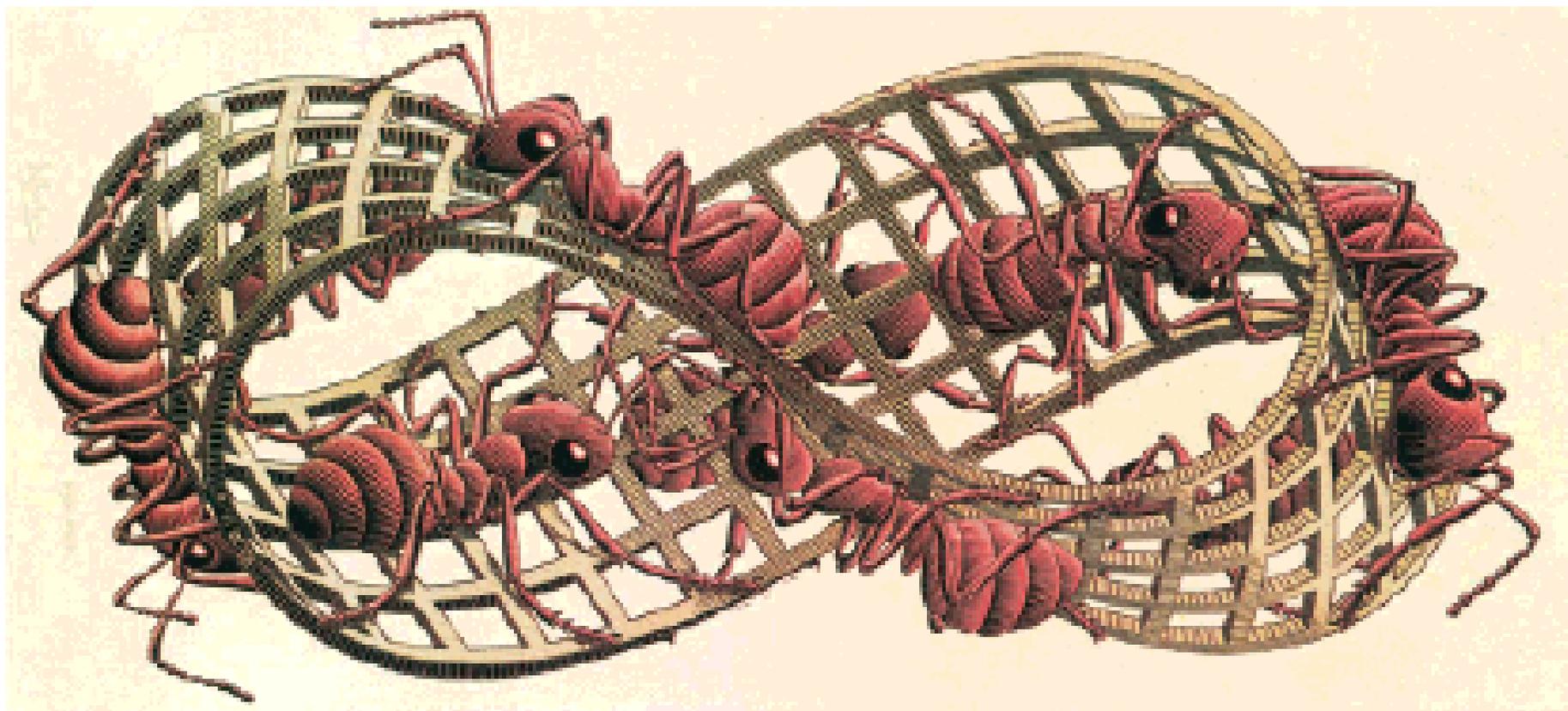


Theory and Design of Mobius Molecules



William Collins
Denmark Research Group Meeting
(04-08-08)

Canon Crancrizans: (Musical Offering, BWV1079)

28

Thematis Regii
Elaborationes Canonicae

1a. Canon a 2 cancrizans

Violine I
Violino II

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The image shows a page of a musical score for 'Thematis Regii Elaborationes Canonicae', specifically the first canon (1a. Canon a 2 cancrizans). The score is written for Violin I and Violin II. It features a complex rhythmic pattern with many sixteenth and thirty-second notes. The page number 28 is in the top left corner. At the bottom left, the code 'BA 1154' is visible, and at the bottom right, the copyright information '© 1987 by Bärenreiter - Verlag, Kassel' is present.

Written in 1747 by Johann Sebastian Bach



Johann Sebastian Bach

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Thematis Regii
Elaborationes Canonicae

1a. Canon a 2 cancrizans

Violine I
Violino II

BA 1154 © 1987 by Bärenreiter - Verlag, Kassel

Written in 1747 by Johann Sebastian Bach



One of the oldest examples of Möbius topology



August Ferdinand Möbius
1790-1866

“Seminal” Publication by Mobius:

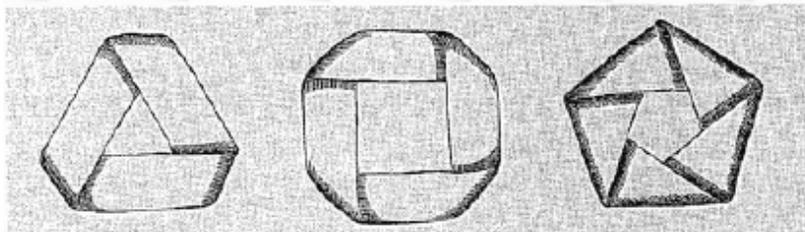
§ 14. Von der verschiedenartigen Form der zweierlei Zonenflächen kann man sich eine sehr anschauliche Vorstellung mittelst eines Papierstreifens verschaffen, welcher die Form eines Rechtecks hat. Sind A, B, B', A' die vier Ecken desselben in ihrer Aufeinanderfolge, und wird er hierauf gebogen, so dass die Kante $A'B'$ sich stets parallel bleibt, bis sie zuletzt mit AB zusammenfällt, so erhält der Streifen die Form einer Cylinderfläche, also einer zweiseitigen Zone, welche die zwei nunmehr kreisförmigen Kanten AA' und BB' des anfänglichen Rechtecks zu ihren zwei Grenzlinien hat. — Man kann aber auch, dafern das eine Paar paralleler Kanten AA' und BB' gegen das andere AB und $A'B'$ hinreichend gross ist, A' mit B , und B' mit A zur Coincidenz bringen, indem man zuvor, das eine Ende AB des Streifens festhaltend, das andere Ende $A'B'$ um die Längsaxe des Streifens halb herumdreht, als wodurch $A'B'$ mit BA einerlei Richtung erhält. Die nach der letztgedachten Coincidenz entstandene Fläche hat nur Eine Grenzlinie, nämlich die aus den jetzt gebogenen und in A und B' , sowie in B und A' an einander grenzenden Linien AA' und BB' zusammengesetzte. Auch hat diese Fläche nur Eine Seite; denn wenn man sie — um dieses noch auf andere Weise vorstellig zu machen — von einer beliebigen Stelle aus mit einer Farbe zu überstreichen anfängt und damit fortfährt, ohne mit dem Pinsel über die Grenzlinie hinaus auf die andere Seite überzugehen, so werden nichtsdestoweniger zuletzt an jeder Stelle die zwei daselbst einander gegenüberliegenden Seiten der Fläche gefärbt seyn.



“...One can, however,...superpose A' with B , and B' with A , by holding the side AB fixed, give the other end $A'B'$ a half-twist...The surface created by this superposition has only one edge...and one side.”



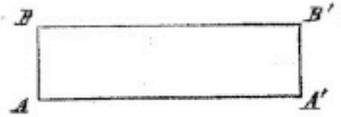
August Ferdinand Möbius
1790-1866



“Zur Theorie der Polyeder und der Elementarverwandschaft”, *diaria Mathematica*, Möbius, A. F. 1858.

Initial work by Mobius / Listing:

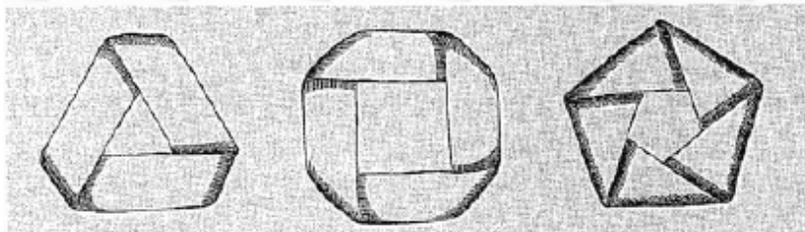
§ 14. Von der verschiedenartigen Form der zweierlei Zonenflächen kann man sich eine sehr anschauliche Vorstellung mittelst eines Papierstreifens verschaffen, welcher die Form eines Rechtecks hat. Sind A, B, B', A' die vier Ecken desselben in ihrer Aufeinanderfolge, und wird er hierauf gebogen, so dass die Kante $A'B'$ sich stets parallel bleibt, bis sie zuletzt mit AB zusammenfällt, so erhält der Streifen die Form einer Cylinderfläche, also einer zweiseitigen Zone, welche die zwei nunmehr kreisförmigen Kanten AA' und BB' des anfänglichen Rechtecks zu ihren zwei Grenzlinien hat. — Man kann aber auch, dafern das eine Paar paralleler Kanten AA' und BB' gegen das andere AB und $A'B'$ hinreichend gross ist, A' mit B , und B' mit A zur Coincidenz bringen, indem man zuvor, das eine Ende AB des Streifens festhaltend, das andere Ende $A'B'$ um die Längsaxe des Streifens halb herumdreht, als wodurch $A'B'$ mit BA einerlei Richtung erhält. Die nach der letztgedachten Coincidenz entstandene Fläche hat nur Eine Grenzlinie, nämlich die aus den jetzt gebogenen und in A und B' , sowie in B und A' an einander grenzenden Linien AA' und BB' zusammengesetzte. Auch hat diese Fläche nur Eine Seite; denn wenn man sie — um dieses noch auf andere Weise vorstellig zu machen — von einer beliebigen Stelle aus mit einer Farbe zu überstreichen anfängt und damit fortfährt, ohne mit dem Pinsel über die Grenzlinie hinaus auf die andere Seite überzugehen, so werden nichtsdestoweniger zuletzt an jeder Stelle die zwei daselbst einander gegenüberliegenden Seiten der Fläche gefärbt seyn.



Johann Benedict Listing
1808-1882



August Ferdinand Möbius
1790-1866



Orientable Space:

- Most 3-D objects in “everyday life” are two-sided (inside and outside). Examples are a sphere, cube and torus.
- For 2-D mathematical objects the definition stands: a normal vector on the surface of a two-sided object cannot be shifted to every other point on the surface w/o crossing a border (walking upright on the outside surface you can't enter the inside)
- The Mobius band is the simplest exception to the above rules.*

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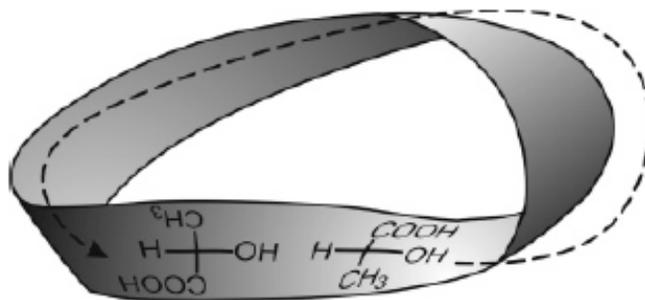
-For 2-D mathematical objects the definition stands: a normal vector on the surface of a two-sided object cannot be shifted to every other point on the surface w/o crossing a border (walking upright on the outside surface you can't enter the inside)

-The Mobius band is the simplest exception to the above rules.

A Mobius band is one-sided and contains an edge.

Unfortunately, sidedness is not an intrinsic property (requires that the surface is embedded in a surrounding space - a closed curve has an inside and outside in 2-D, and is no sided in 3-D)

Orientability: A surface is considered orientable if it is not possible to move a shape on the surface in such a way that it is transformed into its mirror image



Movement of L-lactic acid around the band gives upside-down D-lactic acid
Thus a Mobius band is non-orientable (picture shows transparent band)

Orientable Space:

-Most 3-D objects in “everyday life” are two-sided (inside and outside). Examples are a sphere, cube and torus.

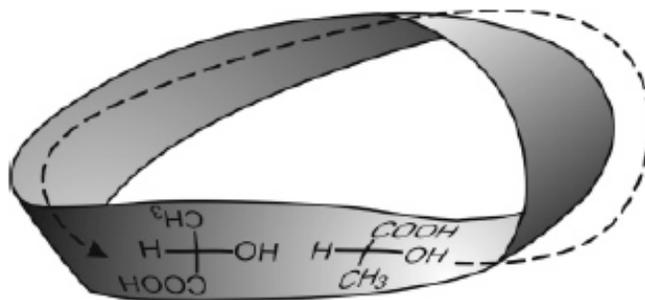
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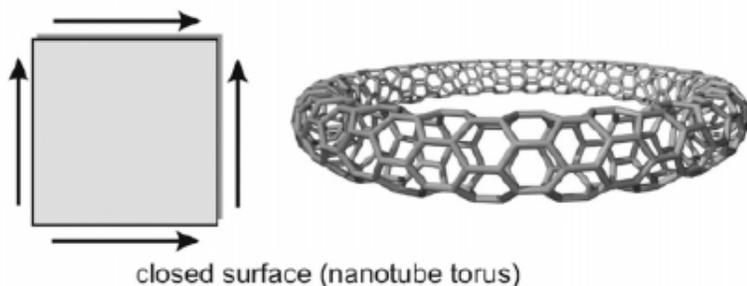
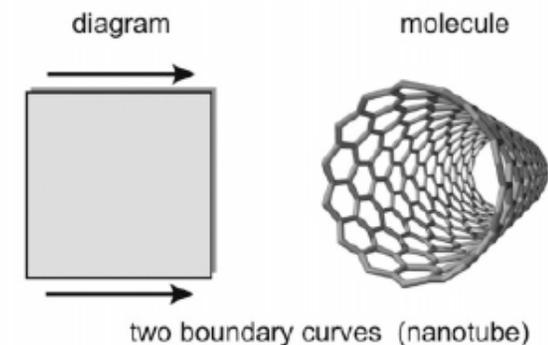


“The space-time manifold of the actual universe is believed to be orientable. Otherwise, you could take a round trip along some noncontractible path through spacetime, then when you arrived back you (or the rest of the universe, from your perspective) would have become left-right reversed, like a mirror image of itself (see chirality /handedness).”

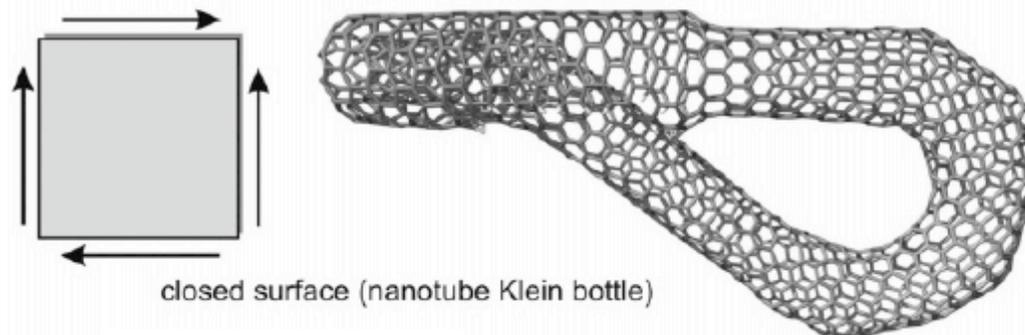
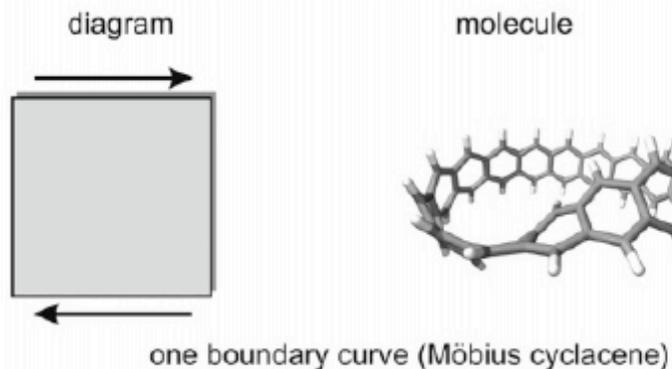
Herges, P. *Chem. Rev.* (2006), 106, 4820

Orientable Space:

Orientable:

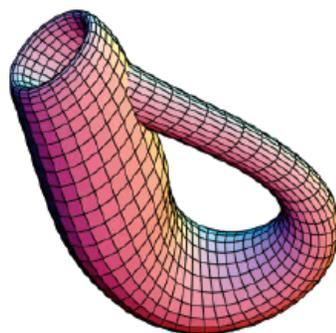


Non-Orientable:



There are a number of patents involving Möbius-type objects: conveyor belts that wear evenly, non-inductive Möbius resistors for high-frequency devices.

