius isomers and the details of their preparation as stable compounds. Our results are in contrast to those published recently by C. Castro, W. L. Karney, P. von R. Schleyer et al.[30]

Strategy to stabilize the twist: To overcome these difficulties we developed a strategy to stabilize the 180° twist in cyclic conjugated molecules. Möbius annulenes exhibit two types of conjugation: 1) "normal" conjugation with p orbitals perpendicular to the ring plane and sp^2 carbon atoms in their preferred trigonal planar configuration (Figure 2, top, blue); 2) "in-plane" conjugation with pyramidalized carbon atoms (Figure 2, top, red). Beside carbon nanotubes, there are only very few examples of experimentally known, in-plane conjugated structures, because the pyramidalization of sp^2-hybridized carbon atoms involves a considerable amount of strain. The strain in Möbius annulenes almost exclusively arises from the pyramidalized (red) part in the ring.

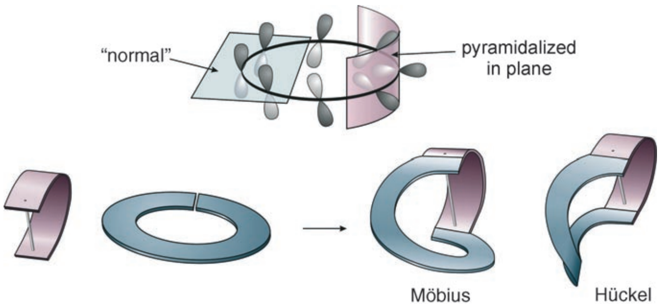


Figure 2. Our strategy to stabilize the twist in a ring.

Consequently, our strategy is based on the idea to use a prefabricated pyramidalized building block that is kept in its strained configuration by a rigid molecular frame and combine it with a "normal" π system. The underlying principle can be easily demonstrated using a simple paper model. (Figure 2, bottom) Bend a rectangular piece of cardboard to a half-open cylinder (pyramidalized part) and fix it in this position using a stick or thread connecting both ends (molecular frame). Cut a disk with a large hole in the middle ("normal" π system) and cut once through the resulting ring. Now try to attach both ends of the half-cylinder with the ends of the dissected disk. There are two ways to form a ring with both components: a 180° twisted Möbius band and a "normal" Hückel band. As you immediately notice during the experiment, the Möbius model is less strained than the Hückel band and therefore should be more stable. How to translate our paper model into chemistry?

We chose the ring enlargement metathesis reaction as the method to combine both parts of the ring (Figure 3), tetradehydrodianthracene (TDDA, bottom, in red) as the pyramidalized part, and cyclooctatetraene as the normal π system.

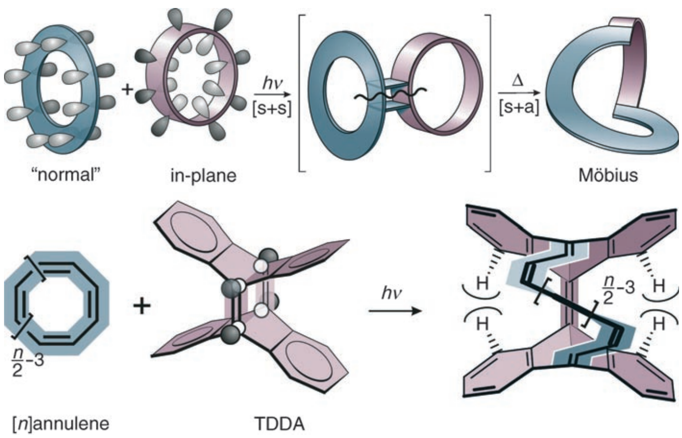
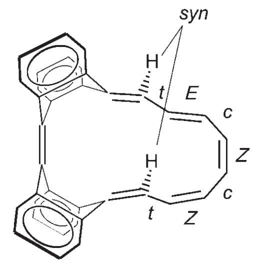


Figure 3. Top: Metathesis strategy to combine a "normal" and an "in-plane"-conjugated unit to form a Möbius ring. Bottom: Synthetic realization using an [*n*]annulene as the "normal" conjugated unit, and TDDA as the "in-plane"-conjugated component.

The ring-enlargement metathesis product contains a bianthraquinodimethane unit (red) and a polyene bridge (blue). The bianthraquinodimethane unit is kept in the pyramidalized configuration by the steric hindrance of the inner *ortho*-hydrogen atoms, which prevent a planar geometry and hence correspond to the stick or thread in our paper model.

To make sure that our simple paper model holds at higher levels of theory we performed DFT calculations. There are 12 *E*/*Z* isomers of our Möbius stabilized [16]annulene, each of which can adopt nine s-*cis*/s-*trans* conformations. We calculated all 108 isomers at the semiempirical PM3 level and reoptimized the most stable conformations of each configuration at the B3LYP/6-31G* level of theory. In Table 2 the 25 most stable isomers of the parent [16]annulene (see Computational Methods) are compared with the 25 most stable isomers of our bianthraquinodimethane-modified system. To denominate the structures we introduce the following stereochemical description. The bianthraquinodimethane unit is rigid and thus the corresponding double bonds don't have to be included in the stereochemical denotation. The two H atoms at the quinoid double bonds are either *syn* or *anti*, *c* and *t* denote the s-*cis* or s-*trans* relationship between two double bonds, and *Z* and *E* define the stereochemistry at the three central double bonds in the bridge. In Scheme 1 the nomenclature is exemplified with the *syn-tZcZcEt* isomer.

As inferred from our simple model the most stable isomer of our bianthraquinodimethane modified [16]annulene has Möbius topology (*syn-tZcZcEt*). There are another six



Scheme 1. Notation of the stereoisomers of the bianthraquinodimethane-stabilized [16]annulene.

Table 2. B3LYP/6-31G* and KMLYP/6-31G* calculated "energy ranking list" of the most stable isomers of the parent [16]annulene and the bianthraquinodimethane-modified system. Relative stabilities (E_{rel}) in kcal mol^{-1}. Note that the structures of the parent [16]annulene and those of the bianthraquinodimethane-modified system with the same entry number are not structurally related.

	Parent [16]annulene			Bianthraquinodimethane modified [16]annulene					
Entry	E_{rel}[a]	Topology	Configuration[b]	Entry	E_{rel}[a]	E_{rel}[c]	Topology	Configuration[d]	[e]
1	0.00	Hückel	0011001100110011	1	0.00	0.00	Möbius	*syn-tZcZcEt*	**8**
2	2.25	Hückel	0011011011001111	2	0.29	1.75	Möbius	*anti-tEcZcEt*	**9a**
3	4.68	Hückel	0001100110011011	3	0.56	0.30	Möbius	*syn-cZtEcZt*	
4	5.14	Möbius	0000110011000111	4	0.56	0.89	Möbius	*syn-cEtZcZt*	
5	5.15	Möbius	0000111000110011	5	2.47	4.95	Möbius	*anti-cEtZcEt*	
6	5.41	Möbius	0001100110011001	6	2.76	1.96	Möbius	*anti-tZtEcZt*	**5**
7	5.41	Möbius	0001001100110011	7	2.77	1.90	Möbius	*anti-tZcZcZt*	**6**
8	5.45	Hückel	0011011011011011	8	4.16	3.26	Hückel	*syn-tEcZcEt*	
9	5.45	Hückel	0011011001101111	9	6.71	5.23	Möbius	*syn-tZcZcEc*	
10	5.47	Hückel	0011011001111011	10	6.91	5.29	Hückel	*syn-tZtZtZt*	**7**
11	5.83	Hückel	0001100110011011	11	8.36	10.74	Möbius	*anti-tEcEtZc*	
12	5.84	Hückel	0001101100110011	12	9.30	8.86	Möbius	*syn-tEtZcZc*	
13	6.03	Hückel	0001101100110101	13	9.34	13.06	Möbius	*anti-cEtZtEc*	**9b**
14	6.05	Hückel	0001010110011011	14	11.20	10.25	Möbius	*anti-tZtZcZc*	
15	6.22	Möbius	0001001100110011	15	11.20	10.25	Möbius	*anti-cZcZxZc*	
16	6.24	Hückel	0011001111001111	16	11.74	11.56	Hückel	*syn-cEtZtEc*	
17	6.37	Hückel	0001111001100101	17	12.38	9.53	Möbius	*syn-cZtZcZc*	
18	6.38	Hückel	0001010011001111	18	12.38	9.53	Möbius	*syn-cZcZtZc*	
19	6.84	Hückel	0001011100011011	19	14.25	13.96	Möbius	*syn-cZtEcEc*	
20	6.85	Hückel	0001101100010111	20	16.20	15.00	Möbius	*syn-cEcZcZc*	
21	6.87	Hückel	0010100110110011	21	23.49	24.35	Möbius	*anti-cZcEcEc*	
22	6.88	Hückel	0010100110011011	22	23.80	27.58	Hückel	*anti-tEtEtEt*	
23	7.09	Möbius	0001101100011111	23	27.10	33.46	Hückel	*syn-tEtEcEt*	
24	7.30	Hückel	0001101100011011	24	28.27	33.01	Hückel	*anti-tEcEcEt*	
25	7.30	Möbius	0001011000110011	25	30.73	34.84	Möbius	*anti-cEcZcEt*	

