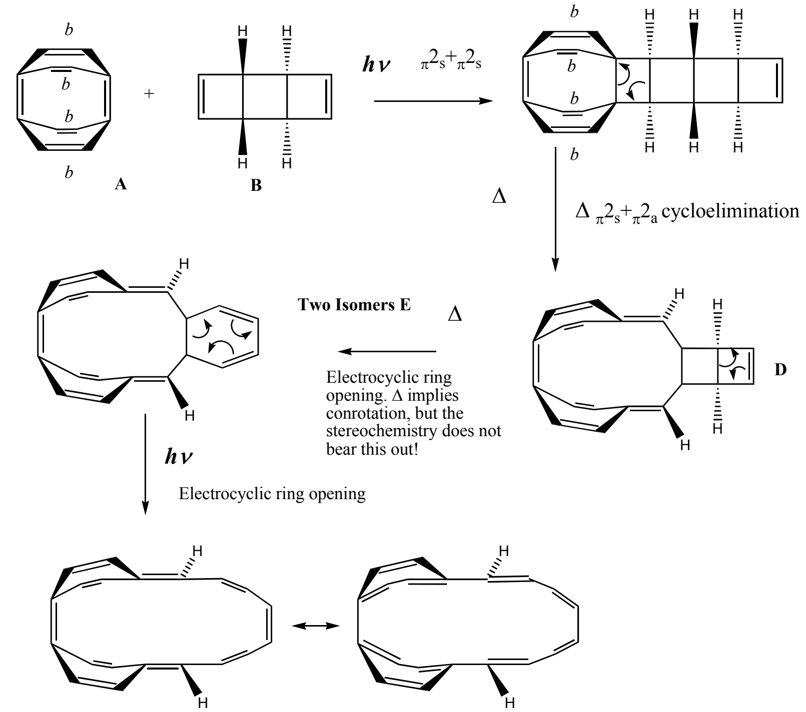
2ND YEAR ORGANIC PROBLEM CLASSES 2004/2005
Class 6. HSR/ACS – Pericyclics & Stereoelectronics – Answers
Class to be held at *3pm on Monday 25th April 2005* in normal tutors groups

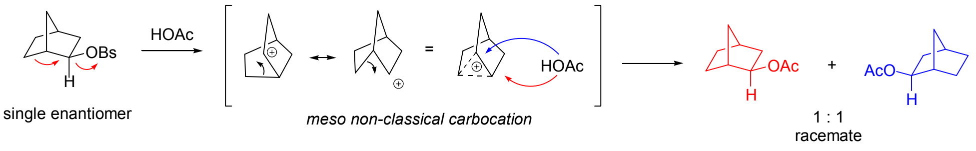
1. Taken from D. Ajami, O. Oeckler, A. Simon and R. Herges, *Nature*, **2003**, *426*, 819-821 and associated Highlight article: *Angew. Chem. Int. Ed.* **2004***, 43,* 4396 (attached below):



Isomer with C2 axis is first known Mobius annulene.

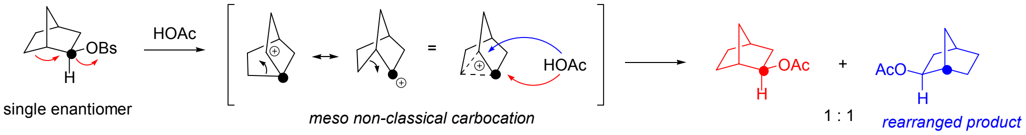
Note that the two isomers of **E** are reported as having C_2 and C_s symmetry, but no stereochemical details are reported for the mechanism of their formation. Neither is any stereomechanistic detail reported for the formation of **F**. The issue of whether these reactions formally obey the Woodward-Hoffmann rules must be regarded as open! A 3D crystal structure for the C_2 isomer of **F** was published, and can be retrieved using the techniques introduced in the CIT course.

2. (a) (i) The reaction proceeds *via* the $\sigma_{C\text{-}C}$ bond anti-periplanar to the brosylate acting as a ‘neighbouring group’ (*i.e.* participating in displacing the brosylate. The resulting *meso* non-classical carbocation (carbonium ion) can then be attacked by the acetic acid nucleophile at either of the two equivalent carbons indicated:



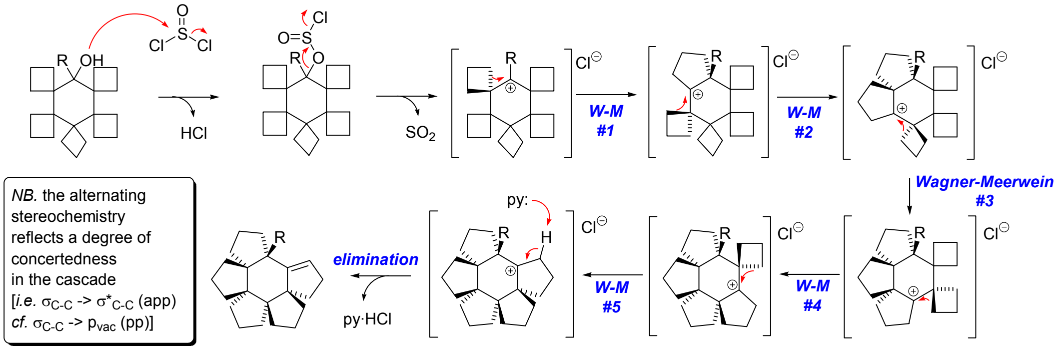
(ii) If the carbon atom to which the brosylate (OBs) group is attached had been ^{13}C labelled then two enantiomerically pure ‘pseudo-enantiomers’ (differing only in the position of a ^{13}C label) would be formed.