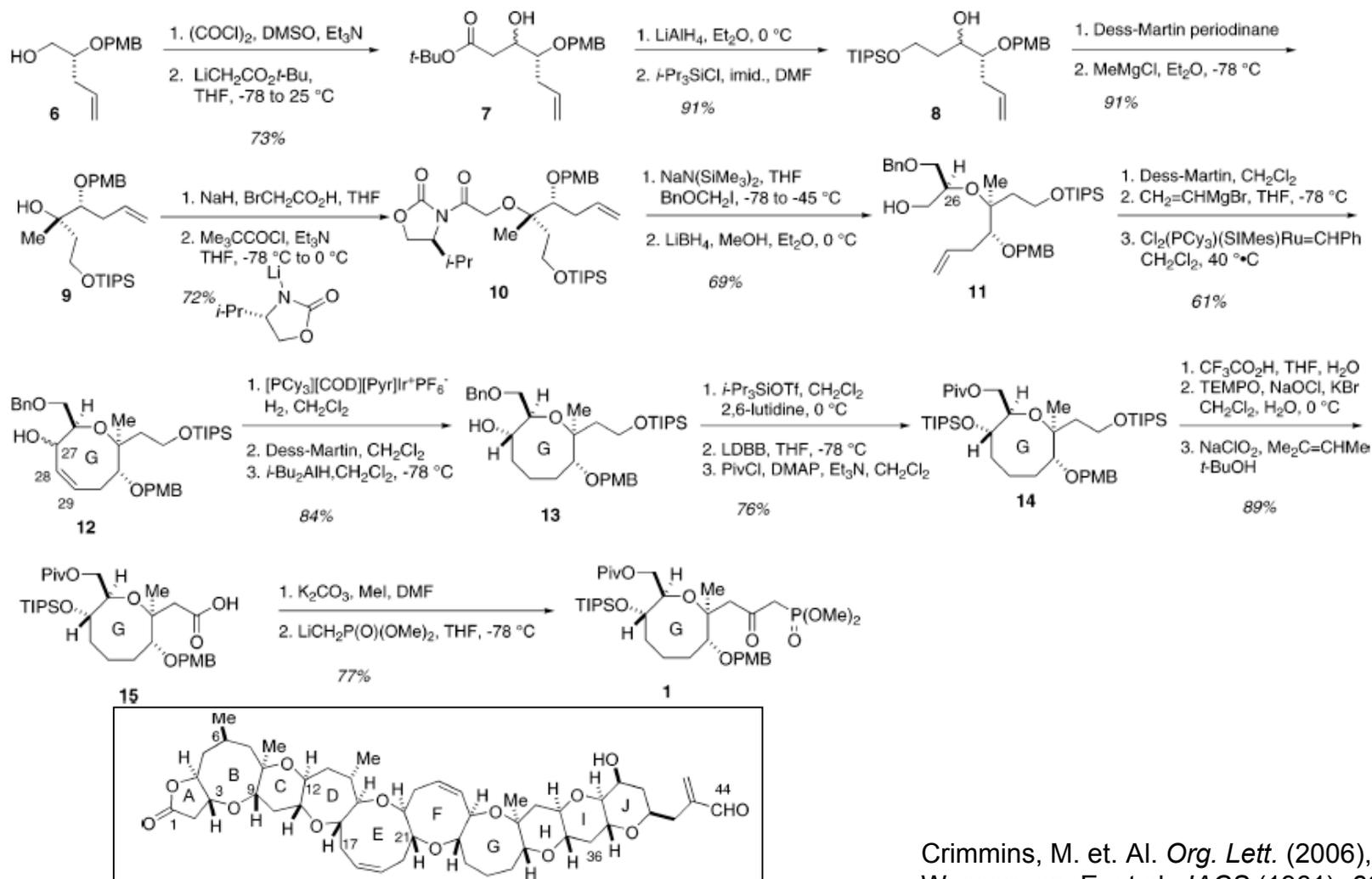
No known examples of naturally occurring Möbius bands exist



Chemical Topology

The structure of a molecule:

- The order in which given numbers of specific atoms are joined
- The types of bonds which connect them
- The spatial arrangement around rigid centers (asymmetric atoms, double bonds, etc.)



Crimmins, M. et al. *Al. Org. Lett.* (2006), 8, 159.
Wasserman, E. et al. *JACS* (1961), 83, 3789.

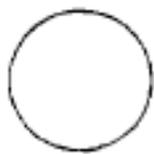
Chemical Topology

The structure of a molecule:

- a) The order in which given numbers of specific atoms are joined
- b) The types of bonds which connect them
- c) The spatial arrangement around rigid centers (asymmetric atoms, double bonds, ect..)

Topological distinctions? Consider the next two examples:

1) 50 carbon atoms in a loop or a trefoil



I



II

2) a 34, 34-catenane and two 34 non-interlocked rings



III

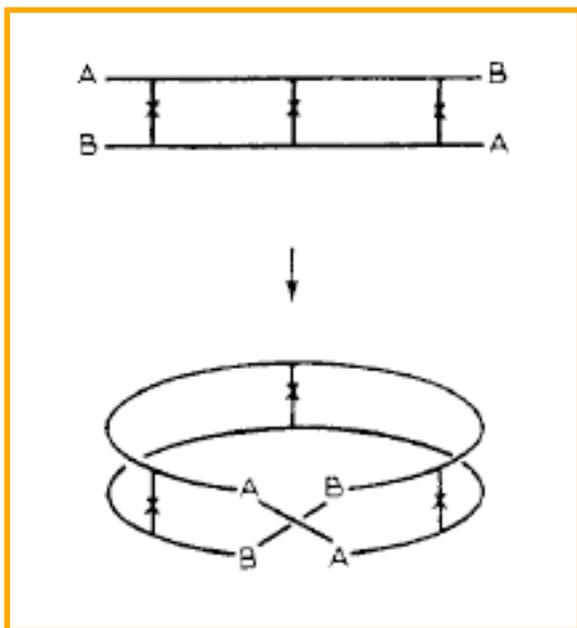


IV

Chemical Topology

The structure of a molecule:

- a) The order in which given numbers of specific atoms are joined
- b) The types of bonds which connect them
- c) The spatial arrangement around rigid centers (asymmetric atoms, double bonds, ect..)
- d) Topology?



Question:

if $A = B$, is the Möbius strip a chiral molecule?

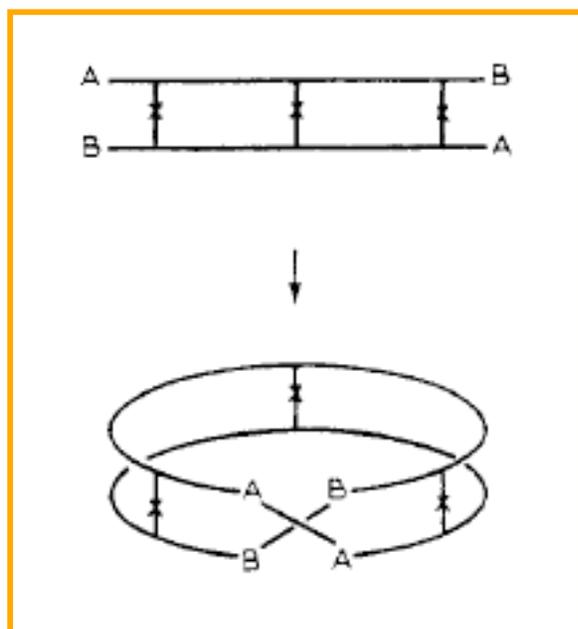
Is there symmetry to the molecule?
And if so, what is the point group?

If the twist moves around the strip through both the space between the bonds as well as the bonds what is the “time-averaged” point-group?

Chemical Topology

The structure of a molecule:

- The order in which given numbers of specific atoms are joined
- The types of bonds which connect them
- The spatial arrangement around rigid centers (asymmetric atoms, double bonds, ect..)
- Topology?



Question:

if $A = B$, is the Möbius strip a chiral molecule?

Yes, the chirality cannot be located on a center, axis, or plane. It is a topological property

Is there symmetry to the molecule?

And if so, what is the point group?

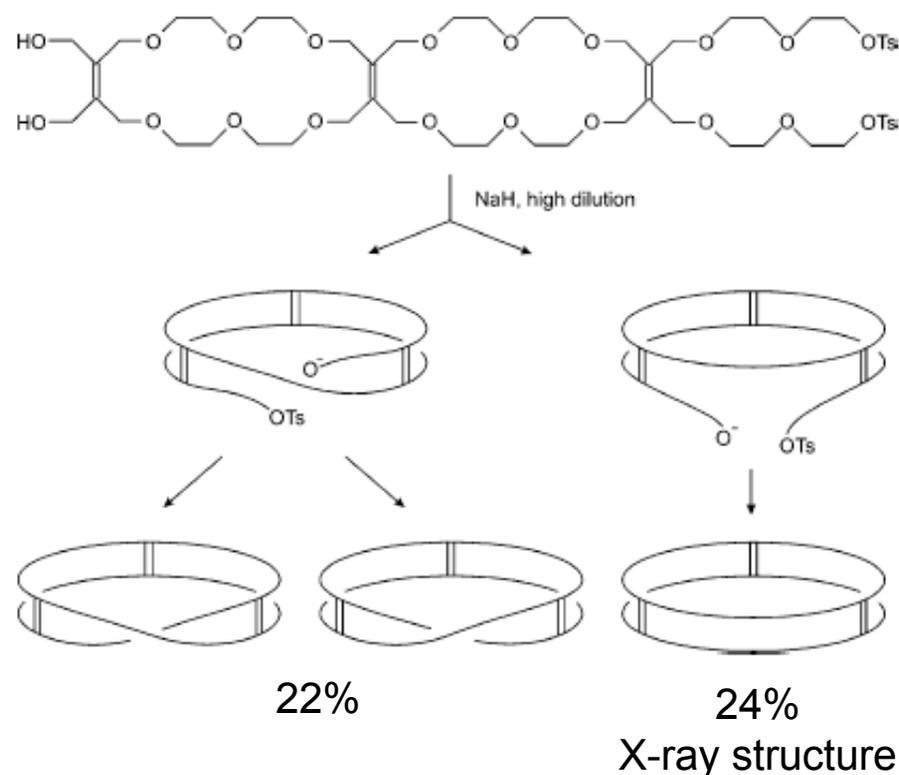
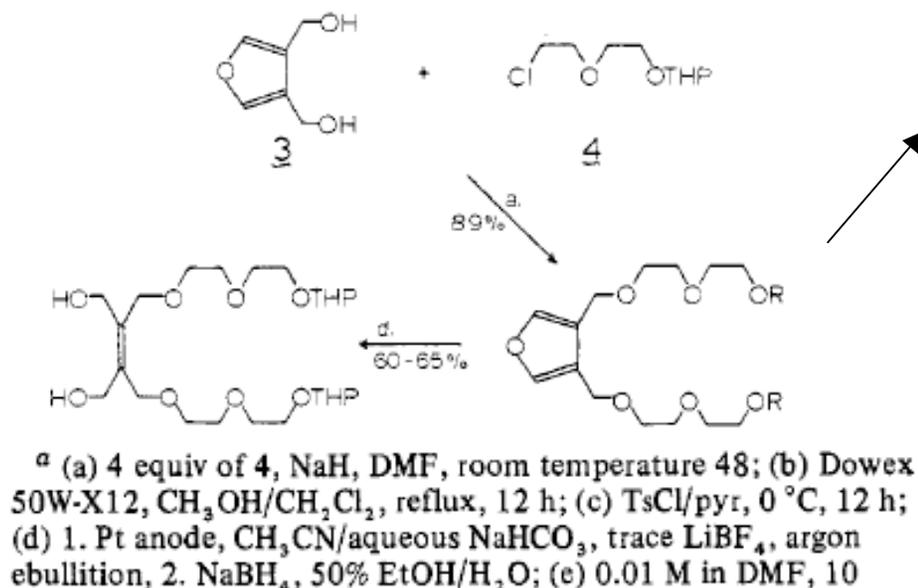
C_2

If the twist moves around the strip through both the space between the bonds as well as the bonds what is the “time-averaged” point-group?

$C_6 \wedge C_2$ (isomorphic to D_6)

Non-Conjugated Molecular Mobius Strips

Coupling repeated 3 times to obtain SM



Spectroscopic data:

Mass spec / gel permeation data show similar but different chemical ionization mass spectra (Mobius Strip: m/z 865 (33% PH⁺), 391 (100%); Cylinder m/z 865 (100% PH⁺), 391 (48%))

Proton NMR for Mobius Strip: 3.65 (br s, 2H), 4.18, 4.29 (AB q, 1H, J=11.8 Hz)

Cylinder: 3.67 (br s, 2H), 4.16, 4.29 (AB q, 1 H, J = 11.8 Hz)

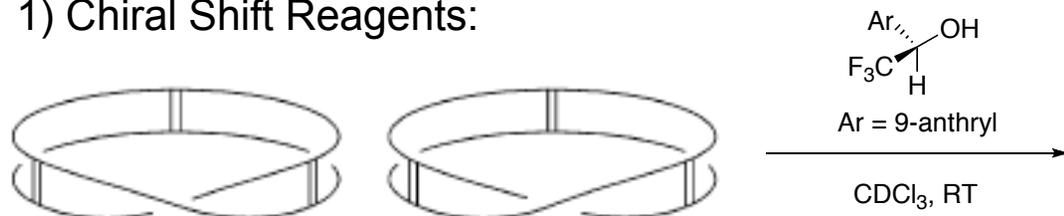
Carbon NMR for Mobius Strip: 137.26, 70.91, 69.9, 68.56

Cylinder: 136.7, 70.89, 69.77, 67.90

Non-Conjugated Molecular Mobius Strips

How can we be sure this is actually the structure?

1) Chiral Shift Reagents:



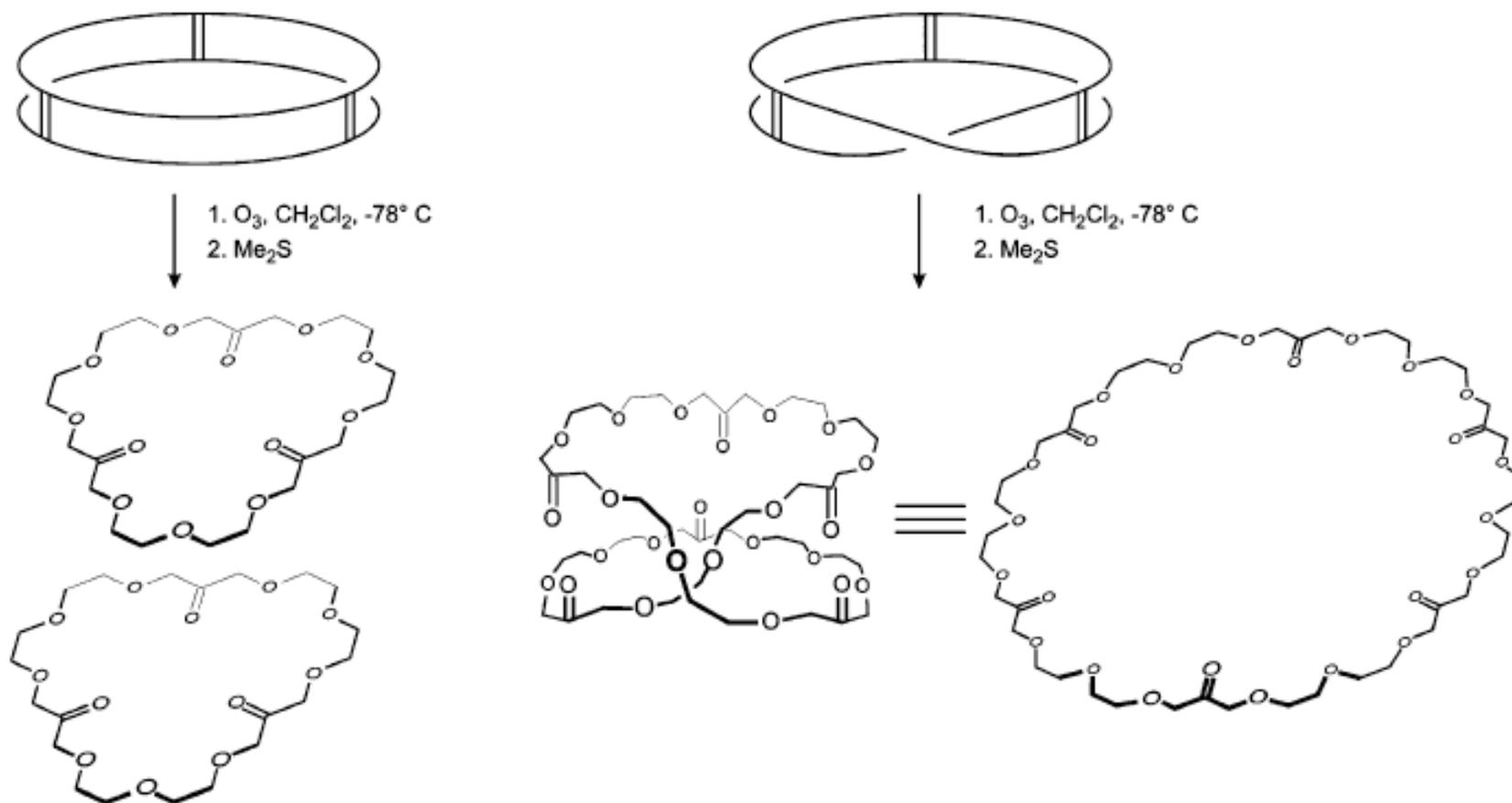
The two olefinic carbon peaks are
Resolved in C13 spectra (1.9 Hz)
No Change is seen in cylinder

“The chirality of compound **2** represents a novel example of optical isomerism. There are no chiral centers, and no molecular rigidity is required to keep the optical antipodes of **2** nonequivalent. *They owe their distinct character to connectivity only, and yet they have identical connectivity.*”

Non-Conjugated Molecular Mobius Strips

How can we be sure this is actually the structure?