[a] B3LYP/6-31G*. [b] $0 = Z$, $1 = E$. [c] KMLYP/6-31G*. [d] For notation see Scheme 1. [e] Compound number.

Möbius isomers within a relative energy of 3 kcal mol^{-1}. The most stable Hückel isomer (*syn-tZtZtZt*) has a relative energy of 4.2 kcal mol^{-1}, which should be formed in very small amounts in a thermodynamically controlled reaction. Thus, based on our theoretical calculations the insertion of a bianthraquinodimethane unit into a [16]annulene stabilizes the Möbius twist to such an extent that the synthesis of a Möbius annulene was expected to be within reach.

Computational Methods

All calculations were performed by using the Gaussian 03 program.[31] Geometries were optimized at the B3LYP/6-31G* level of DFT.[32,33] The bianthraquinodimethane-modified [16]annulenes were additionally optimized at the KMLYP/6-31G* level of DFT.[34] Magnetic susceptibilities were calculated by using the CSGT method[35] and nucleus-independent chemical shift (NICS) values were determined by using the gauge-invariant atomic orbital (GIAO) method.[36] Harmonic oscillator measure of aromaticity (HOMA) values were calculated by averaging of all four cyclic [16]annulene pathways through the bianthraquinodimethane unit. The ring center for calculating the NICS correspondingly was defined as the average center of gravity of the C atoms in each path. The topology of the rings (Hückel or Möbius) was determined by following the normal vectors on the planes defined by each successive triplet of carbon atoms around the ring. The isomers of the [16]annulenes were generated by using a Monte Carlo algorithm, through breaking the ring, varying the dihedral angles in steps of 30°, and rejoining both ends.[37] The structures were submitted to an optimization using the MM+[38,39] force field and then checked for redundancy. The generation procedure was stopped when no new isomers were found by doubling the number of generated structures. All structures within an energy threshold of 60 kcal mol^{-1} were submitted to PM3 single point calculations and those within an energy threshold of 20 kcal mol^{-1} were optimized at the B3LYP/6-31G* level of theory and finally again checked for redundancy.

Results and Discussion

Experiments: Upon irradiation TDDA (tetradehydrodianthracene) reacts with alkenes, cyclic alkenes, and even benzene in ring enlargement metathesis reactions.[40–42] Unfortunately TDDA and cyclooctatetraene (COT) upon irradiation in benzene with a 700 W high pressure mercury lamp in a quartz apparatus did not undergo addition reactions, but furnished bianthryl as the main product. We know from independent investigations with triplet sensitizers (acetophenone and acetone) that the triplet-excited state of TDDA immediately undergoes electrocyclic ring-opening to form 9,10′-didehydroanthracene, which abstracts hydrogen or deuterium from the solvent (e.g. [D$_6$]acetone).[43] This is in agreement with DFT calculations. At the UB3LYP/6-31G* level of DFT the lowest triplet state of TDDA is not even a minimum, but undergoes an electrocyclic ring-opening without barrier. COT is known to be a triplet quencher[44] with a triplet energy of 41 kcal mol^{-1}, but probably still able to sensitize TDDA.

To circumvent this problem we used *syn*-tricyclooctadiene (*syn*-TCOD) as a synthetic analogue for COT. *Syn*-TCOD is difficult to prepare in preparative amounts. The reaction of *syn*-dichlorocyclobutene with sodium amalgam in diethyl ether is not complete even after reaction times of more than several weeks and the reaction mixture has to be purified by preparative GC.[45,46] To avoid the use of hexamethylphosphoramide (HMPTA)[47] we used an ultra sound generator (cell disruptor) to accelerate the heterogeneous reaction and were able to reduce the reaction time to three days. TDDA was irradiated with a tenfold excess of *syn*-TCOD in benzene with a high-pressure mercury lamp for 20 min in a quartz photoreactor. Four products were isolated and characterized: the metathesis product with the solvent benzene (**1**),[40] two metathesis products with *syn*-TCOD (**2** and **3**) and a ladderane (**4**). Compounds **2** and **3** were crystallized and their structures were unambiguously identified by NMR and X-ray analysis as the C_s and C_2 symmetrical isomers of 1,3-cyclohexadiene products. In **2**, two crystallographically independent molecules are found, of which one is disordered. However, in one of the two independent molecules the configuration could be unambiguously elucidated. The X-ray data are also in agreement with NOE spectra. There is a distinct NOE relationship of protons H_a and H_b in **3** and no correlation in **2** (Figure 4). Unfortunately we were not able to isolate any fully ring-opened [16]annulenes. Most probably *syn*-TCOD adds to TDDA in a [2+2]cycloaddition to form the ladderane **4**, which undergoes [2+2]cycloreversion and electrocyclic ring-opening to the 1,3-cyclohexadienes **2** and **3**. (Scheme 2)

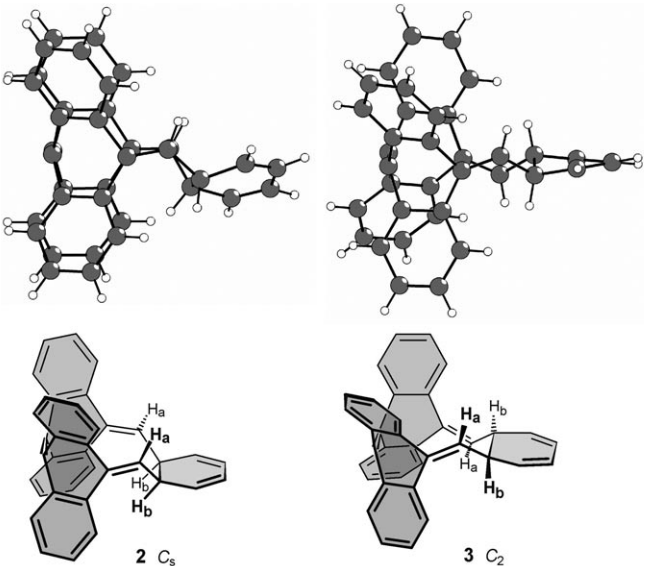
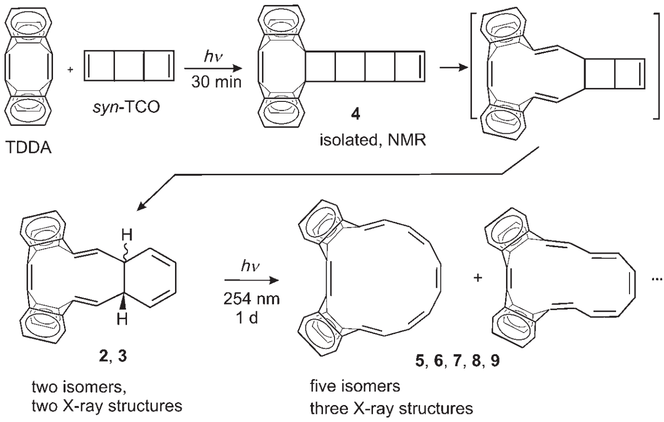


Figure 4. Crystal structures of compounds **2** (left) and **3** (right), isolated after irradiation of TDDA and *syn*-TCOD with light of $\lambda > 300$ nm.