PTO



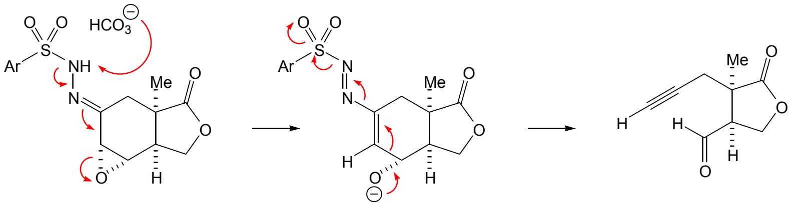
NB. The original reaction was reported by Winstein in the late 1950's and became the subject of a 'heated' debate as to the nature of the intermediate species (*see article attached below*; taken from http://www.chem.umd.edu/courses/chem237/).

(b) This transformation is a cascade rearrangement involving 5 sequential Wagner-Meerwein 1,2-alkyl shifts each one effecting the conversion of a spiro cyclobutane to a fused cyclopentane:

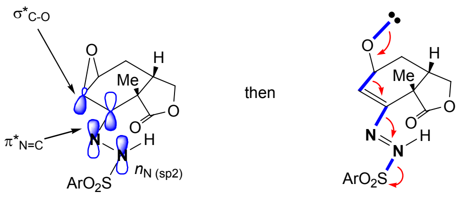


NB. the alternating stereochemistry reflects a degree of concertedness in the cascade [*i.e.* σ_{C-C} -> σ^*_{C-C} (app) *cf.* σ_{C-C} -> p_{vac} (pp)]

(c) (i) Mechanism:



(ii) For the formation of the alkoxide 'intermediate' all the p-orbitals of the hydrazone must be perpendicular to the 'plane' of the ring and therefore overlap well with the epoxide sigma star orbital…which they do. For the fragmentation the (<u>*E*</u>)-stereochemistry about the N=N double bond is important to ensure anti-periplanar overlap in 'step 5' below. Again, any acceptable diagram(s) showing the shapes of the interacting sigma and sigma star orbitals is OK.



NB. bold bonds are all anti-periplanar with respect to each other

1) n_N -> $\pi^*_{N=C}$
2) $\pi_{C=N}$ -> σ^*_{C-O}
3) n_O -> σ^*_{C-C}
4) σ_{C-C} -> σ^*_{C-N}
5) σ_{C-N} -> σ^*_{N-S}

The wires reported here are suitable for low-loss optical wave guiding, and will be promising components in future microphotonic devices for various applications, such as optical communications and optical sensing. Owing to their excellent uniformity, large length, high flexibility, and strength, these wires can be manipulated and assembled with high accuracy and used as micro- or nanoscale tools in physical, chemical, biological, microelectronic and materials research. ☐

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Synthesis of a Möbius aromatic hydrocarbon

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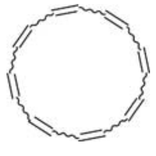
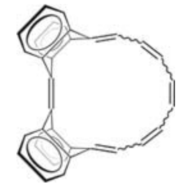
The defining feature of aromatic hydrocarbon compounds is a cyclic molecular structure stabilized by the delocalization of π electrons that, according to the Hückel rule, need to total $4n + 2$ ($n = 1,2,\ldots$); cyclic compounds with $4n$ π electrons are antiaromatic and unstable. But in 1964, Heilbronner predicted[1] on purely theoretical grounds that cyclic molecules with the topology of a Möbius band—a ring constructed by joining the ends of a rectangular strip after having given one end half a twist—should be aromatic if they contain $4n$, rather than $4n + 2$, π electrons. The prediction stimulated attempts to synthesize Möbius aromatic hydrocarbons, but twisted cyclic molecules are destabilized by large ring strains, with the twist also suppressing overlap of the *p* orbitals involved in electron delocalization and stabilization. In larger cyclic molecules, ring strain is less pronounced but the structures are very flexible and flip back to the less-strained Hückel topology[2,3]. Although transition-state species[4], an unstable intermediate[5] and a non-conjugated cyclic molecule[6], all with a Möbius topology, have been documented, a stable aromatic Möbius system has not yet been realized. Here we report that combining a 'normal' aromatic structure (with *p* orbitals orthogonal to the ring plane) and a 'belt-like' aromatic structure (with *p* orbitals within the ring plane) yields a Möbius compound stabilized by its extended π system.

Numerous theoretical calculations have been performed to predict the properties of potential Möbius aromatic systems[7–12]. The twist in the π system is usually introduced by a suitable arrangement of *E* and *Z* double bonds. *Trans*-benzene[13] is the smallest conceivable antiaromatic Möbius annulene. It is only a very shallow minimum on the energy hypersurface, with an energy as much as $107\,\mathrm{kcal\,mol^{-1}}$ above benzene[14]. The next-higher Möbius homologue, *trans*-cyclooctatetraene, indeed comes energetically closer to its Hückel (all-*cis* and global minimum) isomer[14]. Nevertheless, with a relative energy of $21.3\,\mathrm{kcal\,mol^{-1}}$, it is expected to be extremely difficult to synthesize. Moreover, there is almost no conjugation between the *E* and the neighbouring *Z* double bonds

Table 1 **Relative stabilities**





	[16]annulene			Möbius stabilized [16]annulene	
E_{ref}	Topology	Sym.	E_{ref}	Topology	Sym.
0.0	Hückel	S_4	0.0	Möbius	C_1
2.0	Hückel	C_1	0.3	Möbius	C_2
5.1	Möbius	C_1	2.8	Möbius	C_2
7.6	Möbius	C_2	2.8	Möbius	C_1
15.8	Möbius	C_2	6.7	Möbius	C_1
51.4	Möbius	C_2	7.0	Hückel	C_s
			8.3	Möbius	C_1

Calculated relative stabilities (E_{ref} in $\mathrm{kcal\,mol^{-1}}$) of the most stable isomers of the parent [16]annulene and of our modified [16]annulene at the B3LYP/6-31G* level of DFT.