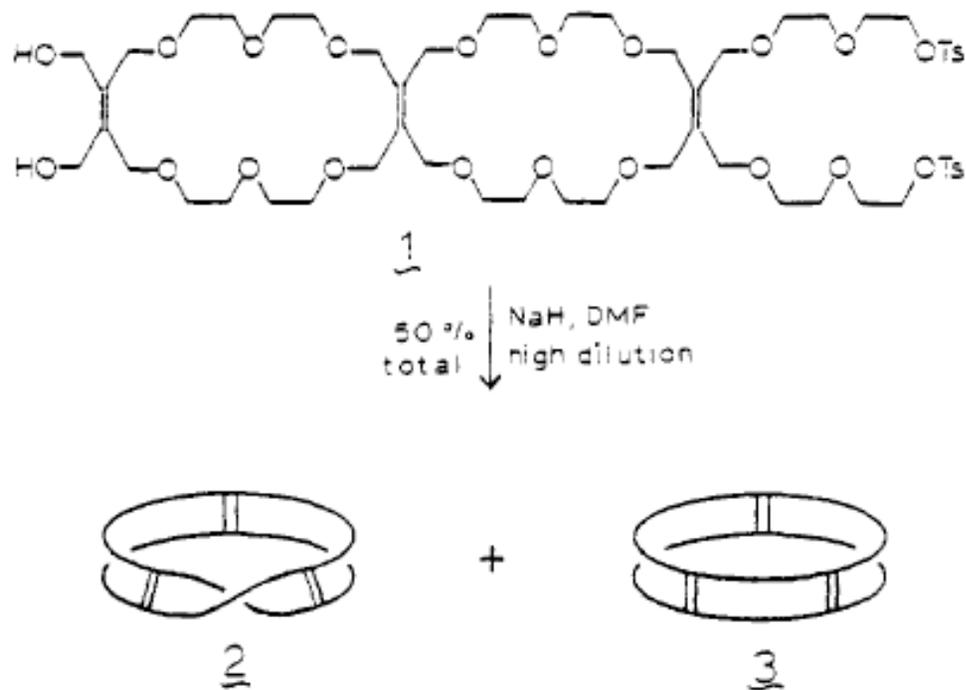
- 1) Chiral Shift Reagents
- 2) Cutting the rungs of the molecular ladder



Wasserman's Proposal / Walba's Experiments:

Walba (1982):

Scheme I



Wasserman's initial proposal was demonstrated experimentally by Walba

Wasserman (1961)

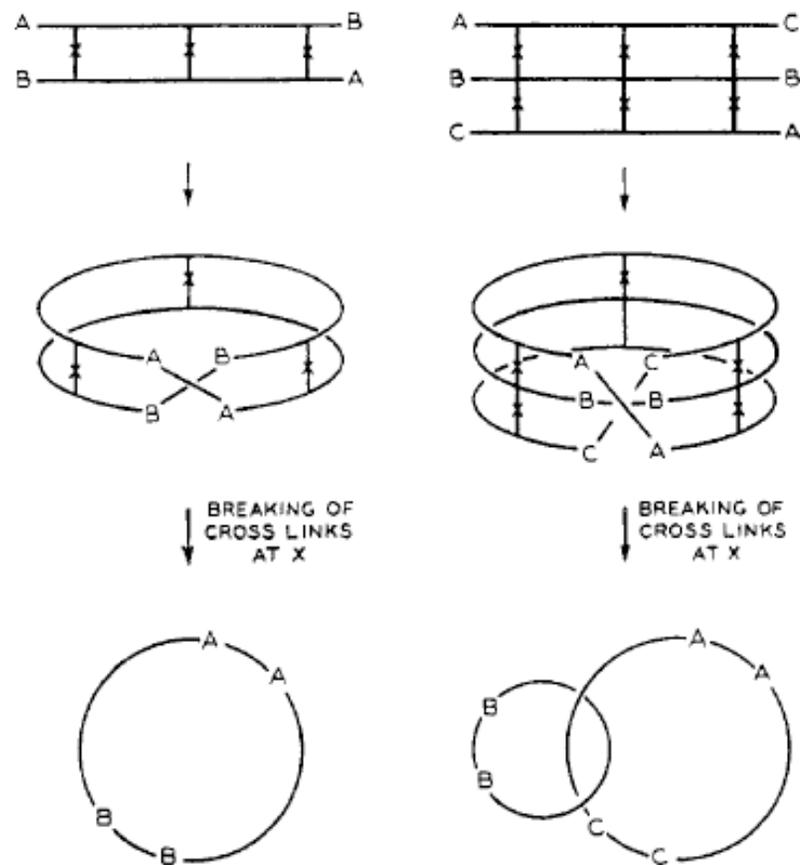
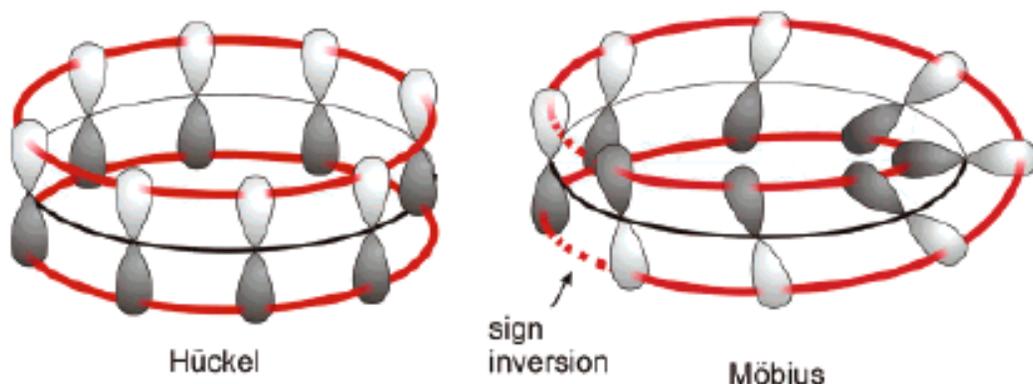


Fig. 2.—Möbius strips.

Wasserman, E. et al. *JACS* (1961), 83, 3789.
Walba, D. et al. *JACS* (1982), 104, 3219

Möbius π Systems

Theoretical Considerations:

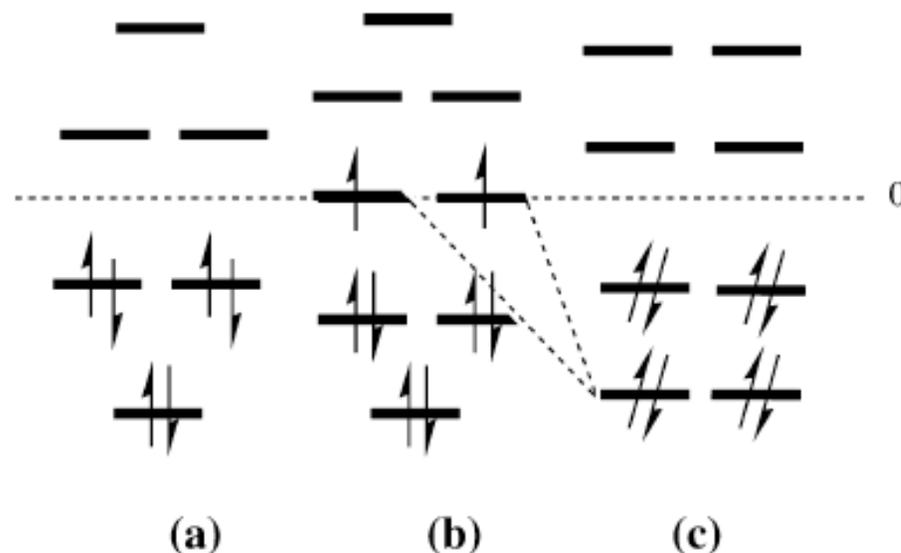


A Hückel and an idealized equilateral (planar) Möbius annulene. The π plane in the Hückel annulene has 2 sides. There is only one side in the Möbius π system. As a result of the twist there is 1 sign inversion between neighboring p orbitals.

Seminal work on Möbius π Systems: Heilbronner, E. *Tett. Lett.* (1964), 29, 1923.

-On the basis of HMO theory predicted that the Hückel rules for aromaticity ($4n+2$) do not apply for Möbius annulenes.

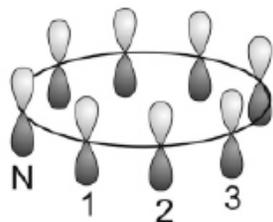
- Double occupancy by $[4n+2]$ electrons of the π molecular orbitals derived from a planar cyclic array of p-AO's results in maximizing the resonance energy per electron and hence the stability of the system
- Occupancy by $[4n]$ electrons leads to an open shell configuration. The singlet diradical electronic config. is regarded as being less stable



Möbius π Systems

Theoretical Considerations:

Hückel Annulenes



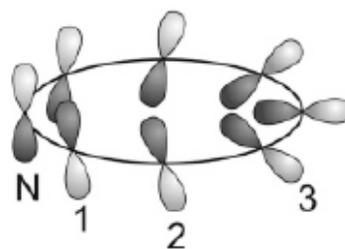
secular equation

$$\begin{vmatrix} \alpha-E & \beta & \dots & \beta \\ \beta & \alpha-E & \beta & \dots \\ \vdots & \beta & \alpha-E & \beta \\ \beta & \dots & \beta & \alpha-E \end{vmatrix}$$

$$E_j = \alpha + 2\beta \cos \frac{2\pi j}{N}$$

N: number p-orbitals
 E_j : π MO energies
 $j = 0, 1, 2, 3 \dots (N-1)$
 α : Coulomb integral
 β : Resonance integral

Möbius Annulenes



secular equation

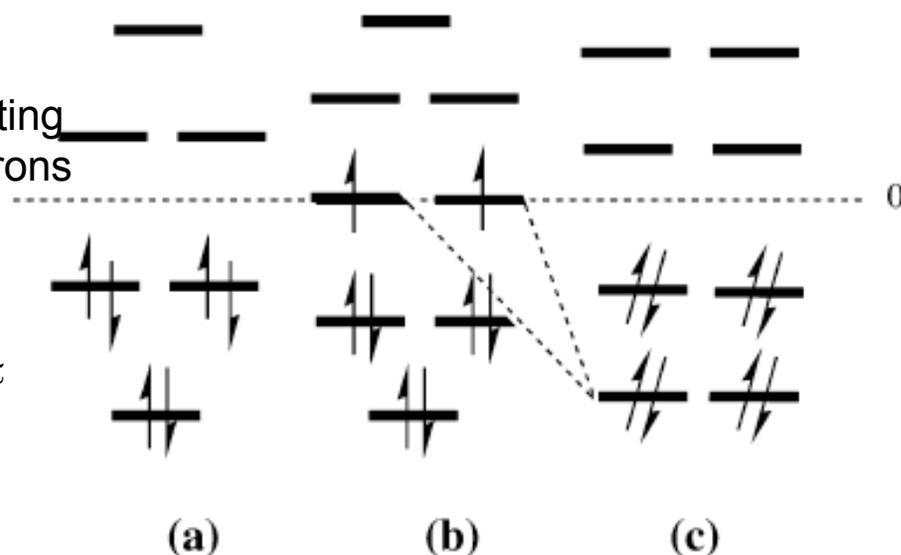
$$\begin{vmatrix} \alpha-E & \beta & \dots & -\beta \\ \beta & \alpha-E & \beta & \dots \\ \vdots & \beta & \alpha-E & \beta \\ -\beta & \dots & \beta & \alpha-E \end{vmatrix}$$

$$E_j = \alpha + 2\beta \cos \frac{\pi(2j+1)}{N}$$

$$\beta^M = \beta \cos(\pi/(4n))$$

c) If the cylinder is twisted into a Möbius strip, a single 180 deg phase shift is introduced into the array of $4n$ $2p$ AOs. HMO theory predicts that for a basis set with an even number of $2p$ AOs the resulting energy levels will be degenerate, and that $4n$ electrons will result in a closed shell config.

*Each energy level is rendered less stable than its untwisted counterpart (b) due to the reduced $p\pi$ - $p\pi$ resonance overlap.



Mobius π Systems

Theoretical Considerations:

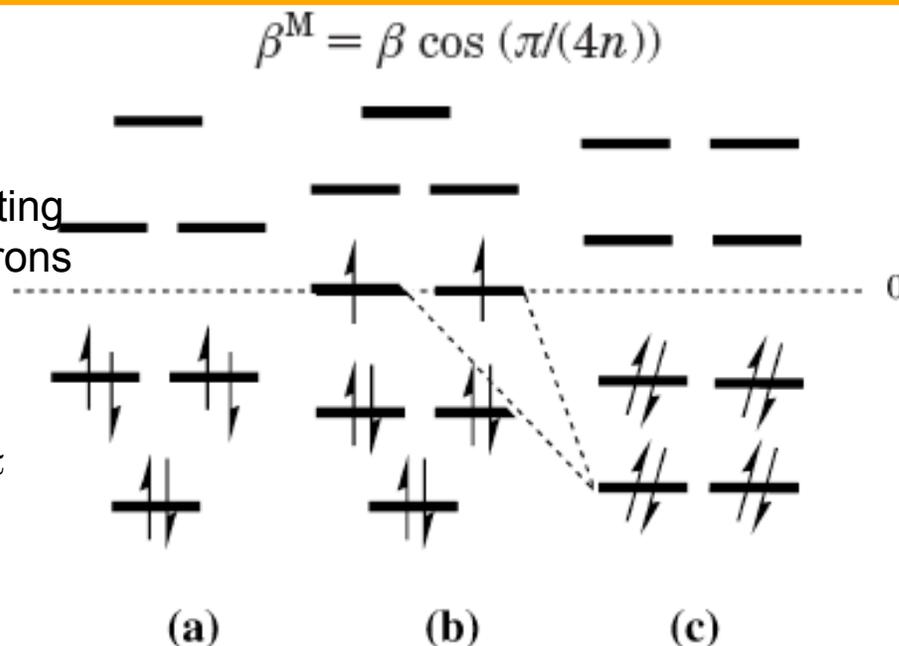
When summed over all $4n$ electrons, the stabilization gained by the phase shift in the AO basis is Exactly offset by the loss of overlap (but only if the twist is evenly distributed around the ring)

Heilbronner's inferences from his proof:

1. $4n-\pi$ Mobius half-twisted bands will favor double occupied closed shell configurations
2. $4n-\pi$ Mobius bands suffer no loss of π resonance energy compared to the untwisted $4n$ p (open shell form **(b, c)**) provided the twist is evenly distributed around the ring
3. Mobius bands have a smaller resonance energy per π -electron than $4n+2$ planar aromatics but for large rings, this may be offset by less ring strain.

c) If the cylinder is twisted into a Mobius strip, a single 180 deg phase shift is introduced into the array of $4n$ 2p AOs. HMO theory predicts that for a basis set with an even number of 2p AOs the resulting energy levels will be degenerate, and that $4n$ electrons will result in a closed shell config.

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Rezpa, H. *Chem. Rev.* (2005), 105, 3697.

Heilbronner, E. *Tett. Lett.* (1964), 29, 1923.