It is known that the photostationary equilibrium in the electrocyclic reaction of 1,3-cyclohexadiene to 1,3,5-hexatriene is shifted towards the ring-opened product upon irradiation with shorter wavelength.[48,49] We therefore irradiated TDDA and *syn*-TCOD with a low-pressure mercury lamp (254 nm) and obtained a complex mixture of isomers in a total combined yield of 50%.



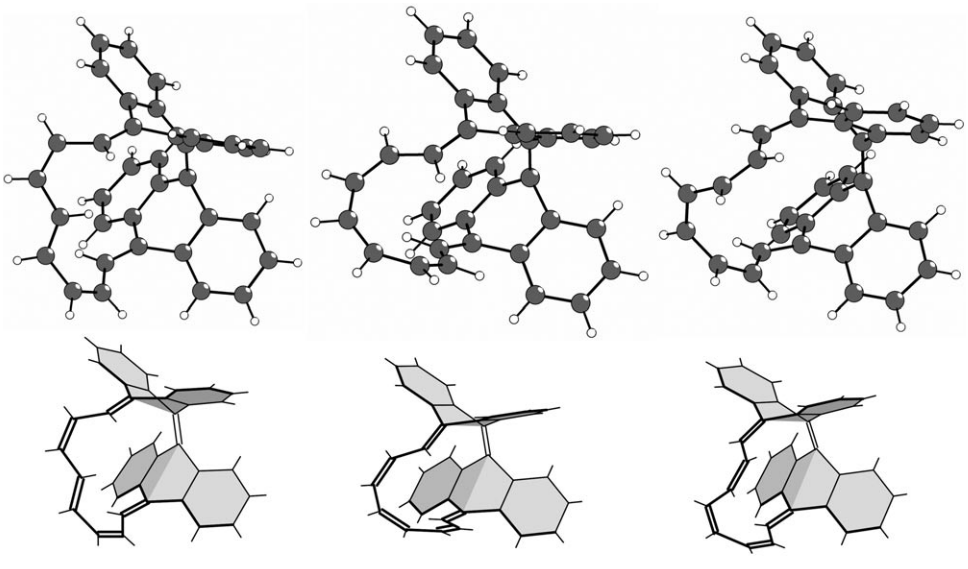
Scheme 2. Reaction of TDDA with *syn*-TCOD upon irradiation with a low-pressure mercury lamp.

Beside the products identified after longer wavelength irradiation, we also isolated five ring-opened [16]annulene compounds (1:1 addition products of TDDA and *syn*-TCOD according to MS and fully conjugated according to ^1H and ^{13}C NMR spectroscopy). The separation was achieved after removing the 1,3-cyclohexadiene structures **2** and **3** by Diels–Alder reaction with tetracyanoethylene (TCNE) and subsequent HPLC on a silica gel column. Three of these isomers were crystallized and their structure was determined by X-ray analysis.

The structures **5** *(anti-tZtEcZt)*, **6** *(anti-tZcZcZt)* and **7** (*syn-tZtZtZt*) are identical (Figure 5) with the entries 6, 7, and 10 in the list of the most stable isomers (Table 2) that had already been calculated at the B3LYP/6-31G* level of density functional theory. Structure **5** has only approximate Möbius topology. One of the torsional angles in the polyene bridge deviates with 124.4° (DFT) or 112.1° (X-ray) from planarity. The structure has no element of symmetry and therefore is chiral. Both enantiomers were found in the unit cell. Compound **5** is stable in dichloromethane and can be exposed to diffuse daylight at room temperature for several months without decomposition.

Structure **6** has a perfect Möbius topology. Both ends of the bianthraquinodimethane unit are connected by a polyene bridge (similar to the model in Figure 2) in such a way that the inner side of the anthracene units is connected to the outer surface and vice versa. The implications on the stereochemistry are interesting. Any attempt to determine the prochirality (*Re*, *Si*) of the central double bond in the bridge according to Prelog and Helmchen[50] leads to an endless loop. Because of the C_2 axis that bisects the double bond, both faces are homotopic. As C_2 is a chiral point group, the molecule should be chiral. The unit cell indeed includes both enantiomers. We have been able to separate both enantiomers by HPLC on a chiral stationary phase (Chiralcel OD) using CH_3OH/H_2O (90:10) as solvent. The CD spectra are given for both isomers in Figure 6.

Structure **7** has C_s symmetry and Hückel topology. The central double bond in the bridge forms a torsional angle of



5 *anti-tZtEcZt* C_1 Möbius **6** *anti-tZcZcZt* C_2 Möbius **7** *syn-tZtZtZt* C_S Hückel

Figure 5. Crystal structures of three ring-opened [16]annulenes **5** (*anti-tZtEcZt*), **6** (*anti-tZcZcZt*), and **7** (*syn-tZtZtZt*).

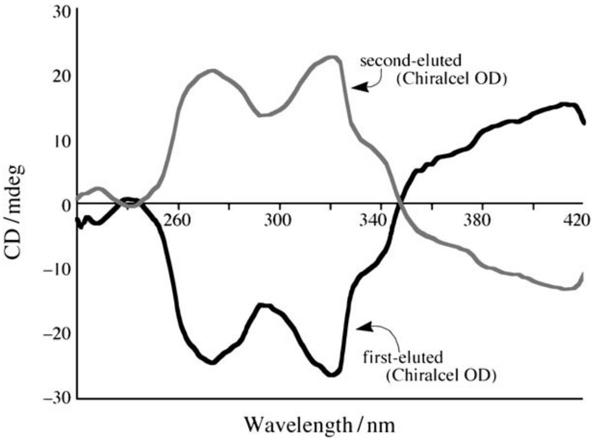


Figure 6. CD spectra of both enantiomers of the Möbius structure **6**.

103° with the two neighboring double bonds. Therefore the conjugation is almost completely interrupted and in contrast to **6**, which forms red rhombic crystals, compound **7** is colorless. The Möbius annulene **6** exhibits an additional band that extends into the visible region and has a stronger absorption compared to **7** (Figure 7).

Two other isomers were isolated, but their structure could not be unequivocally elucidated. One of these compounds (**8**), which is unsymmetrical and has a *syn* relationship of the two quinoid hydrogen atoms, undergoes a clean reaction to the ring-closed 1,3-cyclohexadiene **2** within several hours. According to symmetry considerations and semiempirical calculations the *syn-tZcZcEt* structure (the global minimum of all isomers) is the only unsymmetrical compound within the ten most stable isomers that is able to undergo a thermochemically (Woodward–Hoffmann) allowed ring closure to **2**. We therefore assign this compound to the *syn-tZcZcEt* structure **8**, which has Möbius topology. We isolated a fifth annulene structure in very small amounts that is *anti* with respect to the quinoid hydrogens and C_2 symmetric and therefore must be either **9a** *anti-tEcZcEt* or *anti-cEtZtEc* **9b**. Unfortunately the yield is not large enough to unambiguously assign the conformation.