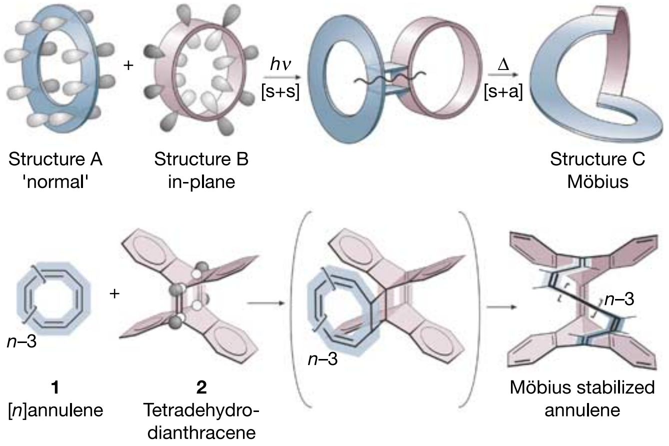


Figure 1 Strategy to stabilize the Möbius structure of annulenes. Möbius bands (structure C) contain a 'normal' trigonal planar conjugated part (shown cyan) and a pyramidalized 'in-plane' part (magenta). The strain arises from the latter. Combining a normal conjugated ring (structure A; for example, [*n*]annulene **1**) with a rigid 'prefabricated' pyramidalized in-plane conjugated building block (structure B; for example, tetradehydrodianthracene **2**) by metathesis leads to rings that are more stable in the twisted Möbius configuration than in the untwisted Hückel configuration. A supra supra allowed [2 + 2] addition ([s + s]) followed by a thermal supra antara cycloreversion ([s + a]) leads to a Möbius system.

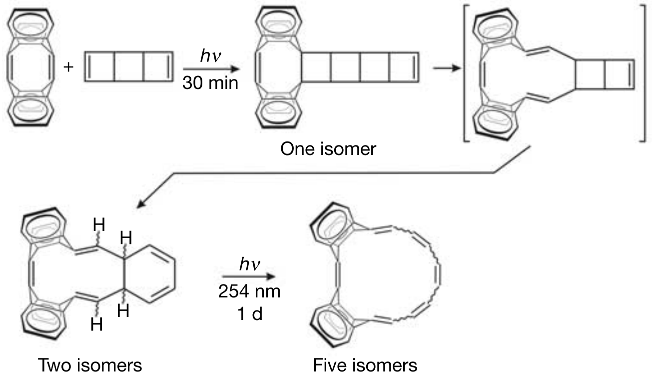


Figure 2 Reaction of *syn*-tricyclooctadiene with tetradehydrodianthracene.

because of the large deformation of the ring induced by the twist. Castro and Schleyer[15] have published an extensive study of various isomers and conformations of higher annulenes. One of the most interesting structures is a [16]annulene with an *E,Z,Z,Z,Z,Z,E,E,Z, E,E,Z,Z,Z,Z,Z* arrangement of conjugated bonds that exhibits distinct Möbius aromaticity. The relative energy is 15.3 kcal mol^{-1} above the global minimum isomer. In view of the large number of conceivable isomers—many of which are more stable than this strongly conjugated Möbius compound—the directed synthesis or isolation of this compound is expected to be a very difficult task.

Our synthetic approach is therefore based on a general strategy that stabilizes Möbius structures (Fig. 1). In 'normal' aromatic structures like benzene, the *p* orbitals are orthogonal with respect to the ring plane (Fig. 1, structure A, cyan) whereas in belt-like systems (for example, carbon nanotubes) the *p* orbitals are perpendicular with respect to the surface of a cylinder (Fig. 1, structure B, magenta). A Möbius system (Fig. 1, structure C) includes both types of conjugation: a 'normal' part with trigonal planar sp^2-hybridized atoms, and a belt-like system with pyramidalized sp^2 atoms. The strain arises from pyramidalization. Thus, introducing a 'prefabricated' pyramidalized building block (Fig. 1, bottom, magenta) in a ring should stabilize the Möbius- versus Hückel-type isomers.

We chose bianthraquinodimethane as this rigid in-plane conjugated part. The steric hindrance of the inner *ortho* protons of the anthracene units enforces the pyramidalization of the central quinoid bond. Ring enlargement metathesis of tetradehydrodianthracene (TDDA) **2** (refs 16–18) with cyclooctatetraene **1** ($n = 1$) should lead to the twisted annulenes.

To test our strategy, preliminary theoretical calculations were performed on the Möbius stabilized [16]annulene. The geometrically fixed anthraquinodimethane part reduces the number of conceivable *E*/*Z* isomers to 12, each of which can have 9 *s-cis*/*s-trans* conformations. We optimized all 108 isomers using the PM3 method[19], and performed density functional theory (DFT) calculations[20] at the B3LYP/6-31G* level[21,22] of theory on the most stable conformation of the 12 most stable isomers. In Table 1 the relative energies of our Möbius stabilized annulene are compared with the results of Castro and Schleyer[15] on the parent [16]annulene. Whereas in the parent [16]annulene the two most stable isomers have Hückel topology, the six most stable isomers of our modified [16]annulene are Möbius-type systems including the global minimum. Hence, the theoretical data confirm our Möbius stabilizing strategy, and on the basis of these thermodynamic data, the synthesis of a Möbius system should be feasible.