Mobius π Systems / Zimmerman's Mnemonic

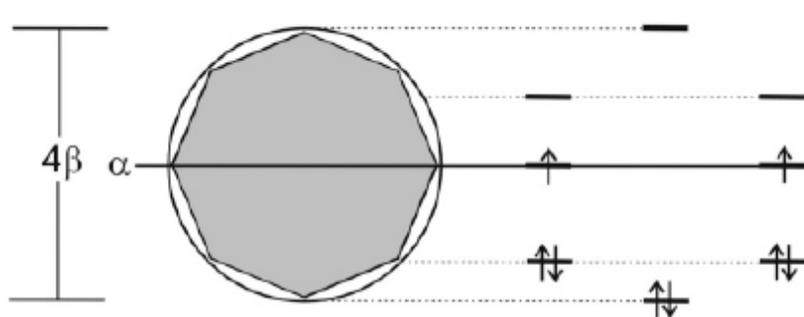
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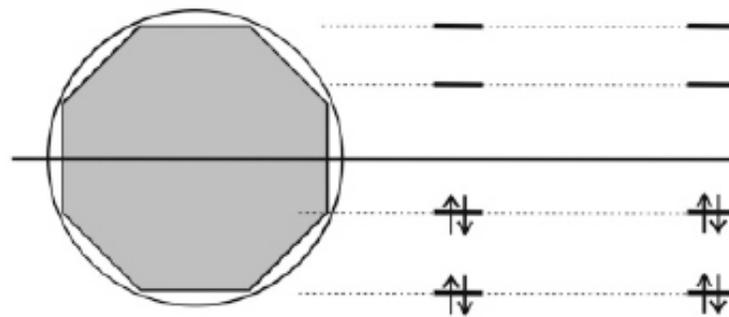
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Similar to the Frost-Musulin Mnemonic for Huckel Systems:



hypothetical planar cyclooctatetraene
(open shell)



hypothetical Möbius cyclooctatetraene
(closed shell)

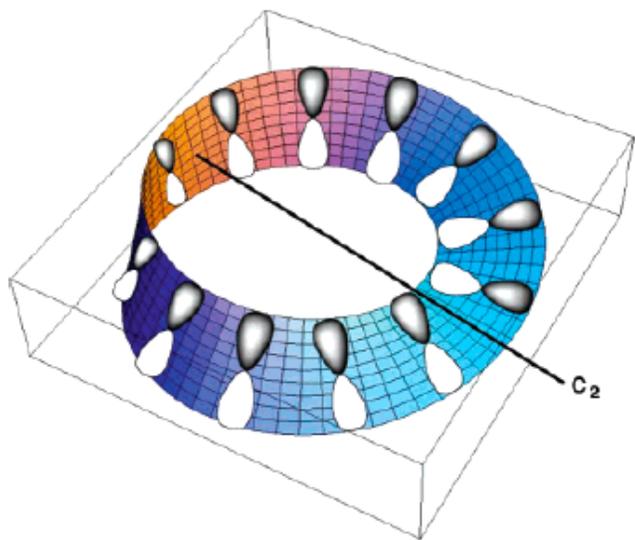
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Despite the large amount of literature on the topic, neither Heilbronner nor Zimmerman mention aromaticity in their seminal contributions.

Heilbronner does suggest (using simple Dreiding) models that for $(\text{CH})_n$ annulenes ($n > 20$) in a Möbius topology showed no apparent bond angle or steric repulsion...

Rezpa, H. *Chem. Rev.* (2005), 105, 3697.

Heilbronner, E. *Tett. Lett.* (1964), 29, 1923.

How do we Quantify Aromaticity?

Table 1. Approximate Ranges for Quantitative Measures of Aromaticity for Möbius Rings

	metric	typical range of values	comments
→	ring bond lengths ^a	C–C \approx 1.37–1.42 Å; $\Delta r \leq 0.05$ Å	typical for both Hückel and Möbius rings of size ~ 4 –18; applies to neutral or charged systems (+, -), triplet states, and transition states; can be expressed as Δr , the maximum difference between the ring bond lengths; sensitive to the method used. ²⁰
	Julg param, A^f	≤ 1.0	based on the degree of bond length equalization; values less than 1.0 indicate reduced aromaticity (with respect to a reference state such as benzene); a value of 0.0 indicates nonaromaticity
→	HOMA ^g	≤ 1.0	validated against experimental bond lengths for cyclic systems only; values less than 1.0 indicate reduced aromaticity (with respect to a reference state such as benzene); a value of 0.0 indicates nonaromaticity; some evaluation for nonplanar cyclic systems
	ring planarity		Hückel aromatic rings size 3 to ~ 8 tend to resist nonplanar distortions; half-twist Möbius aromatic rings size $\sim 7+$ tend to have low-energy C_2 -symmetric conformations with respect to C_s symmetric nonaromatic alternatives
→	ring dihedral angles ^b	0° (180°)– 50° (130°)	measured as R–C–C–R (R = ring substituent); Möbius aromatic rings tend to an ideal even distribution of the AO rotations, totaling $\sim 180^\circ$ for a half-twist system; even one orthogonal dihedral ($\sim 90^\circ \pm 15^\circ$) will interrupt delocalization
	aromatic stabilization energy (ASE) ^c exaltation of diamagnetic susceptibility ^d	~ 1.5 – 3.0 kcal mol ⁻¹ per ring carbon –15 to –120 ppm·cgs	not systematically evaluated for highly nonplanar systems Möbius annulenes show opposite tendency to Hückel annulenes for magnetic susceptibility; ^e dependent on reference fragments; positive values indicate anti-aromaticity.
→	NICS(0) ^h	–10 to –15 ppm	NICS(0) at the heavy atom ring centroid; perturbed by in-plane local effects and associated effects from σ frameworks
	¹ H NMR chemical shifts ⁱ induced current densities ^j π molecular orbitals ^k	7–9 ppm (outer protons) Möbius orbital symmetric with respect to (ideal) C_2 axis	appears typical of both Hückel and Möbius aromatic rings little evaluated for nonplanar Möbius systems one of degenerate pair in Hückel MO theory; ^{4,10} can show characteristic intersecting ring motif; susceptible to contamination from σ -orbitals making interpretation more difficult; qualitative measure only; not yet generally evaluated

^a Schleyer, P. v. R.; Freeman, P.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337. ^b Reference 16. ^c Reference 8c. Wannere, C. S.; Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 865. Schleyer, P. v. R.; Pühlhofer, F. *Org. Lett.* **2002**, *4*, 2873. For a recent review of aromatic stabilization energies, see: Cyranski, M. K. *Chem. Rev.* **2005**, *105*, 3773. ^d Reference 24. ^e Reference 11f. ^f Julg, A.; Francois, P. *Theor. Chim. Acta* **1967**, *7*, 249. ^g Reference 33. ^h References 22 and 23. ⁱ References 8c and 13. ^j For a recent review, see Herges, R. *Chem. Rev.* **2005**, *105*, 3758. See also ref 11j. ^k References 10, 36, and 37.

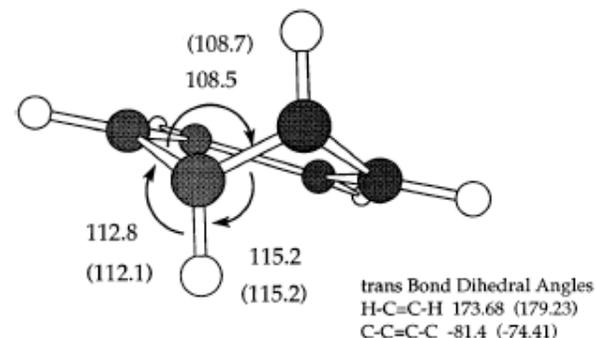
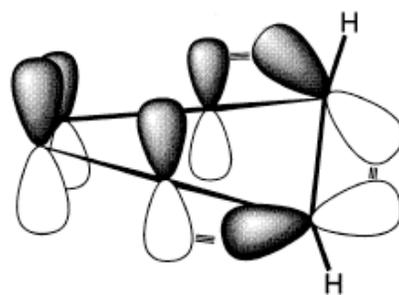
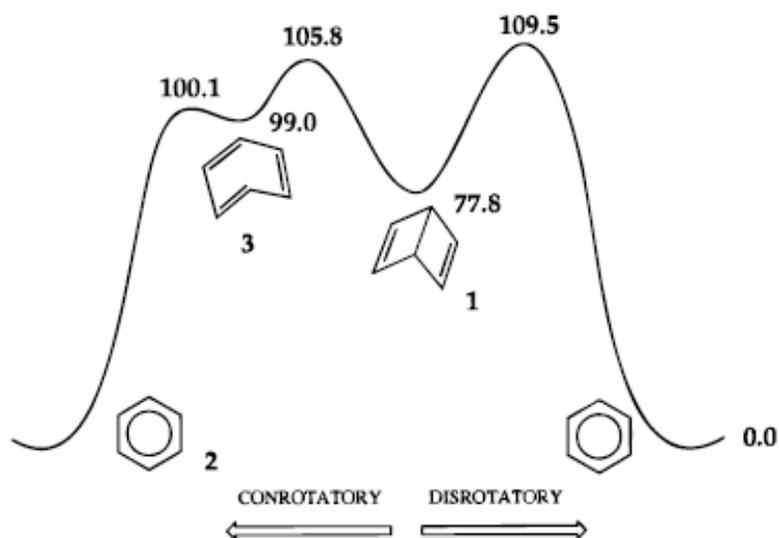
Structure and Stability (*trans*-benzene)

[n]annulenes	n=6	n=8	n=12	n=16	n=20
ΔE [kcal/mol]	107.0	21.3	6.3	5.2	6.3

-*Trans*-benzene is found only to be a shallow minimum on the energy hypersurface.

-Neither of the first two are aromatic according to magnetic criteria (NICS = -1.7 and -1.9). Conjugation between the *trans* and *cis* double bonds is reduced by dihedral angles close to 90 degrees.

Potential Energy diagram (Kcal/mol) for ring opening of Dewar Benzene:



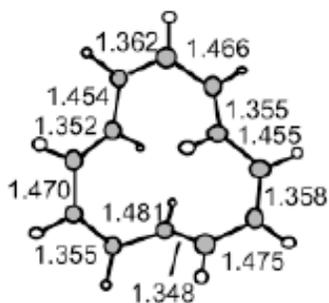
Dihedral 81.4 degrees

The "allowed" conrotatory opening of Dewar PhH to *trans*-PhH is still 3 kcal/mol lower in energy than "forbidden" disrotatory opening!

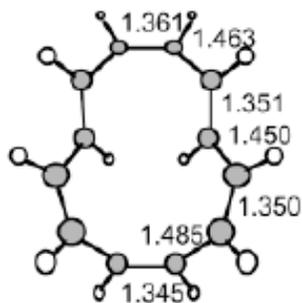
Johnson, R. et. Al. *JACS*, (1996), 118, 7381.
 Herges, P. *Chem. Rev.* (2006), 106, 4820

Structure and Stability ([12] Annulenes)

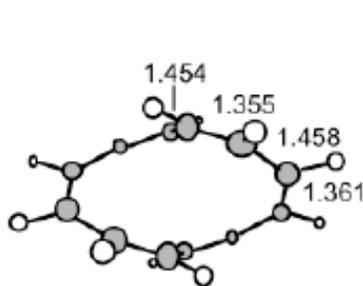
B3LYP/6-31G* Optimized geometries:



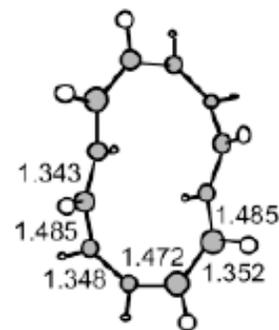
1 (C_7)



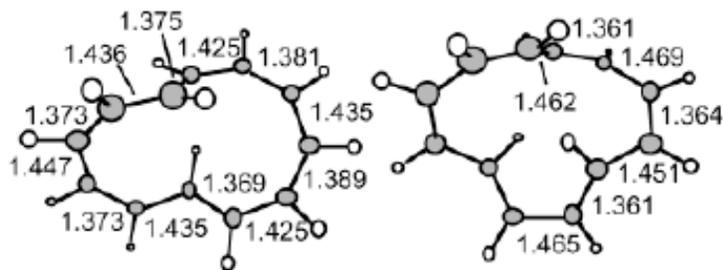
2 (C_s)



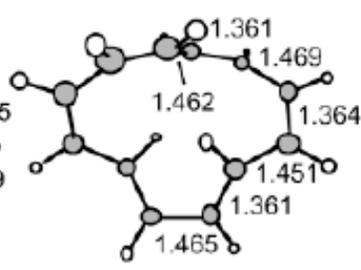
3 (D_2)



4 (C_2)



5 (C_7)

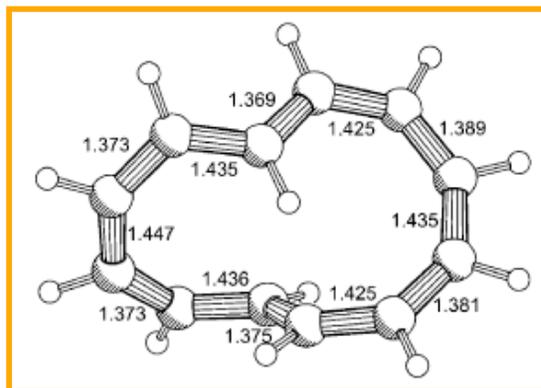


6 (C_2)

cmpd	sym	topol ^a	rel E^b	ΔCC^c
1	C_1	H	0.0	0.133
2	C_s		3.8	0.140
3	D_2	H	-0.3	0.103
4	C_2		2.5	0.142
5	C_1	M	4.4	0.078
6	C_2	M	20.2	0.108

HOMA ^e	NICS(0) [(1)] ^f	$\angle CCCC^g$
annulenes		
0.04	+3.2 [+2.0]	62.4
0.01	-2.4 [-1.7]	79.5
0.27	-8.1 [-9.7]	40.9
-0.32	-4.9 [-1.9]	79.0
0.69	-14.6 [-12.7]	53.6
0.22	-5.4 [-5.4]	45.0

Most stable hypothetical
Mobius Structure:



[12] Annulene originally
synth. by Oth through
irradiation at -100 deg

For cmpds **1-4** and **6**
bond length alternation
parallels dihedral angle
deviation.

Mobius cmpd. **5**, despite
large dihedral deviation
has the smallest bond
length alternation, as
well as HOMA.

The negative NICS
indicates **5** as being the
most aromatic.

The higher energy of **5** to
1 is due to angle strain:
The CCC bond angle avg.
is 130.2 in **5** compared to
125.3 in **1** and an ideal
value of 124.3 in acyclic
polyenes.

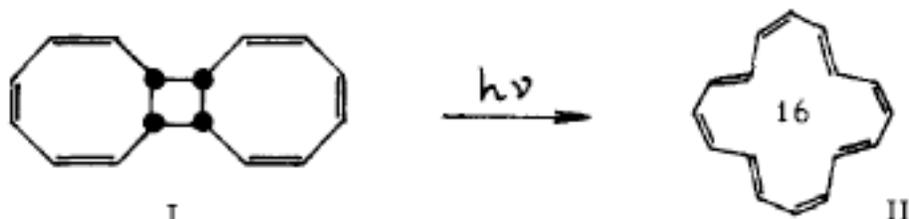
Oth, J.; et. Al. *Tett. Lett.* (1970), 61.

Castro, C. et. Al. *Org. Lett.* (2002), 4, 3431.