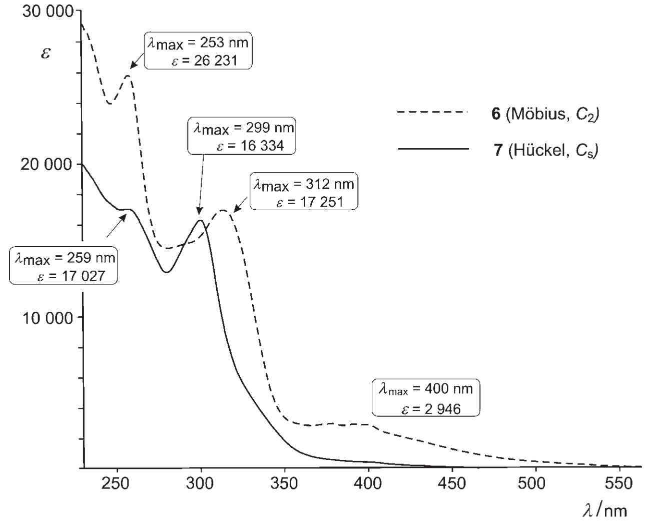
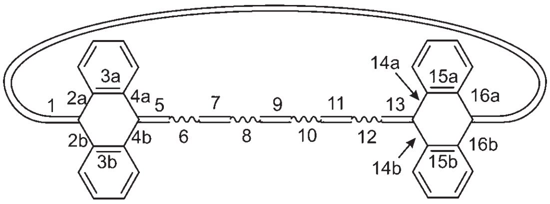


Figure 7. UV/Vis spectra of the Möbius annulene **6** and the Hückel annulene **7**.

Does the twist make a difference? (Theoretical investigations): To analyze the properties of our Möbius annulenes we performed theoretical calculations at the B3LYP/6-31G* and KMLYP/6-31G* of density functional theory. The latter method provided more reliable results in the case of several [4*n*+2]annulenes than the frequently used B3LYP functional.[51] However, applied on our bianthraquinodimethane-modified [16]annulenes KMLYP/6-31G* did not give more accurate geometries when compared with the X-ray structures of **5** and **6**. The mean deviation of the B3LYP/6-31G* calculated bond lengths in **5** relative to the X-ray structure is 0.0093 Å, and 0.0165 Å for the KMLYP-computed geometry. The corresponding mean deviations for **6** are 0.010 Å (B3LYP/6-31G*) and 0.013 Å (KMLYP/6-31G*). The mean difference of the energies of the 25 B3LYP and KMLYP optimized structures also is small (1.91 kcal mol^{-1}). Data for the calculated bond lengths and dihedral angles of compounds **5**–**8** and **9a** and **9b** are given in Tables 3 and 4.

One of the most interesting questions concerning the twisted annulenes is whether there is a significant relationship between topology (Hückel or Möbius) and geometry, energy and magnetic properties or in other words: Does the twist change the properties? Numerous calculations on Möbius structures notwithstanding, a thorough and systematic study has not been made so far. To address the consequences of a twist in the π system, we first analyzed the data of the parent [16]annulene and then turned to the question if this relationship is also valid for our bianthraquinodimethane-stabilized [16]annulenes. Purely based on statistics, there are 2250 conceivable *cis*/*trans* isomers of [16]annulenes, many of which are not minima on the energy hypersurface, because they are highly strained. We used a Monte Carlo algorithm to generate the [16]annulene isomers (see Computational Methods), and optimized the 153 most stable structures at the B3LYP/6-31G* level of theory (the 25 most stable isomers are listed in Table 2). Interestingly, among these structures, which have relative energies up to 19.66 kcal mol^{-1}, there are more Möbius (85) than Hückel isomers (68). However, in agreement with experiment the most stable isomers are Hückel structures. There are two independent X-ray structures available for the global minimum.[52,53] The second most stable isomer was detected by NMR spectroscopy.[25,27] With a relative energy of 5.14 kcal mol^{-1}, the energetically most favorable Möbius compound has little chance to be experimentally detected if a rapid equilibrium of all isomers is assumed. The Möbius structure proposed by Rzepa et al.[17] with a relative energy of 7.1 kcal mol^{-1} is number 24 in the ranking list of the most stable isomers and the Möbius isomer for which a strong aromaticity was predicted by Schleyer and Castro[21] is ranked number 137 with a relative energy of 15.8 kcal mol^{-1}. The energy data confirm our initial assumption that a successful synthesis of a stable parent [16]annulene with Möbius topology is very unlikely and that the twist has to be stabilized by proper substitution.

Table 3. B3LYP/6-31G* calculated bond lengths r_n of Möbius compound **6** and its isomers **8**, **9a**, **5**, **7**, and **9b**. Note that the bonds are numbered not the atoms. Note also that because of the bianthraquinodimethane units there are four different pathways to describe a [16]annulene periphery in each structure.



	r_1	r_{2a}	r_{2b}	r_{3a}	r_{3b}	r_{4a}	r_{4b}	r_5	r_6	r_7	r_8
	r_9	r_{10}	r_{11}	r_{12}	r_{13}	r_{14a}	r_{14b}	r_{15a}	r_{15b}	r_{16a}	r_{16b}
8	1.3656	1.4872	1.4945	1.4137	1.4242	1.4830	1.4855	1.3643	1.4448	1.3603	1.4595
	1.3609	1.4513	1.4398	1.3596	1.3621	1.4808	1.4818	1.4150	1.4225	1.4888	1.4962
9a	1.3721	1.4842	1.4942	1.4139	1.4271	1.4773	1.4798	1.3658	1.4376	1.3599	1.4557
	1.3609	1.4557	1.4376	1.3599	1.3658	1.4773	1.4798	1.4139	1.4271	1.4842	1.4942
5	1.3683	1.4976	1.4948	1.4187	1.4177	1.4823	1.4859	1.3542	1.4721	1.3579	1.4454
	1.3572	1.4575	1.4580	1.3608	1.3607	1.4831	1.4841	1.4226	1.4169	1.4959	1.4927
6	1.3621	1.4960	1.4901	1.4208	1.4153	1.4846	1.4854	1.3626	1.4435	1.3607	1.4561
	1.3618	1.4561	1.4435	1.3607	1.3626	1.4846	1.4855	1.4207	1.4153	1.4960	1.4901
7	1.3649	1.4952	1.4952	1.4165	1.4199	1.4835	1.4866	1.3575	1.4547	1.3490	1.4846
	1.3423	1.4846	1.4547	1.3490	1.3575	1.4835	1.4866	1.4165	1.4199	1.4952	1.4952
9b	1.3944	1.4752	1.4870	1.4191	1.4309	1.4710	1.4767	1.3721	1.4485	1.3649	1.4295
	1.3789	1.4295	1.4485	1.3649	1.3721	1.4710	1.4767	1.4191	1.4309	1.4752	1.4870

Table 4. B3LYP/6-31G* calculated dihedral angles d_n of the single bonds in Möbius compound **6** and its isomers **8**, **9a**, **5**, **7**, and **9b**. For the numbering see Table 3. The dihedral angles are defined by the atoms of the numbered bond and the two neighboring carbon atoms.

	d_1	d_{2a}	d_{2b}	d_{3a}	d_{3b}	d_{4a}	d_{4b}	d_5	d_6	d_7	d_8
	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14a}	d_{14b}	d_{15a}	d_{15b}	d_{16a}	d_{16b}
8	−174.9	115.5	−112.6	−0.3	−6.7	−132.4	136.1	−173.6	168.9	−0.9	−45.5
	−3.6	−22.0	−166.6	170.2	156.5	−127.5	132.8	−1.7	−10.0	111.5	−106.8
9a	−175.7	−117.8	111.8	3.4	11.0	132.0	−138.7	16.0	167.1	−168.0	35.2
	6.4	35.2	167.1	−168.0	−156.5	132.0	−138.7	3.4	11.0	−117.8	111.8
5	−163.7	114.8	−115.9	5.8	−4.0	−137.1	136.3	−174.3	124.4	−12.0	173.3
	175.6	−38.8	150.5	−16.4	−9.3	−139.0	141.1	3.3	−7.3	118.9	−117.4
6	148.7	−108.7	109.6	−4.7	2.4	129.8	−128.2	2.8	167.9	1.3	−34.9
	−3.4	−34.9	167.9	1.3	−167.4	129.8	−128.2	−4.7	2.4	−108.7	109.6
7	0.0	114.0	−116.1	6.5	−1.9	−136.0	133.4	2.2	−153.1	4.2	103.1
	0.0	−103.1	153.1	−4.2	−176.3	136.0	−133.4	−6.5	1.9	−114.0	116.1
9b	−154.6	−133.2	124.0	8.5	12.3	136.9	−146.7	28.6	29.4	164.3	−163.9
	2.6	−163.9	29.4	164.3	−147.0	136.9	−146.7	8.5	12.3	−133.3	124.0