Unfortunately, all attempts to combine TDDA with cyclooctatetraene in a ring enlargement metathesis reaction failed. Even though benzene and a number of alkenes upon irradiation react with TDDA to form metathesis products, cyclooctatetraene under the same conditions only furnished Diels–Alder adducts, isomers of cyclooctatetraene and 9,9′-bianthracene. To circumvent these problems, we used *syn*-tricyclooctadiene (TCOD) as a synthetic equivalent of cyclooctatetraene[23]. Irradiation of TDDA and TCOD in benzene with a high-pressure mercury lamp, using a quartz apparatus, gave as the main products two 1,3-cyclohexadiene derivatives (Fig. 2; see Supplementary Information for a detailed experimental procedure).

In the first step, a [2 + 2]cycloaddition product is formed, which could be isolated and characterized by NMR. This ladder-shaped compound, containing four fused cyclobutane rings, undergoes cycloreversion to give an unstable intermediate, which again opens in an electrocyclic reaction to form a C_2 and a C_s symmetric 1,3-cyclohexadiene. Both isomers were isolated, and characterized by X-ray structure analysis. Only minor amounts of the desired fully ring opened products were detected. As it is known that the photochemical stationary equilibrium between 1,3-cyclohexadienes and hexatrienes is shifted towards the ring opened product at shorter wavelengths, we irradiated the reaction mixture for 24 h with a low-pressure mercury lamp and obtained a mixture of isomers in an overall combined yield of about 50%. Five ring opened isomers were isolated by high-performance liquid chromatography. Two of them exhibit Möbius topology (C_1 and C_2 symmetry) and one has Hückel topology (C_s symmetry). The two Möbius structures were elucidated by NMR, and confirmed by X-ray analysis (for details of the X-ray data of the C_2 Möbius compound, see Supplementary Information; Cambridge Crystallographic Data Centre deposition number 223927). Both geometries are in very good agreement with DFT calculations. Only the C_2 symmetry isomer is significantly conjugated. The structural parameters of the Hückel C_s structure are not accurate because of disorder ($<10\%$ of a second isomer), but the data confirm the structural assignment by NMR. We use the Hückel structure as a reference to investigate the properties of our new Möbius C_2 compound (Fig. 3).

The C_2 symmetry Möbius compound forms red crystals, whereas the C_s symmetry Hückel compound is colourless (for ultraviolet data, see Supplementary Information). In Fig. 3, the most important geometry parameters calculated at the B3LYP/6-31G* level of

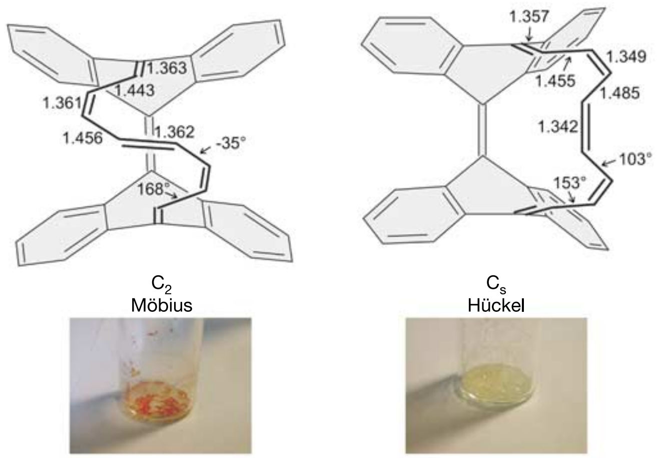


Figure 3 X-ray structures and photographs of the crystals of the C$_2$ Möbius and the C$_s$ Hückel isomer. The structure plots are idealized for clarity (thermal ellipsoids are removed, and the bond orders are indicated by single and double lines). Structural parameters for the Hückel isomer are not reliable because of disorder (see text). Therefore the bond lengths (Å) and C=C–C=C dihedral angles for the polyene bridge shown in the figure are determined by DFT calculations (B3LYP/6-31G*). For the complete set of X-ray data and calculations, see Supplementary Information.

DFT are given. Whereas the rigid bianthraquinodimethane part is almost identical in both isomers, the geometry of the polyene bridge differs substantially. Bond-length equalization, which is used as an aromaticity probe, is more pronounced in the Möbius compound than in the Hückel structure. The HOMA value[24], which quantifies this effect, is 0.50 in the polyene bridge (9 bonds) of the Möbius isomer, and 0.05 in the Hückel isomer. For comparison, the prototype aromatic benzene has a HOMA value of 0.98. The total HOMA (all bonds included) of the Möbius isomer is 0.35, and the HOMA of the Hückel structure is 0.17. A value of 0.35 corresponds to the HOMA in the benzene rings of C$_{60}$, and is somewhat lower than the corresponding value of the central benzene ring in phenanthrene (0.40). The Hückel isomer escapes from the 16-electron antiaromaticity by twisting the central double bond in the polyene bridge by 103° with respect to the two neighbouring double bonds. The dihedral angles in the Möbius system, however, only differ 12° and 35° from the ideal *s-cis* or *s-trans* conformation, still allowing considerable conjugation.