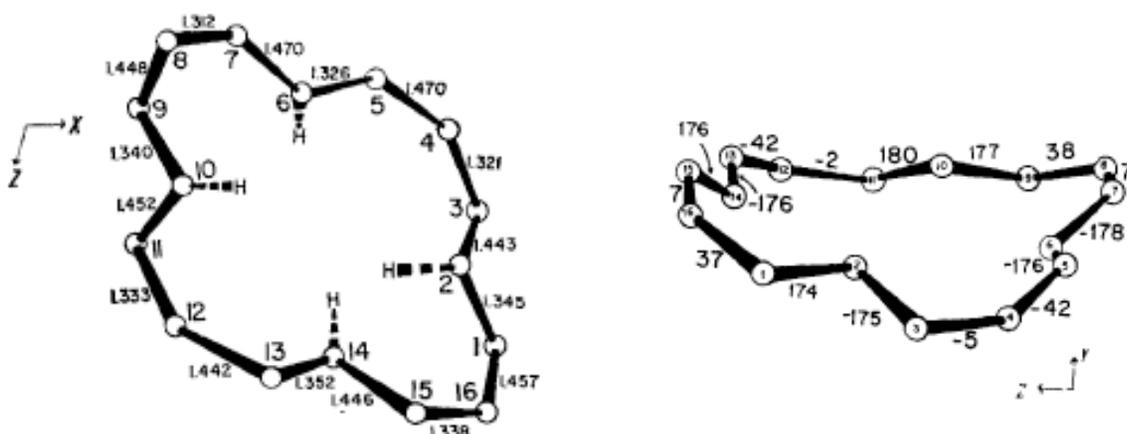
Structure and Stability ([16] Annulenes)

Original Syntheses:

Photolytic ring expansion of a polycyclic valence isomer by Oth:

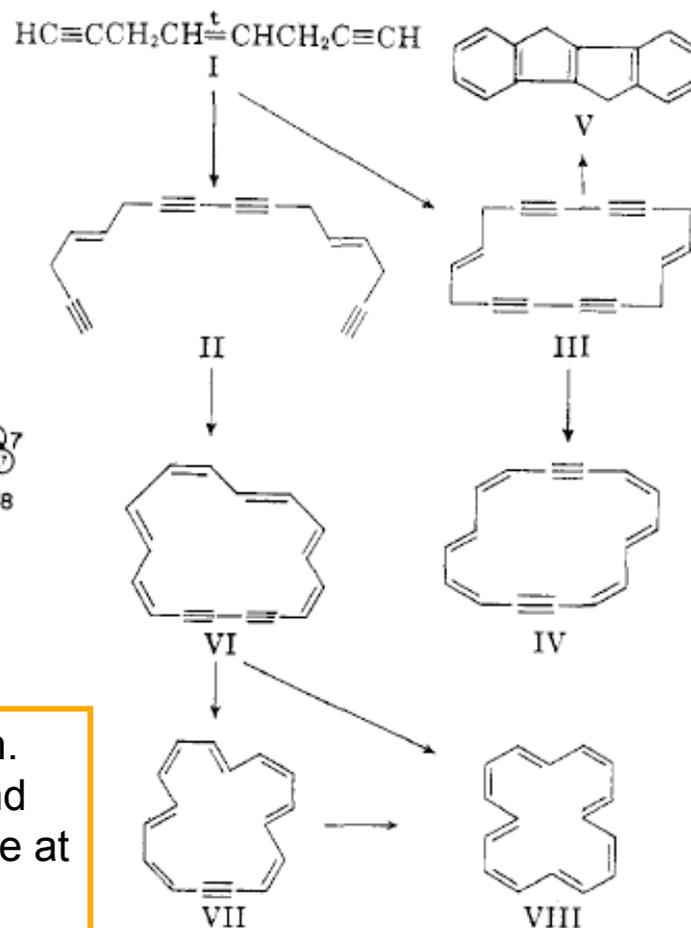


Crystal Structure (S4 Symmetry):



Molecule is non-planar, w/ near complete bond alternation. Single bonds (1.45 Å) are alternately trans and gauche and the double bonds (1.33 Å) cis and trans. Avg. torsion angle at a gauche bond is 41 degrees (relatively flat)

Sondheimer's copper coupling / hydrogenation route:



Oth, J.; et. Al. *Tett. Lett.* (1968), 6259.

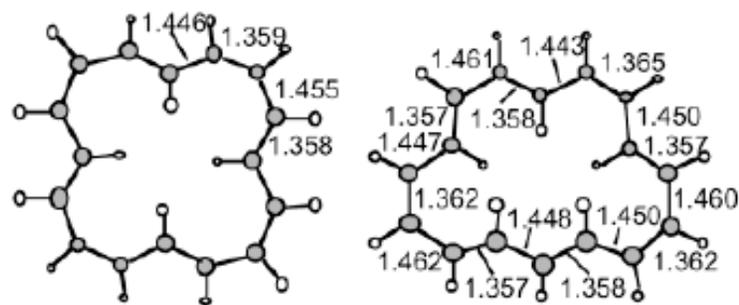
Sondheimer, F. et. Al. *JACS* (1961), 83, 4863.

Sondheimer, F. *Acc. Chem. Res.* (1972), 5i, 81.

Paul, I. et. Al. *J. Chem. Soc.* (1970), 643.

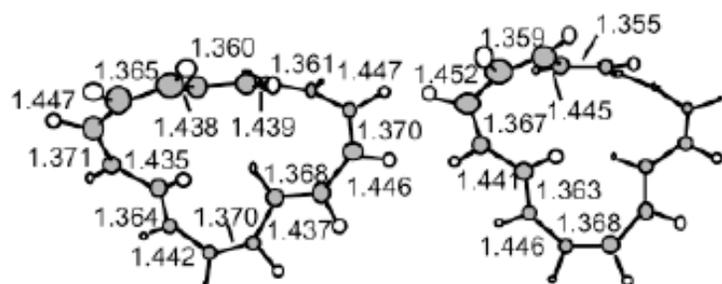
Structure and Stability ([16] Annulenes)

B3LYP/6-31G* Optimized geometries



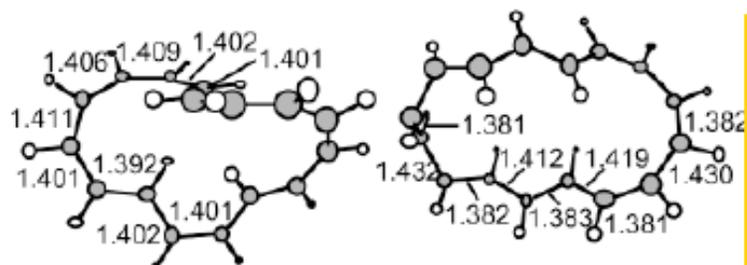
7 (S_4)

8 (C_7)



9 (C_7)

10 (C_2)



11 (C_2)

12 (C_2)

cmpd	sym	topol ^a	rel E^b	ΔCC^c
7	S_4	H	0.0	0.097 ^d
8	C_1	H	2.0	0.105
9	C_1	M	5.1	0.087
10	C_2	M	7.6	0.097
11	C_2	M	15.8	0.019
12	C_2	M	51.4	0.051

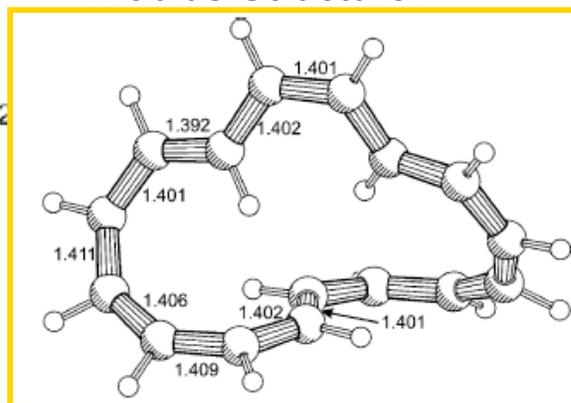
HOMA ^e	NICS(0) [(1)] ^f	$\angle CCCC^g$
0.38	+10.9 [+9.4]	32.6
0.35	+10.7 [+9.3]	26.7
0.57	-6.3 [-4.6]	52.5
0.48	-3.9 [-3.4]	47.1
0.93	-14.5 [-14.4]	29.1
0.81	-15.6 [-11.5]	73.1

Crystal structure of **S4**-symmetric **7** known. Solution NMR shows **7** and **8** in equill.

Both are antiaromatic! (paratropic ring currents)

Cmpd. **11** has nearly perfect bond-length equalization, a NICS value of -14.5 ppm

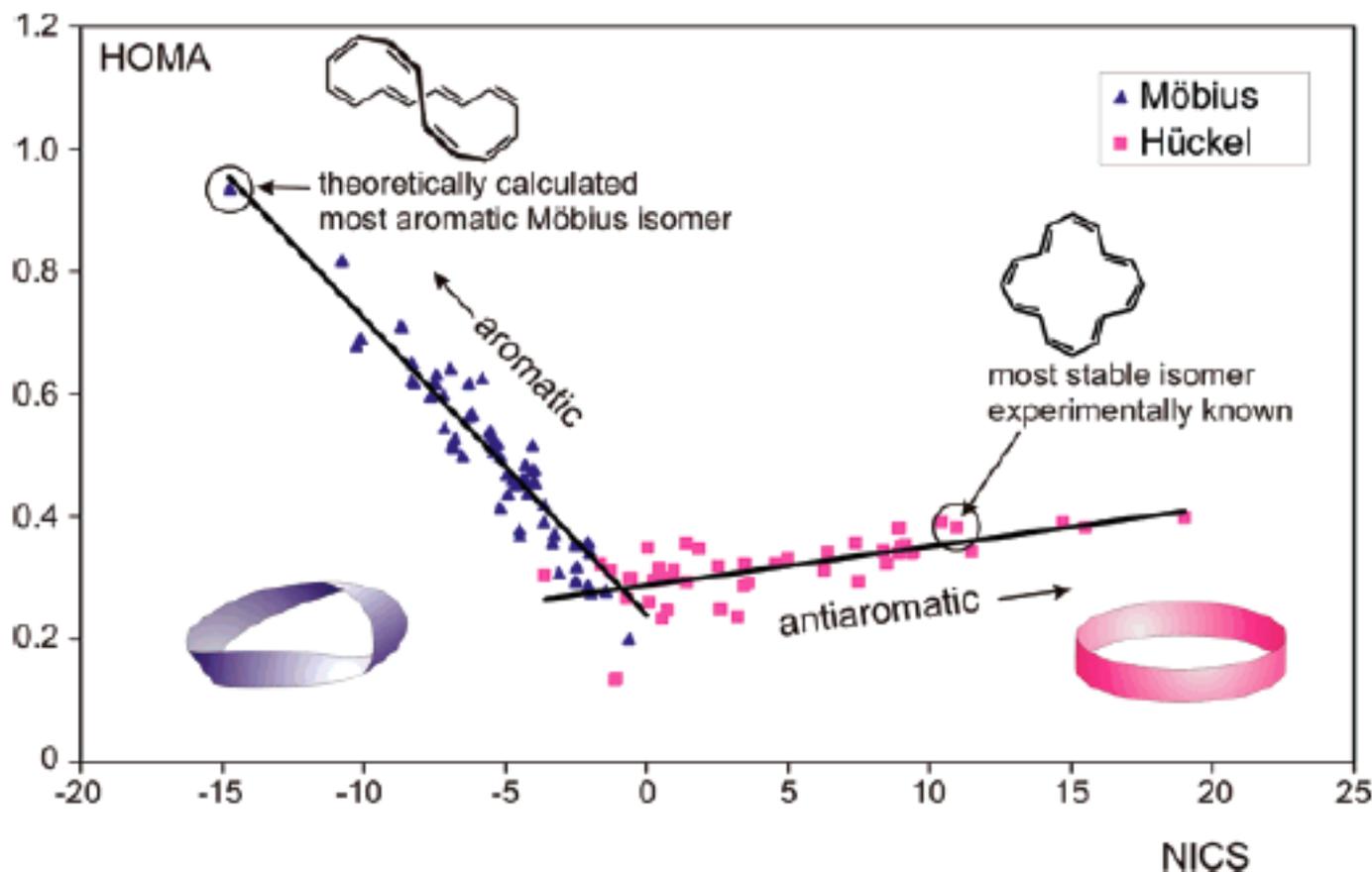
Most stable hypothetical Mobius Structure:



The rel. energies do not correlate with aromaticity. Mobius cmpd. **11** is over 10 KCal/mol than **9**

Aromaticity of [16] Annulenes (HOMA-NICS)

The 153 most stable isomers of [16] annulene: Continuum between truly aromatic, twisted Möbius Isomers, nonaromatic (rings with dihedral angles close to 90 deg), and antiaromatic Huckel



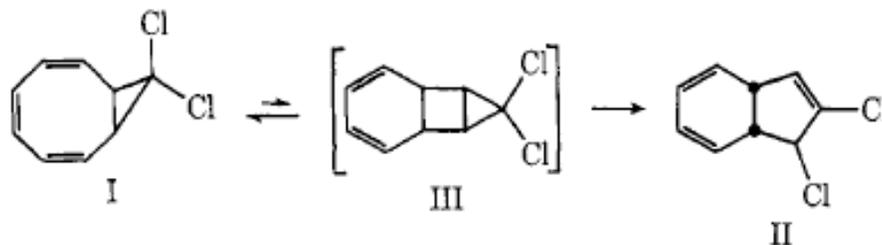
Once again: no correlation between energy and aromaticity.

- For Möbius isomers: good correlation between NICS and HOMA.
- For Hückel isomers: the opposite correlation is found (isomers that exhibit strong bond length correlation, aka more effective conjugation, have a strong paratropic ring current and thus more antiaromatic magnetic properties).

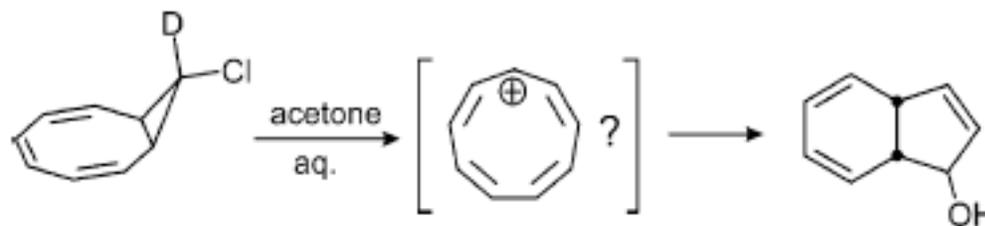
So is it possible to actually make a Mobius π System?

Where the experimentally known neutral $[4n]$ Annulenes all exhibit Huckel topology, the most stable isomer of the $[9]$ annulene cations probably is a Mobius ring:

Benson:



Schneider noted that when the chlorocyclopropane was deuterated (9-position), upon solvolysis gives a dihydroindenol product w/deuterium scrambled to all positions evenly.



Anastassiou and Yakali succeeded in preparing 9-chlorocyclononatetraene. Under ionizing conditions (liquid SO_2 at -66 degrees), D-labeled SM gave the ion-pair return with complete statistical distribution of the label (1/9 D per C atom).

If the cyclononatetraenyl cation is antiaromatic, why does ionization occur in such a facile manner? And why do the positions become equivalent so quickly?

Benson, R. et. Al. *JACS* (1965), 87, 1941.

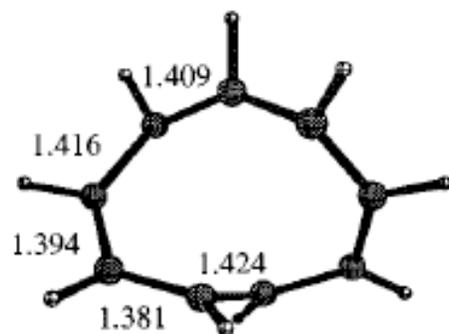
Schneider, J. et. Al. *JACS* (1971), 93, 279.

Anastassiou, A. et. Al. *JACS*, (1971), 93, 3803.

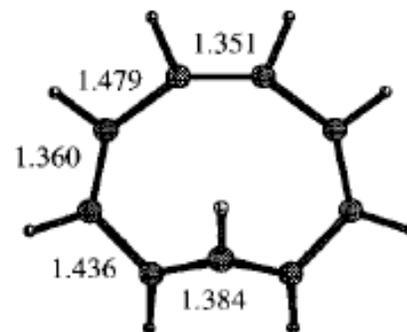
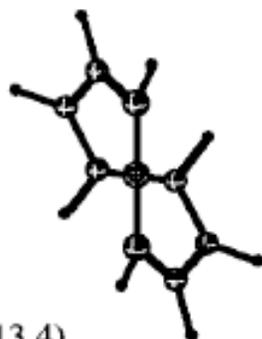
Cyclononatetraenyl Cation:

Computational evaluation of the cyclononatetraenyl cation:

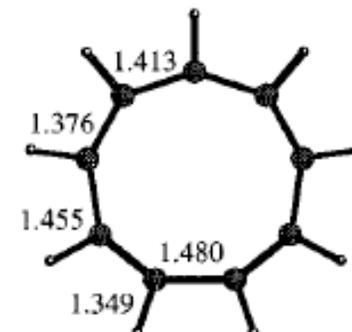
Exploration of the potential energy surface of singlet (CH)₉⁺ with DFT finds 3 structures **4-6**:



4, C₂ (NICS= -13.4)



5, C_s (NICS= 8.6)



6, C_{2v} (NICS= 42.0)

Rel Energies:

0.00 kcal/mol

+21.6 kcal/mol

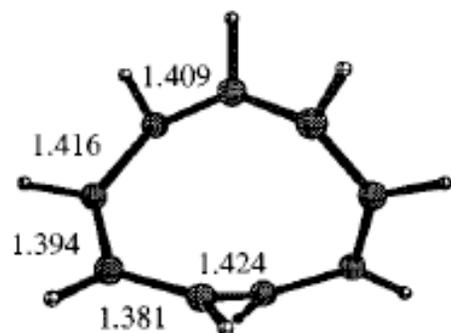
+26.3 kcal/mol

Both **5**, **6** show strong bond length alternations and positive NICS, whereas the Möbius conformer **4** has a small range of C-C bond lengths (maximum difference 0.0043 Å) and a very negative NICS (value for benzene at same level theory -9.7 ppm). It also shows an average chemical shift of 8.5 ppm.