The large set of computed geometries provides a solid basis for the statistical analysis of the properties. Most interesting are those properties that have been related to aromaticity, such as bond-length equalization[54] (HOMA,[55] Julg[56]), maximum deviation from planarity, aromatic stabilization energy[57] (isomerization staili-zation energy; ISE[58]), magnetic susceptibility,[59–61] and NICS.[62,63] All of these methods have drawbacks that have been extensively discussed in the literature. We refrain here from following up this discussion. The most straightforward approach to avoid the problems inherent to each method is to apply all methods to the same data set and to do a principal component analysis (PCA). PCA is a powerful statistical method to reduce the dimensionality and redundancy to find patterns in data of high dimensionality. It has found application in fields such as communication theory, face recognition, image compression, GC-MS, and 2D-NMR spectroscopy. Katritzky et al. used PCA to quantify the aromaticity of a set of heterocyclic compounds.[64,65]

PCA can be used to extract significant information, leaving noise behind. Noises in our case are, for example, local effects disturbing the interpretation of NICS, the influence of the benzene rings in determining the magnetic susceptibility contribution as well as the bond-length equalization of the [16]annulene periphery, the mutual influence of bond-length equalization and out-of-plane distortion of the π system, and numerous other effects interfering with or even obscuring the effect we are interested in, which is the twist in the π system.

The errors and misinterpretations that arise if one relies on a single method and applies it on a single structure can be illustrated with an example from a recent paper of Castro, Karney, Schleyer et al.[30] They calculated the magnetic susceptibility exaltation (Λ) of our Möbius compound **6** by using the incremental system of Dauben et al.[62,63] and obtain a strongly negative value of -30.0 cgs ppm, which is about the value of naphthalene. Hence according to Λ our Möbius compound **6** would be very aromatic. However, Λ is mainly determined by the four perfectly aromatic benzene rings and not only by the [16]annulene periphery, which is the key question. To deduct the strong contribution from the four benzene rings they correct for their large negative value ($\Lambda_{\text{benzene}} = -13.7$ cgs ppm) and end up with a very large positive value of $+19.6$ cgs ppm for the [16]annulene subunit. Thus, our Möbius compound would be extremely antiaromatic in its 16-electron periphery (compare, for example, with the strongly antiaromatic heptalene: $\Lambda = +6$). This is in disagreement with their main conclusion that the Möbius compound **6** is "nonaromatic".

We avoid these problems by applying several methods on a set of very similar structures: the 153 most stable isomers of the parent [16]annulene and the 25 most stable isomers of our bianthraquinodimethane-modified [16]annulenes. For example, in the latter case the influence of the benzene rings largely cancel and local effects are eliminated in the PCA analysis. The first step in PCA is to calculate the correlation matrix that provides information on the linear dependence of the methods (relative energy, maximum deviation of dihedral angles from planarity, HOMA, Julg, magnetic susceptibility, NICS) (Table 5).

It is interesting to note that the relative energy does not correlate strongly with any of the aromaticity parameters. Aromaticity, evidently, does not play an important (or at least not a systematic) role in stabilizing the structures. With a correlation of 0.999, the two methods representing the bond-length equalization (HOMA and Julg) correlate perfectly. The same is true for the two magnetic parameters, the magnetic susceptibility (MAGS) and NICS (correlation: 0.969). Both MAGS and NICS methods provide almost exactly the same information for our data set. Geometry and magnetic properties, however, correlate more weakly (HOMA/NICS: -0.651). Our findings thus are in agreement with those of Katritzky et al.[64] The next step in PCA is the diagonalization of the correlation matrix. The largest eigenvectors (based on the size of the eigenvalues) are the most important parameters describing the system. The eigenvectors (principle components, PCs) are linear combinations of the parameters used in the initial analysis (see Table 6).

Table 5. Correlation matrix for the PCA analysis of the 153 most stable isomers of the parent [16]annulene. The parameters used are E_{rel} (relative energy), Tmax (maximum deviation of dihedral angles from planarity), HOMA (bond-length equalization index), Julg (bond-length equalization index), MAGS (magnetic susceptibility), and NICS (nucleus independent shift).

	E_{rel}	Tmax	HOMA	Julg	MAGS	NICS
E_{rel}	1.000	0.314	−0.075	−0.054	−0.209	−0.246
Tmax	0.314	1.000	−0.218	−0.218	−0.330	−0.399
HOMA	−0.075	−0.218	1.000	0.999	−0.721	−0.651
Julg	−0.054	−0.218	0.999	1.000	−0.725	−0.653
MAGS	−0.209	−0.330	−0.721	−0.725	1.000	0.969
NICS	−0.246	−0.399	−0.651	−0.653	0.969	1.000

Table 6. Principal components of the PCA analysis for the 153 most stable isomers of the parent [16]annulene. The following parameters were used: Tmax (maximum deviation of dihedral angles from planarity), HOMA (bond-length equalization index), Julg (bond-length equalization index), MAGS (magnetic susceptibility), and NICS (nucleus independent shift).

	PC1	PC2	PC3	PC4	PC5
Tmax	0.063	−0.807	0.588	0.004	−0.003
HOMA	0.495	0.321	0.392	−0.087	0.701
Julg	0.495	0.320	0.382	−0.008	−0.711
MAGS	−0.513	0.229	0.375	−0.736	−0.044
NICS	−0.493	0.302	0.463	0.671	0.034

For visualization, the PC's are plotted as a function of each other. In Figure 8 (top) the most important (PC1) is plotted as a function of the second most important principle component (PC2). Both components account for 95.7% of the variance.

The plot is a text book example of the clustering capability of the PCA method. Without using the information on the topology of the structures in the analysis, the PCA plot clearly separates two classes of structures the Hückel (Figure 8, gray) and the Möbius isomers (Figure 8, black; the colors were assigned after the PCA analysis!). Following the traditional interpretation of the aromaticity parameters, the most aromatic structures are on the top right part of the plot and the most antiaromatic isomers are located top left. The global minimum synthesized by Schröder[24] and Sondheimer[23] is clearly located on the antiaromatic side, which is in agreement with the ^{1}H NMR spectrum ($\delta = 10.4$ ppm for the "inner" protons and 5.4 ppm for the "outer" protons). The most aromatic isomer is the Möbius structure calculated by Castro, Karney, and Schleyer.[21] Evidently, there is a continuum between aromatic and antiaromatic structures.

Having analyzed the parent [16]annulenes we turned to the question if our bianthraquinodimethane-modified

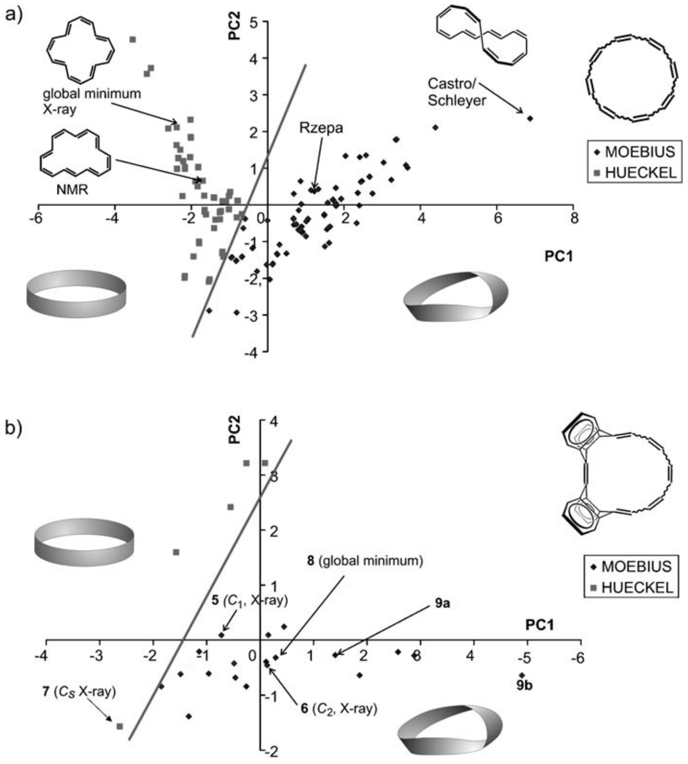


Figure 8. Principle component analysis (PCA) of [16]annulenes by using the parameters Tmax (maximum deviation of dihedral angles from planarity), HOMA (bond-length equalization index), Julg (bond-length equalization index), MAGS (magnetic susceptibility) and NICS (nucleus independent shift) based on the B3LYP/6-31G* optimized geometries (see text). a) PCA of the 153 most stable isomers of parent [16]annulene. The two theoretically predicted Möbius isomers and the two experimentally known structures are labeled. b) PCA of the 25 most stable isomers of Möbius stabilized [16]annulenes. Compounds **5**–**8** have been isolated and characterized by X-ray crystallography or NMR spectroscopy. An unambiguous assignment of one of the isomers to **9a** or **9b** was not achieved.