Aromaticity is a multidimensional property[25], and arguments exclusively based on geometric parameters may be misleading. For example, the maximum bond-length difference between single and double bonds in our C$_2$ Möbius compound (0.095 Å) is still quite large, comparable to the value for the non-aromatic anti-bismethano-[14]annulene[26]. We therefore also investigated a second, independent, aromaticity measure based on energy considerations, by using the 'indene–isoindene method' (ref. 27) to estimate the stabilization caused by conjugation in the Möbius structure. At the B3LYP/6-31G* level of DFT we computed a stabilization energy due to conjugation, ISE$_{\mathrm{II}}$, of 4.04 kcal mol^{-1} for the C$_2$ Möbius compound (20% of the ISE$_{\mathrm{II}}$ of benzene) and an antiaromatic destabilization energy of -2.22 kcal mol^{-1} for the Hückel C$_s$ structure. Both values are uncorrected, and can be expected to be more positive if *syn–anti* corrections are included[28]. We also find that the strain energy of the Möbius compound is slightly higher than that of the Hückel isomer, clearly indicating that it is the more efficient conjugation that makes the Möbius compound more stable than the Hückel compound.

Taken together, the observed trends in bond-length equalization and stabilization energy indicate that the Möbius structure is moderately aromatic, whereas the Hückel structure is non-aromatic. In the C$_2$ Möbius structure, all C–C bonds are conjugated, yet the molecule has only one π surface. The properties investigated here finally confirm Heilbronner's prediction for Möbius twisted [4*n*]annulenes. □

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Authors' contributions R.H. together with D.A. conceived the experiment; D.A. carried it out; R.H. wrote the Letter; and A.S. and O.O. determined the X-ray structure of the Möbius C$_2$ compound.

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Aromaticity

Möbius Aromatic Hydrocarbons: Challenges for Theory and Synthesis

Takeshi Kawase and Masaji Oda**

Keywords:
annulenes · aromaticity · carbocycles · hydrocarbons

In memory of Masazumi Nakagawa

Since the beginnings of organic chemistry the concept of aromaticity has been studied by both theoretical and synthetic chemists, and their interaction has resulted in exciting developments in this field.[1] In the nineteenth century it was recognized that benzene exhibits unusual stability for a highly unsaturated hydrocarbon and that all six carbon atoms are equivalent. In 1865 Kekulé put forward the hexagonal formula now used and introduced the hypothesis of valence oscillation between two cyclohexatriene structures to explain the absence of double-bond isomers for 1,2- and 1,3-disubstituted benzenes. However, the unusually high stability of benzene was not explained satisfactorily for a long time.

In the 1930s Hückel published his detailed treatise on the theoretical foundations of aromaticity which led to the formulation of his now famous "$4n+2$" rule: for ground-state molecules with a cyclic array of p orbitals, $(4n+2)$ π electrons, where n is zero or any positive number, lead to special stability based on the presence of a closed electronic shell. Calculations also predicted that systems having $4n$ π electrons are unstable, namely "antiaromatic" owing to open-shell electronic structures. The Hückel rule not only accounted for the unusual stability of benzene but it also stimulated synthetic organic chemists to construct various carbocyclic conjugated systems. Annulenes $(CH)_n$ were the main targets of synthesis. The scope and limitation of the Hückel rule have thus been established: the rule is applicable to planar or nearly planar cyclic systems without any apparent twist of the π frameworks interrupting the conjugation.

However, while the development of synthetic methodology has expanded the chemistry of conjugated systems, some difficulties have emerged. It is not easy to determine experimentally whether a compound is aromatic, particularly for non-benzenoid systems. In this context, computational analyses of bond-length equalization and magnetic properties such as the harmonic oscillator model of aromaticity (HOMA)[2] and nucleus-independent chemical shifts (NICS)[3] are now used as probes of aromaticity.

In 1964 Heilbronner conceived of "Möbius aromaticity" based on simple Hückel molecular orbital theory and predicted that [4n] Möbius systems would be stable because they possess a closed-shell structure in contrast to [4n] Hückel systems (Figure 1).[4] His idea was extended in the formulation of a selection rule for inferring the aromaticity of the transition states of pericyclic reactions: Zimmerman generalized the idea as the "Möbius–Hückel" concept.[5] However, Möbius annulenes conforming to Heilbronner's concept have not been realized up until recently, probably because it is difficult for even large macrocyclic annulenes to adopt Möbius geometries without any apparent angle or steric strain.

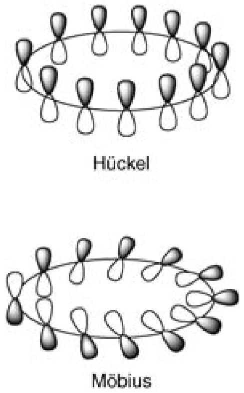
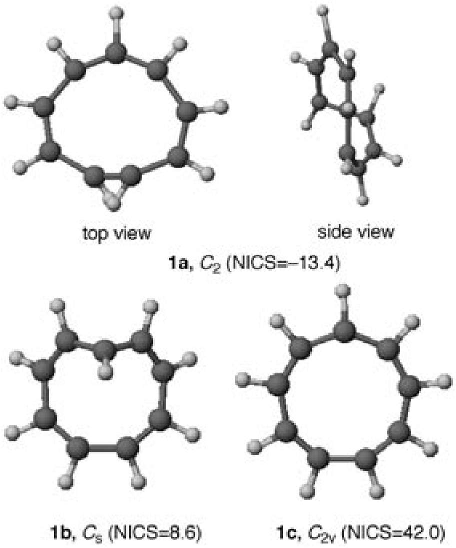


Figure 1. The π system labeled "Hückel" is a destabilized [4n] system, whereas that labeled "Möbius" is a stabilized [4n] system.