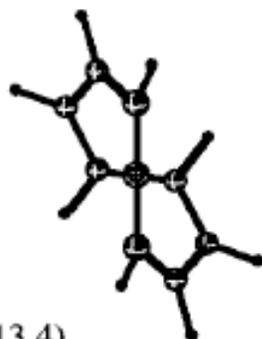
Cyclononatetraenyl Cation:

Computational evaluation of the cyclononatetraenyl cation:

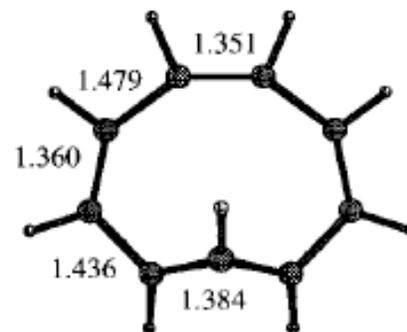
Exploration of the potential energy surface of singlet (CH)₉⁺ with DFT finds 3 structures **4-6**:



4, C₂ (NICS= -13.4)



5, C_s (NICS= 8.6)



6, C_{2v} (NICS= 42.0)

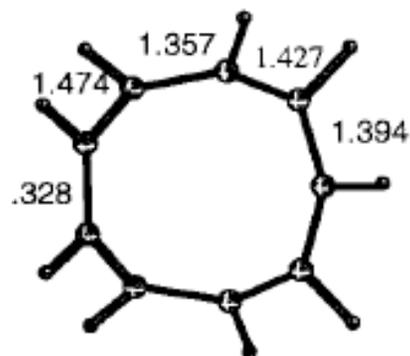
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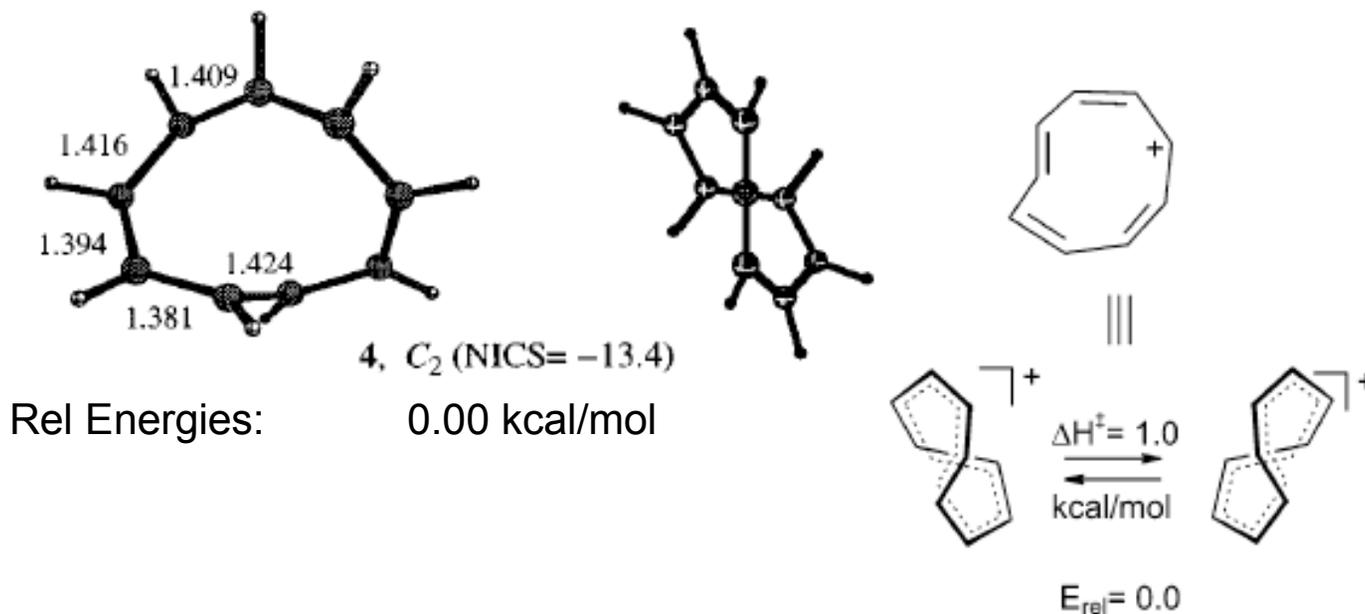
7, C_s (NICS= -0.9)

A low kinetic barrier of 1.1 kcal/mol for the enantiomerization of **4** could be found through the non-aromatic compound **7**. Despite the loss of Möbius aromaticity compound **7** has considerably less strain associated with it.

Cyclononatetraenyl Cation:

Computational evaluation of the cyclononatetraenyl cation:

Exploration of the potential energy surface of singlet (CH)₉⁺ with DFT finds 3 structures **4-6**:



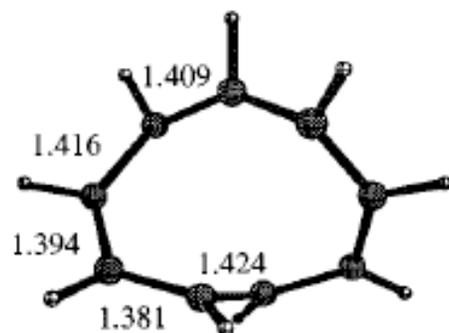
The complete scrambling of the D-label even at -66 deg is consistent w/ the low barrier for **7**. Nine-fold repetition of the helical enantiomerization completely scatters the label

A low kinetic barrier of 1.1 kcal/mol for the enantiomerization of **4** Could be found through the non-aromatic compound **7**. Despite The loss of Mobius aromaticity compound **7** has considerable less strain associated with it.

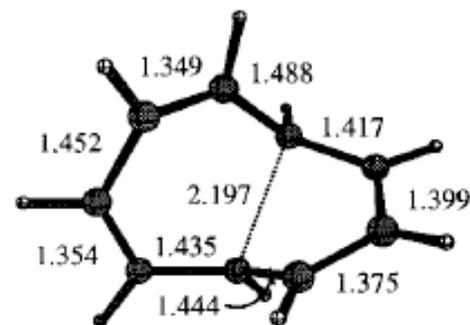
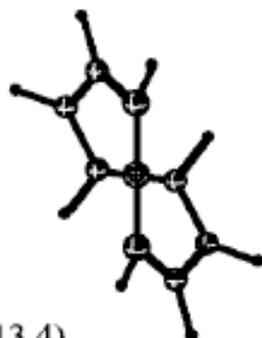
Cyclononatetraenyl Cation:

Computational evaluation of the cyclononatetraenyl cation:

Mobius conformation **4** can also undergo disrotatory ring closure via TS **8**



4, C_2 (NICS= -13.4)



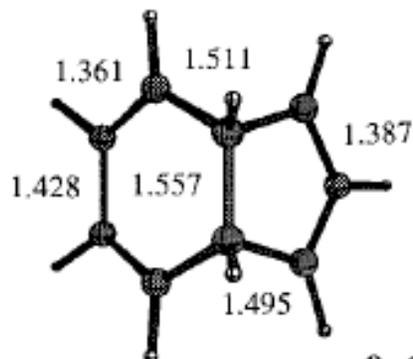
8, C_1 (NICS= -6.0)

Rel Energies:

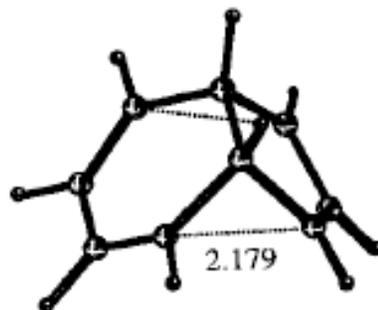
0.00 kcal/mol

8.1 kcal/mol

This is in accord with experimentally determined half-life of 10 min at -66 deg



9, C_s (NICS= -11.8)

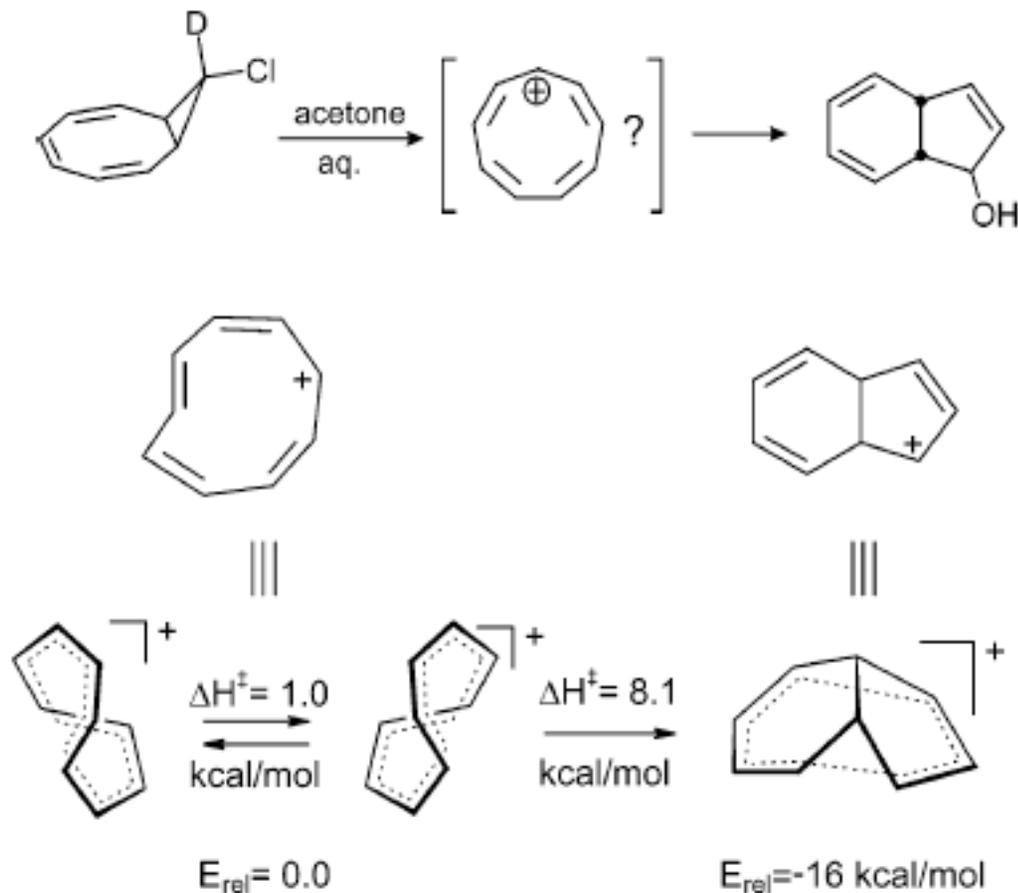


The bicyclic bishomotropylium cation **9** product is 16.6 kcal/mol more stable than **4** and is a known aromatic compound

Cyclononatetraenyl Cation:

Computational evaluation of the cyclononatetraenyl cation:

Complete mechanistic picture

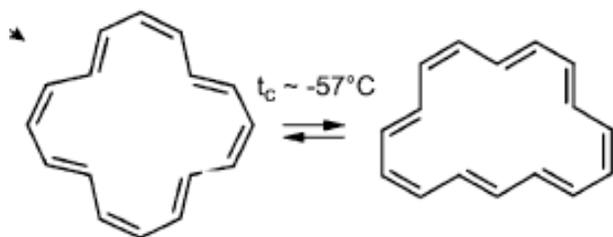


But is it possible to synthesize a neutral, observable Mobius strip?

Synthesis of a Neutral Mobius Annulene

The main challenge in preparing Mobius annulenes is that all parent annulenes with a ring size 4 - 20 are more stable in a non-twisted topology (the stabilization of the π -system cannot overcome the strain induced by the 180 degree twist)

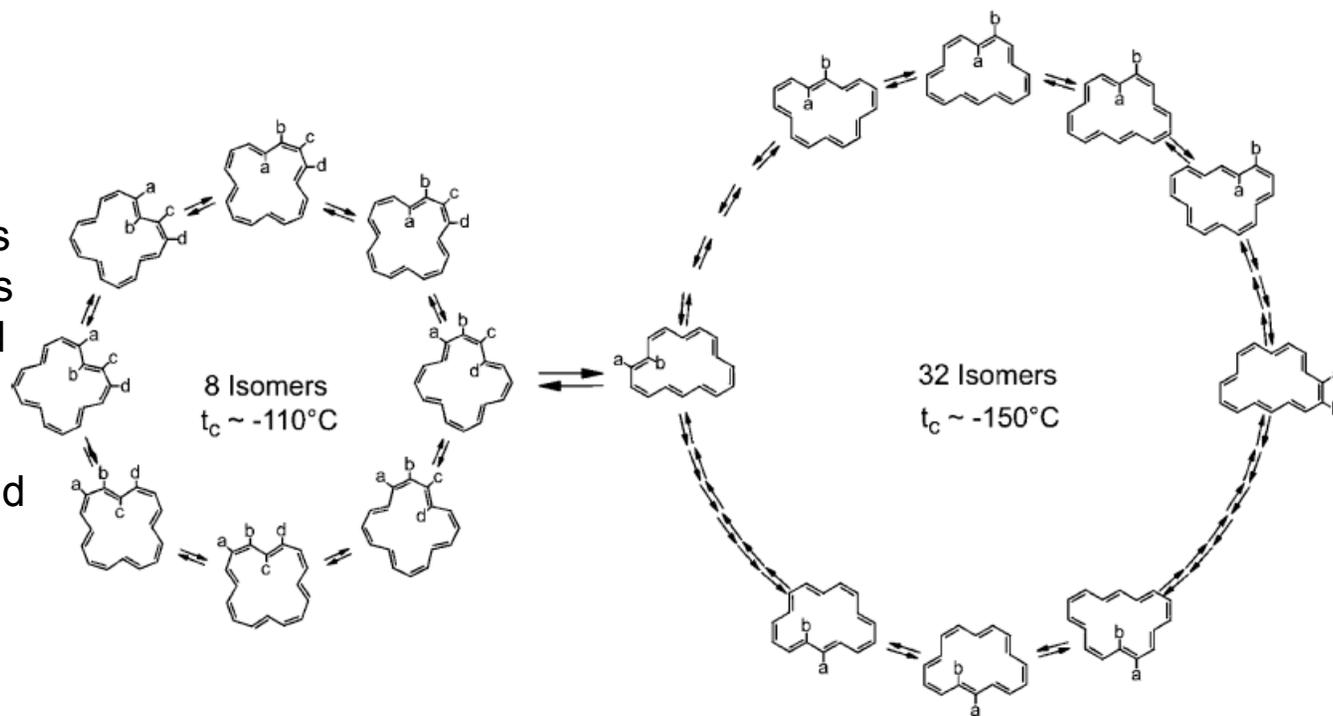
Additionally if you consider the following example of the ease of isomerization:



When synthesized, the coalescence T in the proton NMR for The [16]annulene is -57 degrees

Moreover, the 2 isomers are in equilibrium with 8 or 32 symmetry equivalent isomers which are formed by cis/trans isomerization or double bond shifts.

The automerizations are rapid on the NMR time scale even below -100 degrees.