[16]annulenes would exhibit similar properties. This is indeed the case. The PCA analysis with the two most important PC's is plotted in Figure 8 (bottom). Again, the Hückel and the Möbius structures are clearly clustered on the basis of the aromaticity probes. Hence, the twist also makes a difference in our bianthraquinodimethane-modified annulenes. The experimentally isolated and characterized compounds are indicated with their structure number. The Möbius structure **6** that we isolated and characterized by X-ray analysis and the global minimum **8** are located within the cluster of aromatic Möbius compounds. Structures **5** and **7** (characterized by X-ray analysis) are rather nonaromatic because they are located very close to the dividing line of both topologies. The most aromatic is structure **9b**. Unfortunately, we have so far not been able to elucidate its conformation, which could be either **9a** or **9b**. On an absolute scale, the aromaticity of our benzoannelated [16]annulenes is reduced; however, the Möbius twisted isomers are clearly more aromatic than the nontwisted structures, as this is the case with the parent [16]annulenes.

Conclusions

Heilbronner's prediction that a planar [4*n*]annulene "…can be twisted into a closed shell Möbius strip perimeter without loss in π electron energy" is only valid at the level of Hückel molecular orbital theory. In the parent [4*n*]annulenes, any Möbius aromatic stabilization does not overcome the strain induced by the twist. Other effects, such as strain energy determine the topology. The three most stable isomers of the parent [16]annulene are not twisted.

By inserting a bianthraquinodimethane unit into the ring we were able to stabilize the twist. Structures with Möbius topology are now more stable than Hückel isomers and we were able to isolate and characterize the first three Möbius annulenes.

By using a principle component analysis with five different aromaticity parameters on a set of 153 parent [16]annulene isomers, we were able to confirm previous assumptions that [4*n*]annulenes with a Möbius twist exhibit properties that can be assigned to aromaticity. We applied the same analysis also to 25 isomers of our bianthraquinodimethane-modified [16]annulene and observe the same functional relationship between the aromaticity parameters and the topology. The Möbius isomers exhibit enhanced aromaticity relative to the Hückel structures. Thus, the benzoannelation may reduce the aromaticity but not to zero as stated previously.[30]

Experimental Section

Single-crystal structure analysis: All data were measured using an STOE Imaging Plate Diffraction System (IPDS-1). Structure solutions were performed with direct methods using SHELXS-97. Structure refinement was done against F^2 using SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The C–H hydrogen atoms in compound **2**, **3**, **5**, and **7** were positioned with idealized geometry and were refined with isotropic displacement parameters using a riding model. In compound **6** the hydrogen atoms were refined with varying coordinates and varying isotropic displacement parameters. In compound **2** two crystallographically independent molecules are found of which one shows some disordering and therefore, was refined using a split model. Details of data collection and structure refinement are given in Table 7.

Synthesis of *syn*-TCOD: Sodium (6.5 g) was added to mercury (650 g) in small portions under an argon atmosphere at room temperature. The sodium amalgam was cooled to room temperature and diethyl ether (250 mL) was added. The mixture was sonicated with an ultrasonic probe (cell disruptor 250 W, 50% output) for 30 min at 5 °C under argon and 3,4-*cis*-dichlorocyclobutene (5 mL) was added. The mixture was sonicated at 5–10 °C for 2–7 d (the reaction was monitored by GC (column temperature 30 °C). The reaction was allowed to run until all 3,4-*cis*-dichlorocyclobutene was converted to tricyclooctadiene). The mixture was filtrated with Celite and the diethyl ether was evaporated carefully first at 30 °C (800 mbar) and then 0 °C (200 mbar). A flow of argon was passed through the yellowish liquid until no diethyl ether was detected in the NMR spectrum. The *syn*-tricyclooctadiene (1.5 g, 68%) was stored in benzene (10 mL). ^{1}H NMR (500 MHz, $CDCl_3$/TMS): $\delta = 6.03$ (s, 4 H), 3.13 ppm (s, 4 H).

Preparation of compounds 2–4: A suspension of TDDA (100 mg, 0.28 mmol), TCOD (300 mg, 2.88 mmol), and naphthalene (20 mg, 0.15 mmol) was irradiated with a 700 W high-pressure mercury lamp in a quartz photoreactor and agitated with a flow of argon. After 10–20 min

Table 7. Selected crystal data and results of the structure refinements for compounds **2**, **3**, **5**, **6** and **7**.

	2	**3**	**5**	**6**	**7**
formula	$C_{36}H_{24}$	$C_{36}H_{24}$	$C_{36}H_{24}$	$C_{36}H_{24}$	$C_{36}H_{24}$
M_r [g mol^{-1}]	456.55	456.55	456.55	456.55	456.55
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$
a [Å]	8.6822(7)	10.1574(8)	9.6883(7)	16.280(2)	8.9779(5)
b [Å]	29.245(3)	8.7109(6)	16.5449(12)	10.959(1)	29.007(2)
c [Å]	19.284(2)	28.100(2)	15.3416(9)	14.373(2)	9.3982(5)
β [°]	101.43(1)	100.07(1)	100.90(1)	110.41(2)	94.09(1)
V [Å^3]	4799.4(7)	2448.0(3)	2414.7(3)	2403.5(2)	2441.3(3)
T [K]	170	170	150	173	150
Z	8	4	4	4	4
ρ_{calcd} [g cm^{-3}]	1.264	1.239	1.256	1.262	1.242
2θ range [°]°	3–46	3–48	3–52	2–55	3–45
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.07	0.07	0.07	0.07	0.07
measured reflns	25066	14086	9917	28913	7739
$R_{int.}$	0.0953	0.0535	0.0771	0.0813	0.0759
independent reflns	6826	3651	4658	2766	3150
observed reflns [$I>2\sigma(I)$]	4850	3064	2757	2356	1773
parameters	723	326	326	212	326
R_1 [$I>2\sigma(I)$]	0.0872	0.0495	0.0542	0.0400	0.0599
wR_2 (all data)	0.2212	0.1341	0.1397	0.1132	0.1488
Goof	1.105	1.070	0.959	1.046	0.951
residual electron density [e Å^{-3}]	0.49/−0.39	0.26/−0.19	0.23/−0.20	0.25/−0.22	0.34/−0.19

irradiation, the solvent was evaporated and the residue was dissolved in dichloromethane and passed through a short column of silica gel. By using preparative HPLC (90:10 heptane/dichloromethane) three isomers were separated and characterized: 1,3-cyclohexadiene structure **2** (C_s symmetry; 12 mg, 9.4 %), 1,3-cyclohexadiene structure **3** (C_2 symmetry; 8 mg, 6.3 %) and ladderane **4** (2 mg, 1.6 %). For a copy of the HPLC chromatogram (UV detector, 254 nm) see the Supporting Information. Single crystals of **2** and **3** were obtained from a heptane/dichloromethane mixture.