In 1998 Schleyer and co-workers reported that cyclononatetraenyl cation **1** with 8 π electrons is Möbius aromatic rather than nonaromatic on the basis of calculated NICS values (Figure 2). The cation **1** is formed easily in spite of the anticipated antiaromaticity of the planar structure.[6] According to calculations (B3LYP 6-311+G*), the Möbius conformation (C_2) **1a** is 21.6 kcal mol^{-1}



1a, C_2 (NICS=−13.4)

1b, C_s (NICS=8.6) **1c**, C_{2v} (NICS=42.0)

Figure 2. Conformations of $(CH)_9^+$.

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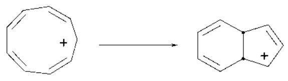
lower in energy than a second minimum conformation, **1b**, which has strong bond alternation. The energy difference between **1a** and the planar Hückel conformation (C_{2v}) **1c** is 26.3 kcal mol^{-1}. The NICS value of **1a** (−13.4) is more negative than that of **1b** (+8.6) and even than that of benzene (−9.7). Although formed easily, **1a** is a short-lived species; it isomerizes readily to the more stable bicyclo[4.3.0]nonatrienyl cation **2**, a bishomoaromatic cation (−11.8), through an electrocyclic ring closure (Scheme 1).

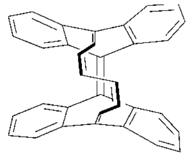


1 **2**

Scheme 1. Electrocyclization of **1** to **2**.

The electronic properties of small-ring compounds containing a strained allene bond or a *trans* double bond have also been discussed by theoreticians in connection with Möbius aromatic properties.[7] Although these computational studies predicted the importance of Möbius conjugation, the twisted cyclic molecules are destabilized by strong ring strain. In larger cyclic systems, however, ring strain is less pronounced. Rzepa's and Schleyer's groups have explored various isomers and conformations of [4*n*]annulenes (*n* = 3–5) computationally. These annulenes exist in equilibrium mixtures of geometrical isomers because of their structural flexibility. The calculations predict that some isomers of these systems adopt Möbius aromatic structures as energy minima, but the structures are very flexible and tend to flip back to the less strained Hückel structures with low activation energies.[8]

To display Möbius aromaticity, therefore, the target molecules should have rigid frameworks that enforce a smoothly twisted conjugation. Moreover, the molecular strain should be dispersed over the entire molecule. Almost the same concept was applied in the molecular design of "belt-shaped" conjugated systems.[9] The systems, in which the p orbitals are aligned horizontally on a rigid surface, have also been sought as attractive synthetic targets. Since the discovery of fullerenes and carbon nanotubes, these belt-shaped conjugated systems have been regarded as good models for the new carbon materials. The first examples, picotubes **3** and **4** and carbon nanorings **5** and **6**, were synthesized as relatively stable substances by Herges et al. and by our research group in 1996.[10,11] It is notable that a Möbius structure can be regarded as a combination of a "normal" aromatic structure and a belt-shaped aromatic structure as illustrated graphically in Scheme 2.[10]



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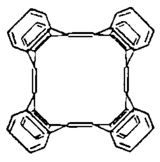

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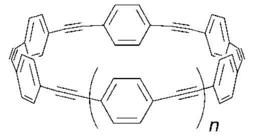
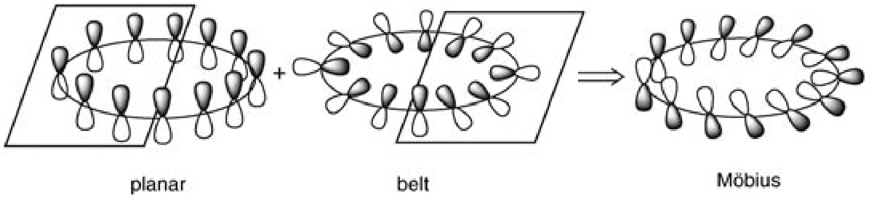
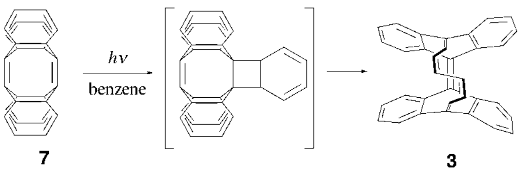


5: *n*=1, **6**: *n*=3



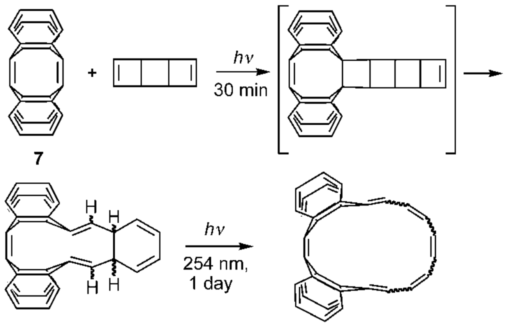
Scheme 2. Schematic construction of a Möbius structure.