Oth, J.; et. Al. *Tett. Lett.* (1968), 6259.
Stevensen, C. *JACS*, (1999), 121, 1623

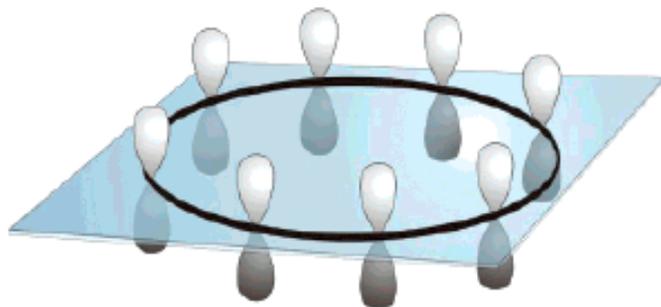
The larger annulenes are even more flexible

Stabilization of the Twist

Examination of the π system in more detail:

There are 2 types of cyclic π conjugation

a) “normal” aromatic p orbitals perpendicular to the ring



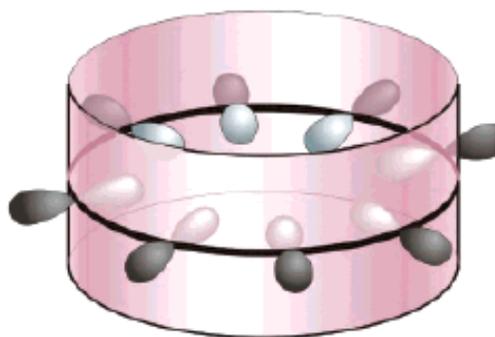
“normal”
aromatic



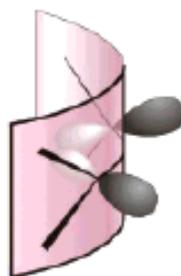
trigonal planar

Retention of preferred
trigonal planar conformer
(pure sp^2 hybrids)

b) “in-plane” (belt like) conjugated systems in which the p orbitals point toward the axis



in plane or belt-like
aromatic



pyramidalized

Exhibit pyramidalized sp^2 centers
(partial sp^3 character). In rings with small
diameters pyramidalization cause strain,
thus are much less common

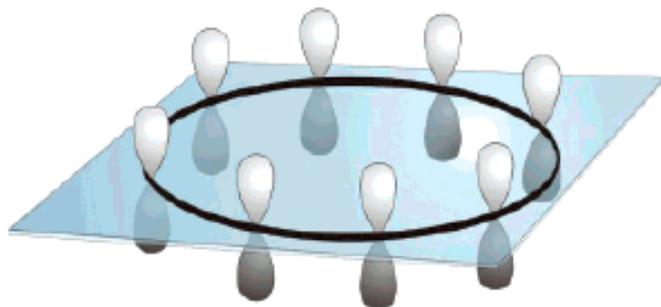
Question: Can you give a naturally
occurring example of this type of aromaticity

Stabilization of the Twist

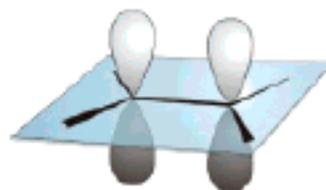
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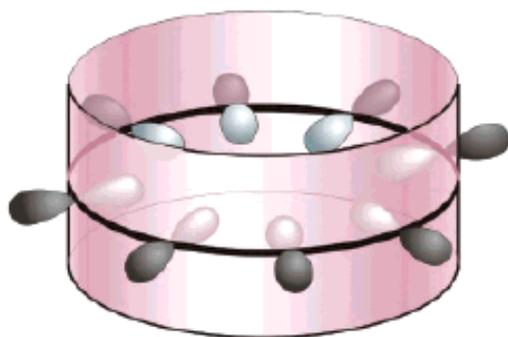
“normal”
aromatic



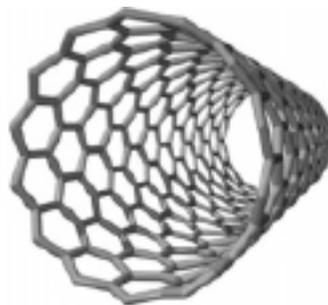
trigonal planar

Retention of preferred
trigonal planar conformer
(pure sp² hybrids)

b) “in-plane” (belt like) conjugated systems in which the p orbitals point toward the axis



in plane or belt-like
aromatic

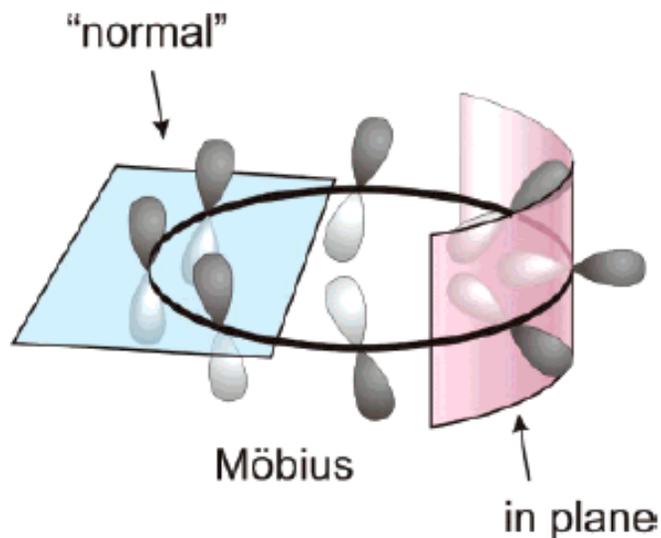


Nanotubes / Fullerenes are
examples of this type of aromatic
structure (avoids strain through
very large diameters)

Stabilization of the Twist

Examination of the π system in more detail:

Möbius annulenes contain both types of aromaticity (normal and in-plane) and it is the pyramidalized in-plane section that cause the most strain.



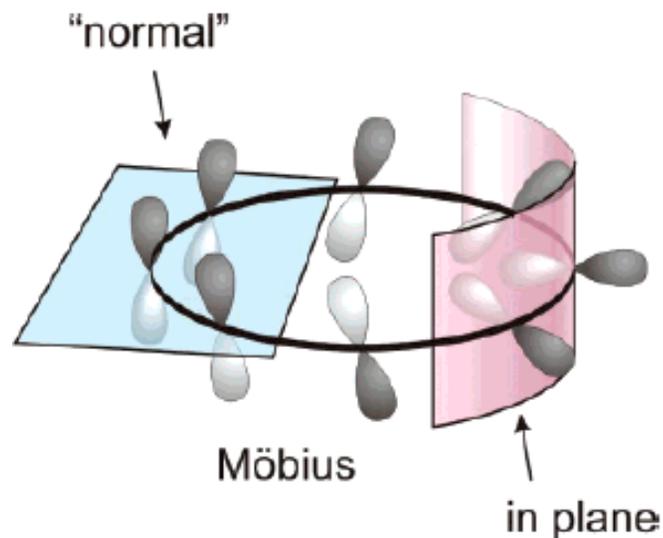
Strategically, a method to stabilize the pyramidalized double Bond should also stabilize the twist.

Question: Give a hypothetical molecule / example that would pyramidalize a double bond. Could it be used in the context of designing a Möbius band?

Stabilization of the Twist

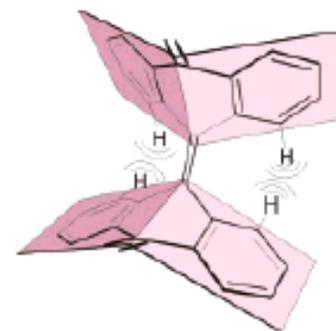
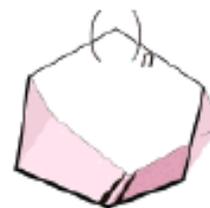
Examination of the π system in more detail:

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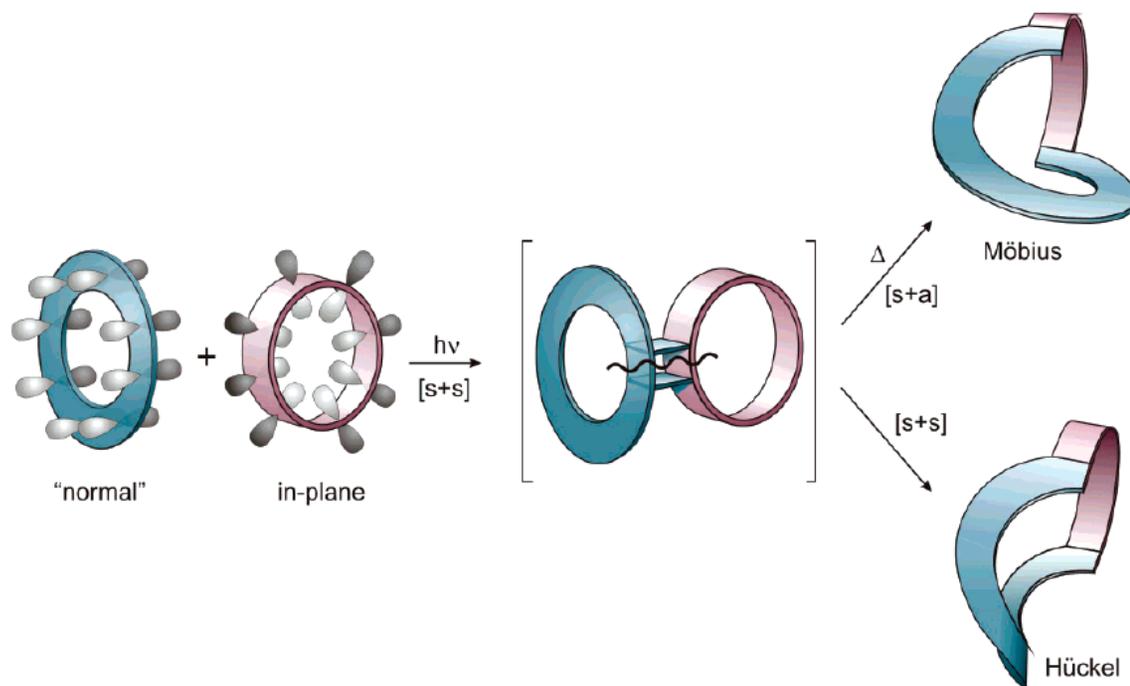
Question: Give a hypothetical molecule / example that would pyramidalize a double bond. Could it be used in the context of designing a Möbius band?



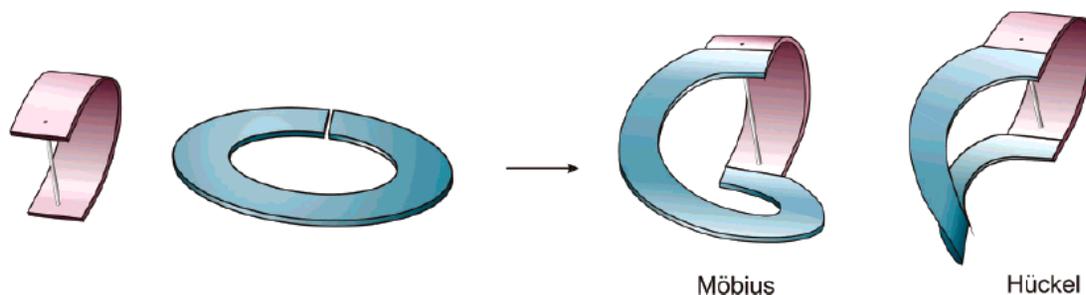
Two strategies: pyramidalization is induced by ring strain
-In the bianthraquinodimethane pyramidalization is enforced by the steric hindrance of the inner hydrogen atoms

Building the Mobius Strip

To connect the pyramidalized building block and the normal p component, the ring enlargement Metathesis method was utilized by Herges:



It is hypothesized that in this system the Möbius ring should be less strained than the Hückel:



Ajami, D. et. A; *Chem. Eur. J.* (2006), 12, 5434.
Ajami, D. et. Al. *Nature* (2003), 426, 819.

Building the Mobius Strip

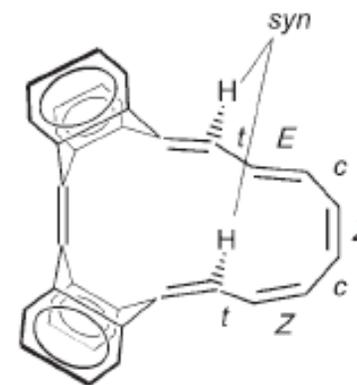
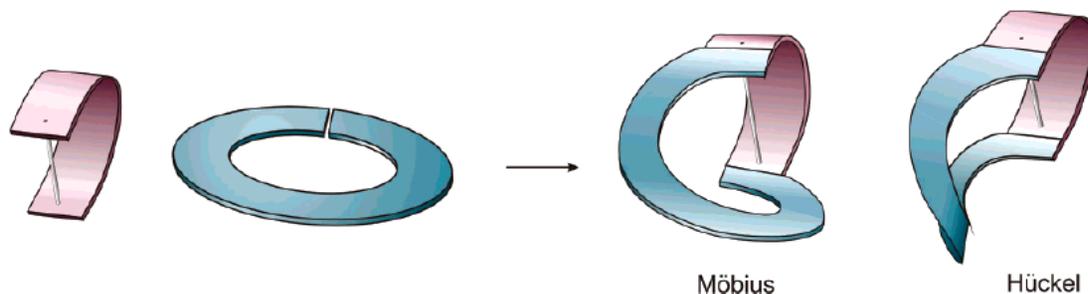
Do the cartoons hold up to theoretical predictions?

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	<i>syn-tZcZcEt</i>	8
2	2.25	Hückel	0011011011001111	2	0.29	1.75	Möbius	<i>anti-tEcZcEt</i>	9a
3	4.68	Hückel	0001100110011011	3	0.56	0.30	Möbius	<i>syn-cZtEcZt</i>	
4	5.14	Möbius	0000110011000111	4	0.56	0.89	Möbius	<i>syn-cEtZcZt</i>	
5	5.15	Möbius	0000111000110011	5	2.47	4.95	Möbius	<i>anti-cEtZcEt</i>	
6	5.41	Möbius	0001100110011001	6	2.76	1.96	Möbius	<i>anti-tZtEcZt</i>	5
7	5.41	Möbius	0001001100110011	7	2.77	1.90	Möbius	<i>anti-tZcZcZt</i>	6
8	5.45	Hückel	0011011011011011	8	4.16	3.26	Hückel	<i>syn-tEcZcEt</i>	
9	5.45	Hückel	0011011001101111	9	6.71	5.23	Möbius	<i>syn-tZcZcEc</i>	
10	5.47	Hückel	0011011001111011	10	6.91	5.29	Hückel	<i>syn-tZtZtZt</i>	7

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

There are 7 Möbius structures within 3 kcal/mol relative energy, the first Hückel structure over 4 Kcal/mol higher in energy

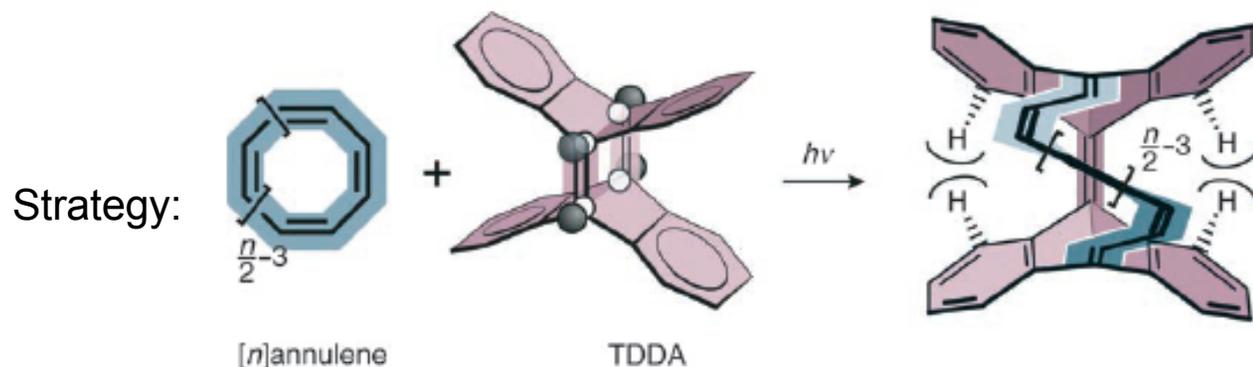
It's hypothesized that in this system the Möbius ring should be less strained than the Hückel:



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

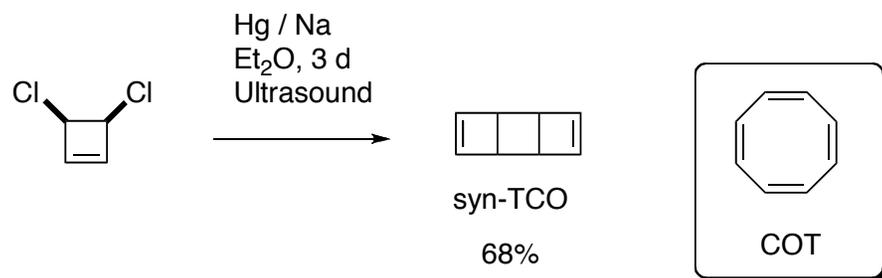
Ajami, D. et. A; *Chem. Eur. J.* (2006), 12, 5434.
Ajami, D. et. Al. *Nature* (2003), 426, 819.

Synthesis of the Strip:



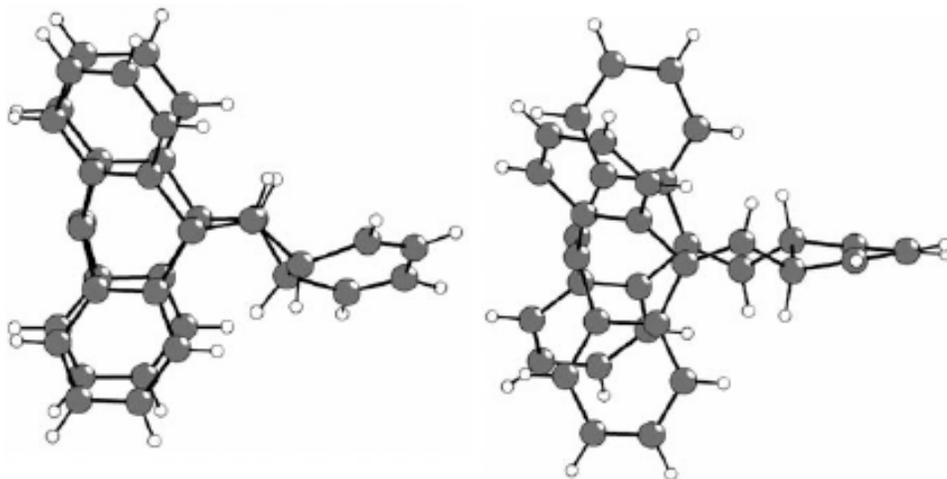
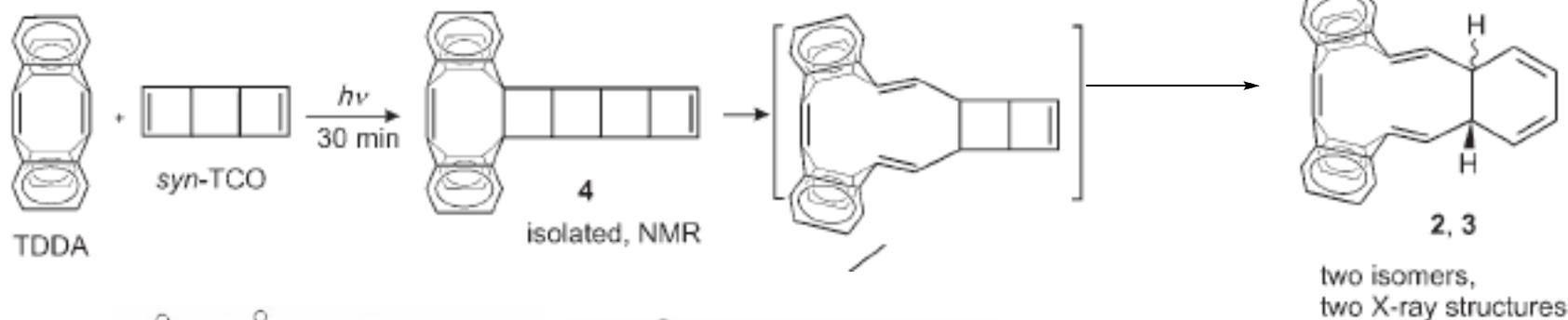
Initial reaction of cyclooctatetraene with TDDA (tetrahydrodianthracene) under irradiation conditions failed. Bianthryl was the main product produced. It is suspected that COT could sensitize TDDA to form the triplet excited state of TDDA which, after ring opening abstracts a hydrogen from benzene.