*Data for compound **2** (C_s symmetry)*: ^{1}H NMR (500 MHz, $CDCl_3$/TMS): $\delta=7.61$ (d, $J=7.0$ Hz, 2H), 7.26 (d, $J=7.0$ Hz, 2H), 7.21 (dd, $J=7.0$, 7.0 Hz, 2H), 7.16 (m, 2H), 7.13 (dd, $J=7.0$, 7.0 Hz, 2H), 7.01 (d, $J=7.0$ Hz, 2H), 6.91 (dd, $J=7.5$, 7.5 Hz, 2H), 6.86 (dd, $J=7.5$, 7.5 Hz, 2H), 5.92 (d, 10.5 Hz, 2H), 5.67 (d, $J=10.5$ Hz, 2H), 5.14 ppm (d $J=10.5$ Hz, 2H), 3.40 ppm (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$/TMS): $\delta=141.40$ (C_q, C=C bridgehead), 141.08 (C_q, CR_2=CHR), 140.27 (C_q), 138.58 (C_q), 137.6 (C_q), 134.47 (C_q), 131.13 (CH, olefinic), 127.42 (CH, arom), 127.33 (CH, cyclohexadiene), 127.28 (CH, arom), 125.21 (CH, arom), 125.16 (CH, arom), 125.12 (CH, arom), 124.90 (CH, arom), 124.86 (CH, arom), 124.68 (CH, arom), 123.15 (CH, cyclohexadiene), 40.75 ppm (CH, aliphatic); MS (70 eV): m/z (%): 456 (100) [M^+].

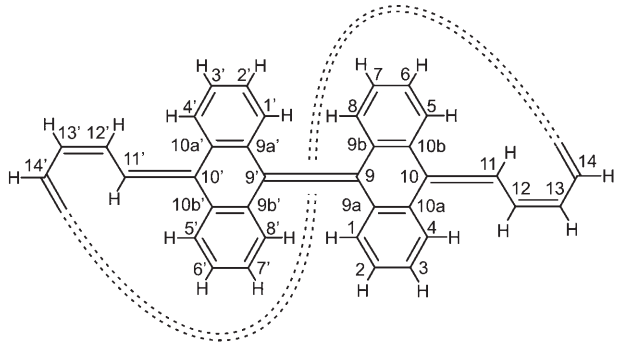
*Data for compound **3** (C_2 symmetry)*: ^{1}H NMR (500 MHz, $CDCl_3$/TMS): $\delta=7.53$ (m, 4H), 7.26 (d, $J=7.0$ Hz, 2H), 7.15 (d, $J=7.0$ Hz, 2H), 7.11 (d, $J=7.0$ Hz, 2H), 7.06 (m, 2H), 7.02 (m, 2H), 6.99 (dd, $J=7.0$, 1.3 Hz, 2H), 5.92 (d, $J=10.0$ Hz, 2H), 5.66 (dd, $J=10.0$, 1.5 Hz, 2H), 5.54 (dd, $J=10.0$, 2.8 Hz, 2H), 3.67 ppm (dd, $J=7.0$ Hz, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$/TMS): $\delta=140.68$ (C_q, C=C bridgehead), 140.48 (C_q, CR_2=CHR), 140.40 (C_q), 140.05 (C_q), 137.17 (C_q), 134.88 (C_q), 129.28 (CH, olefinic), 127.96 (CH, cyclohexadiene), 127.18 (CH, arom), 126.52 (CH, arom), 126.36 (CH, arom), 125.89 (CH, arom), 125.50 (CH, arom), 125.03 (CH, arom), 124.48 (CH, arom), 122.38 (CH, arom), 121.86 (CH, cyclohexadiene), 36.99 ppm (CH, aliphatic); MS(70 eV): m/z (%): 456 (100) [M^+].

*Data for compound **4** (ladderane)*: ^{1}H NMR (500 MHz, $CDCl_3$/TMS): $\delta=7.85$ (dd, 2H), 7.45 (dd, 2H), 7.40 (dd, 2H), 7.33 (dd, 2H), 7.22 (dd, 2H), 6.10 (dd, 2H), 7.02 (dd, 2H), 6.67 (dd, 2H), 6.50 (s, 2H; olefinic), 4.31 (dd, 2H), 3.27 (dd, 2H), 2.86 ppm (dd, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$/TMS): $\delta=144.20$ (C_q, C=C bridgehead), 143.38 (C_q, CR_2=CHR), 138.11 (C_q), 137.78 (C_q), 137.56 (C_q), 134.47 (C_q), 129.27 (CH, olefinic), 129.12 (CH, arom), 128.78 (CH, arom), 128.45 (CH, arom), 128.31 (CH, arom), 128.08 (CH, arom), 126.90 (CH, arom), 126.7 (CH, arom), 125.37 (CH, arom), 125.12 (CH, arom), 124.12 (CH, arom), 121.60 (CH, arom), 46.76 (CH, aliphatic), 39.10 (CH, aliphatic), 29.71 ppm (CH, aliphatic); MS(70 eV): m/z (%): 456 (100) [M^+].

Preparation of compounds 5–9: A solution of TDDA (100 mg, 0.28 mmol), TCOD (300 mg, 2.88 mmol) and naphthalene (20 mg, 0.15 mmol) was irradiated with a 15 W low-pressure mercury lamp in a quartz photoreactor and agitated with an argon gas flow. After 24 h of irradiation, the solvent was evaporated and the solid residue was dissolved in dichloromethane and passed through a short column of silica gel. The combined yield of isomers was 50 %. For separation of the products a semipreparative HPLC column and a mixture of 95:5 of heptane and dichloromethane was used. For a copy of the HPLC chromatogram (UV detector, 254 nm) see Supporting Information. The cyclohexadiene compound **2** (C_s symmetry), Möbius compound **6** (C_2 symmetry), and Möbius compound **8** (C_1 symmetry) have very close retention times. Isolation of **6** was only possible after removal of **2** by titration with TCNE. The cyclohexadiene isomer reacts faster and forms a polar [4+2] adduct, which can be easily separated. Compound **8** is thermolabile and has to be separated at low temperatures. Single crystals of **5**, **6**, and **7** were obtained by the diffusion method from heptane/dichloromethane.

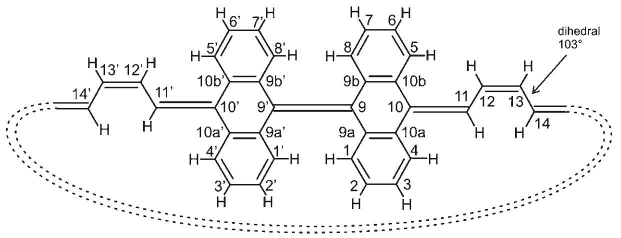
*Data for compound **5** (Möbius C_1)*: Yield: 8 mg; ^{1}H NMR (500 MHz, $CDCl_3$/TMS): $\delta=7.83$ (m, 4H), 7.44 (dd, $J=5.5$, 3.4 Hz, 2H), 7.20 (dd, $J=7.5$, 7.5 Hz, 4H), 7.09 (m, 4H), 6.72 (dd, $J=9.4$, 6.9 Hz, 2H; olefinic), 6.41 (dd, $J=6.9$, 1.7 Hz, 2H; olefinic), 6.22 ppm (d, 4H; olefinic); ^{13}C NMR (125.8 MHz, $CDCl_3$/TMS): $\delta=139.81$ (C_q, C=C bridgehead), 138.09 (C_q, CR_2=CHR), 136.98 (C_q), 136.52 (C_q), 135.90 (C_q), 135.5 (C_q), 132.97 (CH, olefinic), 132.72 (CH, olefinic), 128.72 (CH, arom), 128.65 (CH, arom), 127.75 (CH, olefinic), 126.78 (CH, arom), 126.14 (CH, arom), 125.01 (CH, arom), 124.81 (CH, arom), 124.77 (CH, arom), 123.97 (CH, arom), 123.84 ppm (CH, olefinic); UV/Vis ($CHCl_2$): λ_{max} (ε)$=250$ (19528), 300 nm (15199); MS (70 eV): m/z (%): 456 (100) [M^+].