Recently Herges and co-workers have synthesized the first stable Möbius molecule based on this consideration.[12] They found that tetradehydrodianthracene (TDDA, **7**) reacts with a number of alkenes upon photoirradiation to form rigid macrocyclic compounds by metathesis of the corresponding [2+2] cycloadducts. The twisted[14] annulene **3** was obtained from the [2+2] adduct of **7** with benzene (Scheme 3).[10a] The steric interaction of the inner *ortho* protons of the anthracene units forces the molecule to assume a tubelike structure. This interesting synthetic strategy was also applied to the synthesis of the twisted [16]annulene **9** using *syn*-tricyclooctadiene, a valence-bond isomer of cyclooctatetraene, in place of benzene (Scheme 4). In this case, the first metathesis proceeded thermally, but the second one proceeded photochemically. Although it contains rigid anthraquinodimethane moieties, annulene **9** has a number of geometrical and conformational isomers. According to calculations of all 108 isomers, the six most stable isomers, including the global minimum, possess Möbius-type structures.[12]



7 **3**

Scheme 3. Reaction of benzene with **7**.



7 **8** **9**

Scheme 4. Reaction of *syn*-tricyclooctadiene with **7**.

Five isomers were separated by HPLC and fully characterized by spectroscopic and crystallographic analysis. The orange crystalline *Z*,*E*,*Z* isomer **9a** (C_2) exhibits relatively little bond alternation (HOMA value = 0.50), whereas the colorless crystalline *Z*,*Z*,*Z* isomer **9b** exhibits strong bond alternation (HOMA value = 0.05) (Figure 3). The authors concluded that **9a** is Möbius

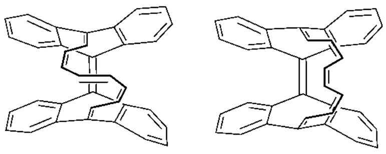


Figure 3. Molecular structures of isomers of **9**.

aromatic and that **9b** is a Hückel structure but nonaromatic. The orange color of **9a** clearly indicates the extension of conjugation.

Schleyer's group have predicted that "[4n+2] trannulenes" having in-plane cyclic conjugation are aromatic like Hückel annulenes;[13] however, it is not yet clear how orbital pyramidalization can cause a change in cyclic conjugation. Moreover, it is well known that a benzene nucleus in polycyclic conjugated systems drastically reduces the peripheral conjugation in the molecules. Actually, the families of picotubes and carbon nanorings do not exhibit much effect of peripheral conjugation.[11b] Despite these disadvantages, the hydrocarbon prepared by the Herges group is the first stable molecule having a Möbius structure. Thus, synthetic organic chemists have now realized Heilbronner's idea about 40 years after it was proposed. Theoretical studies on other Möbius conjugated systems have been advanced recently, and the synthesis of such compounds will be a highly interesting subject.[14] Thus, the synthesis of aromatic compounds has now entered a new stage, and bent cyclophanes, twisted polycyclic aromatic hydrocarbons, and, notably, fullerenes are just some examples of new targets.

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Non-Classical Carbonium Ions

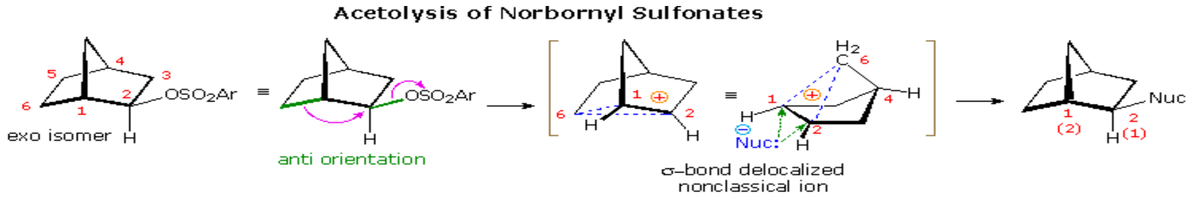
Marcus Clark, May Lee, Ashley Sacramo, Jaclyn Wolfe

DeShong

CHEM247

The term non-classical carbonium ion was first used by J.D. Roberts referring to the tricyclobutonium structure for the cyclopropylcarbinyl cation[1]. This non-classical carbonium ion was proposed in order to differentiate from the currently accepted “classical ions,” positively charged species which can be represented by a single Lewis structure. The classical ion has two electron- two center bonds while the non-classical carbonium ion is a positively charged species which cannot be drawn by a single Lewis structure. These non-classical carbonium ions have delocalized sigma electrons and have two electron-three center bonds. Roberts’ use of the term, “non-classical carbonium ion” sparked an interest in the ions which lead to further investigation by many big names in chemistry including Saul Winstein, H.C, Brown, and George Olah.

Saul Winstein was second, behind J.D. Roberts to use the term “nonclassical structures.”[1] Winstein used the term in order to explain what he observed in the acetolyses, a form of solvolysis, of exo-2-norbornyl brosylate and endo-2-norbornyl brosylate. In the reactions it was found that the exo-2-norbornyl brosylate was three-hundred fifty times more reactive than the endo-2-norbornyl brosylate. [2] Also, in the acetolyses of the molecules, both the exo-2-norbornyl brosylate and endo-2-brosylate yield racemic exo-norbornyl acetate.[3] Winstein proposed with this information that the loss of the brosylate anion created a bridged cation which could undergo a nucleophilic attack by a solvent at either carbon position one or two to yield the product.[3]



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[1] H.C.Brown, *Tetrahedron*, **32**, 179(1976).
[2] *Advanced Organic Chemistry*, Carey, Sundberg; Plenum Press: New York, 1984; p 304.
[3] *Organic Chemistry*, Morrison, Boyd; Allyn and Bacon, Inc.: Boston, 1973; p.916.
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To explain with more familiar ideas, the reaction of the exo-2-norbornyl brosylate can be compared to a Sn2 reaction where the carbon at position six helps to push out the brosylate and creates the bridged non-classical ion in one step.[3] The endo-2-norbornyl brosylate reaction can be compared to the Sn1 reaction where the there is a cation intermediate which forms, but then it changes quickly into the bridged non-classical ion.[3] Though it is possible to compare the two reactions, they are not exactly the same. Only the exo-2-norbornyl brosylate can actually form the non-classical ion because it has the proper spatial relationship between bonds. The endo-2-norbornyl brosylate can only form the bridged non-classical ion with the assistance of a rate-determining ionization.[2] Therefore, the non-classical carbonium ion that Winstein proposed was a molecule where a saturated carbon could use its sigma electrons as a neighboring group to explain the loss of the leaving group and to form the bridged intermediate. [3]