Synthesis of a COT Surrogate:



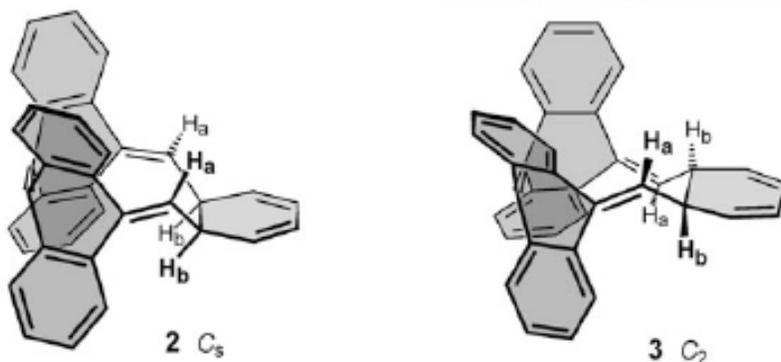
Synthesis of the Strip:

Irradiation with a 700 W high-pressure mercury lamp (light >300 nm):



Three products isolated. Ladderane,
and 2 metathesis products **2**, **3**
Syn-TCOD

Strong NOE between H_a and H_b in **3**
And no NOE in **2**

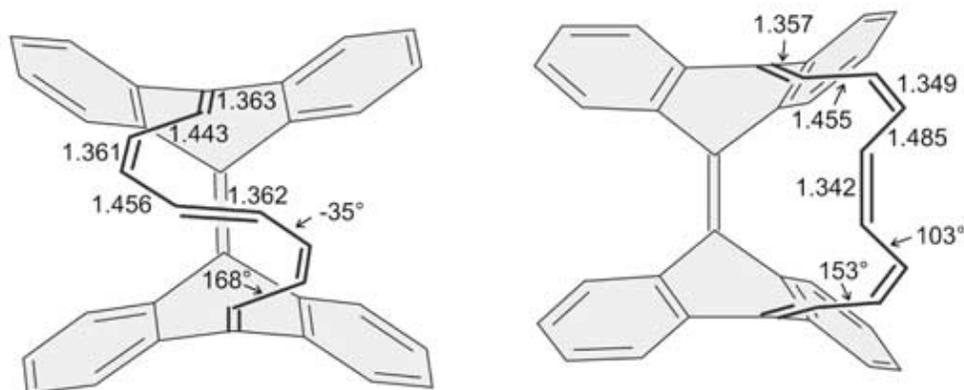
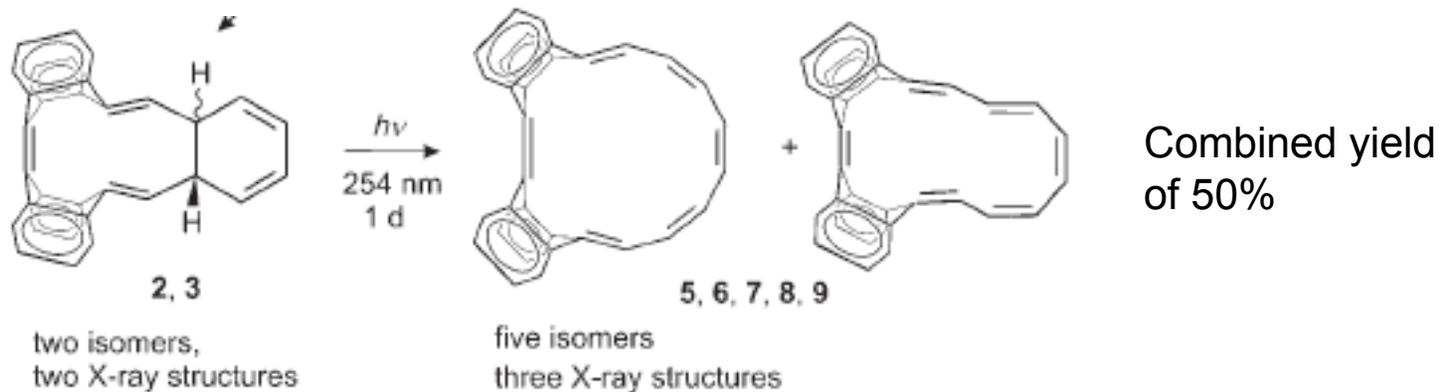


No [16] annulene detected

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Synthesis of the Strip:

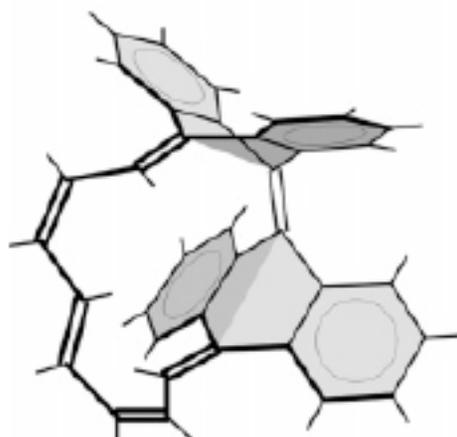
Known that the photostationary equilibrium in the electrocyclic reaction of 1,3-cyclohexadiene To 1,3,5-hexatriene is shifted toward the ring opened product upon short wavelength irradiation.



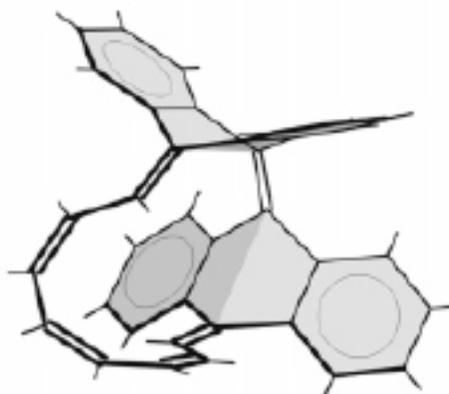
After removal of the SM
(through diels alder with tetracyanoethylene)
three structures could be crystallized.



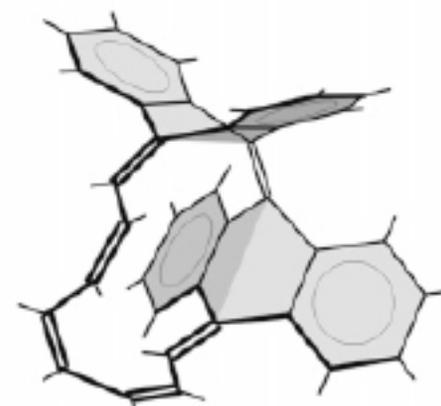
Synthesis of the Strip:



anti-tZtEcZt C_1 Möbius

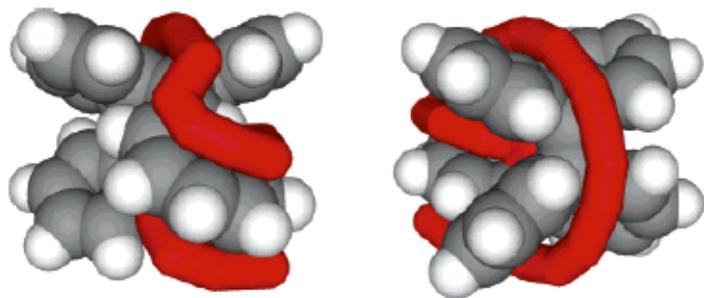


anti-tZcZcZt C_2 Möbius

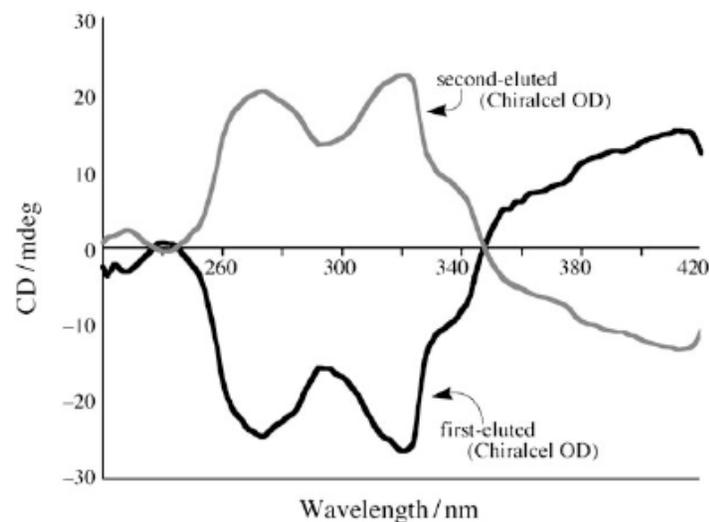


syn-tZtZtZt C_S Hückel

Stereochemical implications are interesting:
Attempts to assign prochirality (*Re* or *Si*) of the
Central bond in the bridge leads to an endless loop.
Both faces of the double bond are homotopic

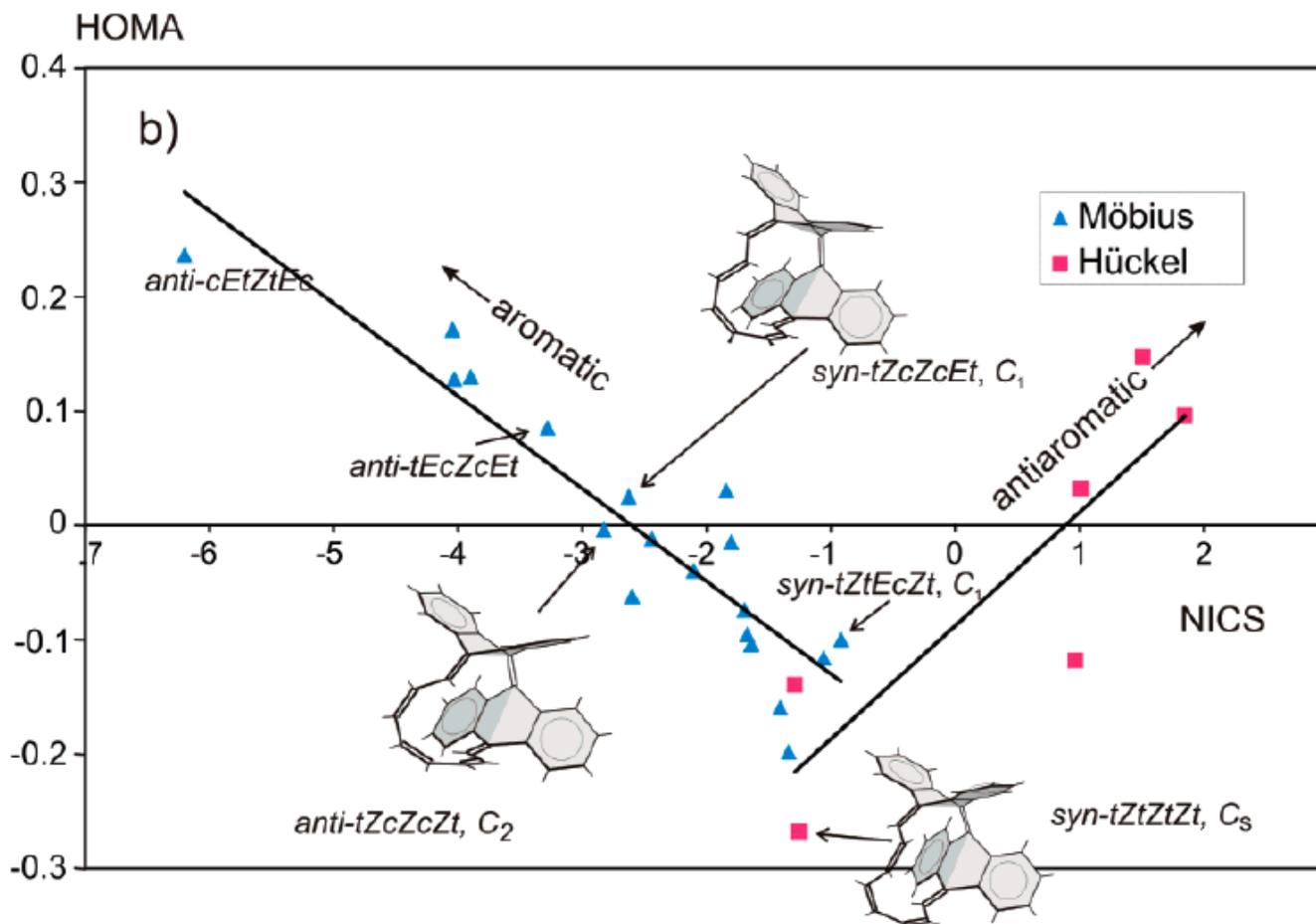


Molecular walk around anti-tZcZcZt Möbius



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Are they Aromatic?



Shows good inverse correlation between NICS and HOMA for Möbius systems and vice-versa for Hückel aromatic

Despite structural features, all three structures are non-aromatic. NICS values show very little diatropic ring current and considerable bond-length alternation (low HOMA)

“It is probably not a simple endeavor to synthesize neutral Möbius annulenes with an aromaticity Comparable... to benzene. Most of the measures to stabilize the twist, reduce the conjugation.”

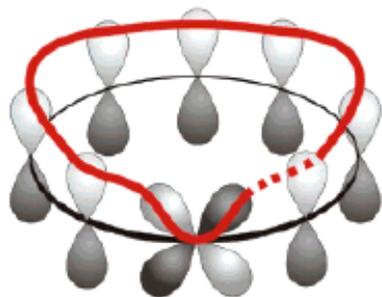
Conclusions - Other Mobius Systems

Despite a large synthetic communities efforts, Heilbronner's prediction of a stable, "aromatic" Mobius annulene (neutral) in 1964 has yet to be truly realized.

As the bar for synthetic challenge for organic chemists has continued to rise, the focus has dramatically shifted from "*whether it can be made*" to "*the most efficient route*". It is important to realize that there are molecules of theoretical and practical interest that still exist that cannot be made (despite how many times the synthetic community claims that today's technology can synthesize any compound).

Mobius-like Systems not covered:

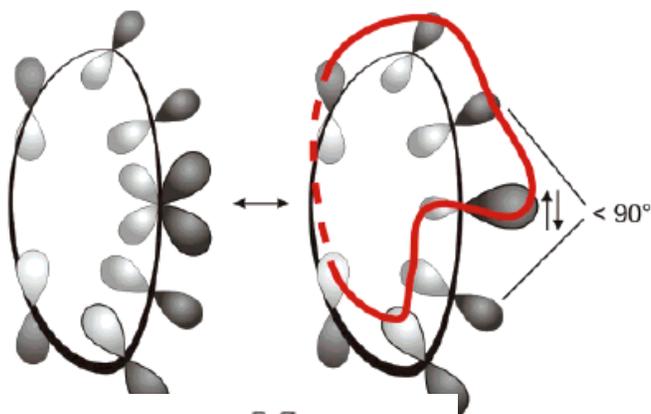
d-orbital participation:



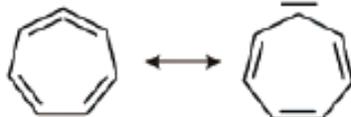
e.g.



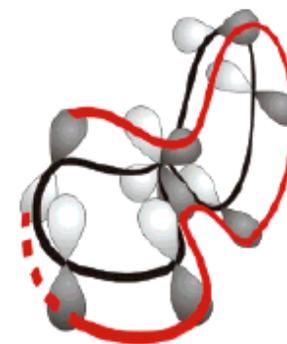
Allenes in strained rings:



e.g.



Coarctate spiro system:



e.g.