*Data for compound **6** (Möbius C_2)*: Yield: 6 mg; ^{1}H NMR (500 MHz, $CDCl_3$/TMS): $\delta=7.709$ (ddd, ^3J(1-H,2-H)$=7.5$ Hz, ^4J(1-H,3-H)$=1.3$ Hz, ^5J(1-H,4-H)$=0.5$ Hz, 2H; 1-H), 7.516* (m, 2H; 8-H), 7.209* (m, 2H; 4-H), 7.201* (m, 2H; 5-H), 7.184 (ddd, ^3J(2-H,1-H)$=7.5$ Hz, ^4J(2-H,4-H)$=1.3$ Hz, 2H; 2-H), 7.098 (ddd, ^3J(3-H,2-H)$=7.5$ Hz, ^3J(3-H,4-H)$=7.5$ Hz, ^4J(3-H,1-H)$=1.3$ Hz, 2H; 3-H), 7.009 (ddd, ^3J(7-H,6-H)$=7.4$ Hz, ^3J(7-



H,8-H) = 7.4 Hz, ^{4}J(7-H,5-H) = 2.0 Hz, 2H; 7-H_A), 7.003 (ddd, ^{3}J(6-H,7-H) = 7.4 Hz, ^{3}J(6-H,7-H) = 7.4 Hz, ^{4}J(6-H,8-H) = 2.0 Hz, 2H; 6-H_B), 6.486 (dd, ^{3}J(11-H,12-H) = 12.5 Hz, ^{4}J(11-H,13-H) = 1.5 Hz, 2H; 11-H), 6.118 (dd, ^{3}J(12-H,11-H) = 12.5 Hz, ^{3}J(12-H, 13-H) = 11.9 Hz, 2H; 12-H), 5.940 (dd, ^{3}J(14-H,13-H) = 4.7 Hz, ^{4}J(14-H,14′-H) = 1.9 Hz, 2H; 14-H), 5.690 ppm (dddd, ^{3}J(13-H,12-H) = 11.9 Hz, ^{3}J(13-H,14-H) = 4.7 Hz, ^{4}J(13-H,14′-H) = 1.9 Hz, ^{n}J = 0.9 Hz, 2H; 13-H); *chemical shifts were assigned from HSQC spectra; ^{13}C NMR (125.8 MHz, $CDCl_3$/TMS): $\delta = 140.67$ (10-C), 139.92 (9-C), 139.36 (10b-C), 138.93 (9a-C), 138.34 (9b-C), 135.91 (10a-C), 128.09 (1-C), 127.79 (12-C), 127.04 (14-C), 126.42 (6-C), 126.27 (8-C), 126.15 (4-C), 125.97 (3-C), 125.41 (2-C), 125.24 (7-C), 124.89 (11-C), 122.05 ppm (5-C); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 253 (26231), 312 (17251), 400 nm (br, 2946); MS (70 eV): *m*/*z* (%): 456 (100) [M^+].

*Data for compound **7** (Hückel C_s)*: ^{1}H NMR (500 MHz, $CDCl_3$/TMS): $\delta = 7.733$ (ddd, ^{3}J(8-H,7-H) = 7.5 Hz, ^{4}J(8-H,6-H) = 1.3 Hz, ^{5}J(8-H,5-H) = 0.6 Hz, 2H; 8-H), 7.609 (ddd, ^{3}J(1-H,2-H) = 7.3 Hz, ^{4}J(1-H,3-H) = 1.5 Hz, ^{5}J(1-H,4-H) = 0.6 Hz, 2H; 1-H), 7.332 (ddd, ^{3}J(5-H,6-H) = 7.3 Hz, ^{4}J(5-H,7-H) = 1.5 Hz, 2H; 5-H), 7.114 (m, 2H; 4-H), 7.087 (ddd, ^{3}J(7-H,8-H) = 7.5 Hz, ^{3}J(7-H,6-H) = 7.3 Hz, ^{4}J(7-H,5H) = 1.5 Hz, 2H; 7-H), 7.043 (ddd, ^{3}J(6-H,7-H) = 7.3 Hz, ^{3}J(6-H,5-H) = 7.5 Hz, ^{4}J(6-H,8-H) = 1.3 Hz, 2H; 6-H), 7.005 (ddd, ^{3}J(2-H,1-H) = 7.3 Hz, ^{3}J(2-H,3-H) = 7.3 Hz, ^{4}J(2-H,4-H) = 1.5 Hz, 2H; 2-H), 6.978 (ddd, ^{3}J(3-H,2-H) = 7.3 Hz, ^{3}J(3-H,4-H) = 7.5 Hz, ^{4}J(3-H,1-H,=1.5 Hz, 2H; 3-H), 6.624 (dd, ^{3}J(12-H,11-H) = 11.0 Hz, ^{3}J(12-H,13-H) = 10.8 Hz, 2H; 12-H), 6.260 (dd, ^{3}J(11-H,12-H) = 11.0 Hz, ^{4}J(11-H,13-H) = 1.3 Hz, 2H; 11-H), 6.238 (ddd, ^{3}J(14-H,14′-H) = 11.0 Hz, ^{3}J(14-H,13-H) = 2.4 Hz, ^{4}J(14-H,13′-H) = 1.1 Hz, 2H; 14-H), 5.875 ppm (dddd, ^{3}J(13-H,12-H) = 10.8 Hz, ^{3}J(13-H,14-H) = 2.4 Hz, ^{4}J(13-H,14′-H) = 1.1 Hz, ^{4}J(13-H,11-H) = 0.9 Hz, 2H; 13-H); ^{13}C NMR (125.8 MHz, $CDCl_3$/TMS): $\delta = 139.76$ (9-C)*, 138.19 (10-C)*, 137.93 (10a-C)*, 137.65 (9b-C)*, 137.47 (9a-C)*, 136.31 (10b-C)*, 131.52 (13-C), 129.83 (14-C), 128.45 (8-C), 128.02 (12-C), 127.94 (1-C), 126.44 (3-C), 126.06 (6-C), 125.41 (5-C), 125.23 (7-C), 124.60 (2-C), 123.29 (4-C), 122.00 ppm (11); * assignement according to a CSGT B3LYP/6–31G* calculation; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 259 (17027), 299 nm (16334); MS (70 eV): *m*/*z* (%): 456 (100) [M^+].



*Data for compound **8** (Möbius C_1, global minimum)*: ^{1}H NMR (500 MHz, $CDCl_3$/TMS): $\delta = 7.75$ (dd, 2H), 7.37 (dd, 2H), 7.20 (dd, 2H), 7.15 (m, 2H), 7.12 (m, 2H), 6.94 (dd, 2H), 6.80 (t, 2H), 6.72 (dd, 1H; olefinic), 6.25 (d, 1H; olefinic), 6.15 (t, 1H; olefinic), 5.97 (d, 1H; olefinic), 5.90 (dd, 1H; olefinic), 5.85 (dd, 1H; olefinic), 5.78 (dd, 1H; olefinic), 5.72 ppm (dd, 1H; olefinic); MS(70 eV): *m*/*z* (%): 456 (100) [M^+]. The compound isomerizes at room temperature to give the C_s symmetric cyclohexadiene structure **2**.

*Data for compound **9** (Möbius C_2)*: ^{1}H NMR (500 MHz, $CDCl_3$/TMS): $\delta = 7.75$ (dd, 2H), 7.37 (dd, 2H), 7.20 (dd, 2H), 7.15 (m, 2H), 7.12 (m, 2H), 6.94 (dd, 2H), 6.80 (t, 2H), 6.72 (dd, 1H; olefinic), 6.25 (d, 1H; olefinic), 6.15 (t, 1H; olefinic), 5.97 (d, 1H; olefinic), 5.90 (dd, 1H; olefinic), 5.85 (dd, 1H; olefinic), 5.78 (dd, 1H; olefinic), 5.72 pm (dd, 1H; olefinic); MS (70 eV): *m*/*z* (%): 456 (100) [M^+]. The data are not sufficient to distinguish between the two possible conformations **9a** and **9b**.

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