Not everyone agreed with Roberts and Winstein's interpretation of data. One of the major opponents of the non-classical carbonium ion theory was Herbert C. Brown. At a Symposium on Carbonium Ions held at the St. Louis Meeting of the American Chemical Society in March of 1961, Brown pointed out that "many of the non-classical structures for carbonium ions rested on exceedingly fragile experimental foundations, and suggested the need for further experimental work to test and reaffirm these foundations."[5] Instead of attributing the increased rates of solvolysis to the formation of a non-classical ion, Brown believed the observed rates were due to the relief of steric strain from the departure of an ion or molecule from a sterically crowded molecule.[6] For example, work done by Ingold on the rate of solvolysis of camphene

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[5] *The Nonclassical Ion Problem*, Brown, Herbert C., Schleyer, Paul Von R.; Plenum Press: New York and London, 1977; p 7.

[6] *The Nonclassical Ion Problem*, Brown, Herbert C., Schleyer, Paul Von R.; Plenum Press: New York and London, 1977;p 5.

hydrochloride, was shown to be 6,000 times faster than tert-butyl chloride. Ingold concluded that the formation of a non-classical carbonium ion was the driving force behind the increase solvolysis rates as opposed to the relief of steric strain from the departure of the chloride ion.[6] Brown also believed that the racemic product from Winstein's work on the exo-derivatives of norbornyl was due to a rapidly equilibrating classical carbocation instead of the formation of a non-classical carbocation. [7]

Brown's criticisms were damaging to the non-classical carbonium ion theory but experiments done by George Olah ended the controversy. In the early 1960s NMR spectroscopy techniques improved and allowed for direct observations of carbocations.[8] Olah performed spectroscopy work using "superacids" at low temperatures. Through the use of superacids Olah was able to stabilize and create long living carbonium ions and by performing his work at such low temperatures he was able to effectively eliminate the potential for hydride shifts within the carbocation being analyzed. Using H1 and C13 NMR spectroscopy Olah analyzed 2-norbornyl in SbF5/SO2ClF/SO2F2 solvent systems and at temperatures from -100 degrees Celsius to -158 degrees celsius. By performing the experiment at such low temperatures, Olah was able to freeze out 2,3 hydrogen shifts and 6,1,2 hydrogen shifts. [8] The spectrums remained unchanged at the different temperatures, as low as -160 degrees Celsius and had no low signals that were expected for a classical secondary carbocation. [8] The results from C13 and H1 NMR indicates a

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[6] *The Nonclassical Ion Problem*, Brown, Herbert C., Schleyer, Paul Von R.; Plenum Press: New York and London, 1977;p 5.
[7] *The Nonclassical Ion Problem*, Brown, Herbert C., Schleyer, Paul Von R.; Plenum Press: New York and London, 1977; p 89.
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symmetrical structure and based on this work have shown that the 2-norbornyl cation is symmetrically bridged. Further experimentation on 2-norbornyl done by Yannoni and Myhre using solid-state spectroscopy at –144 and –268 degrees Celsius demonstrated that if hydride shifts were occuring, allowing for the rapid equilibration between the 2-norbornyl carborcations, then the activation barrier for rearrangement would have to be less than .2 kcal/mol.[9] This activation barrier for rearrangement was measured to be too low for the extensive bonding and geometrical reorganization that would have to occur for classical ions, thus suggesting the existence of the non-classical bridging ions. [9] The symmetrically bridged, non-classical norborynl carbocation exists as an intermediate and not as a transition state as proposed by H.C. Brown. Olah, along with the majority of the scientific community, concluded from his studies that "…the long standing controversy as to the nature of the norborynl cation is unequivocally resolved in favor of the non-classical carbonium ion." [10]

When Winstein proposed the non-classical carbonium ion around 1950, he was met with opposition from Brown. For several years an academic feud ensued over whether or not the norbornyl cation had a structure containing a penta-coordinated carbon or if the norbornyl cation had a tri-coordinated carbon that was rapidly equilibrating with the charge moving to another carbon. Finally, Olah was able to solve the question through use of his superacids and NMR spectroscopy at low temperatures. He found that the structure of the 2-norbornyl cation was Winstein's non-classical symmetrical bridged structure with a penta-coordinated carbon. This method of analysis developed by Olah was the first to use NMR to address this sort of structure questions. Now, practically all carbocation intermediates can be studied using this method. His

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[9] Olah, G. A.; Prakash S. G. K.; Saunders, M.; Am. Chem. Soc. 1983, 16, 443.

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work has allowed for the protonation of saturated hydrocarbons in superacid media. Isomerization and alkylation of saturated hydrocarbons is of great importance to the petroleum industry in processes such as the production of high-octane gasoline. Superacid catalysis has made it possible to hydro-treat coals, shale oil, tar sands, and other heavy petroleum sources and residues, and yield liquid hydrocarbons under mild conditions.[11] Though the existence of the non-classical carbonium ion has been solved, the rigorous intellectual battle will be remembered as will the methods which are presently in use.

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