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Möbius Aromaticity and Delocalization

Henry S. Rzepa

Department of Chemistry, Imperial College London, Kensington Campus, London SW7 2AY, U.K.

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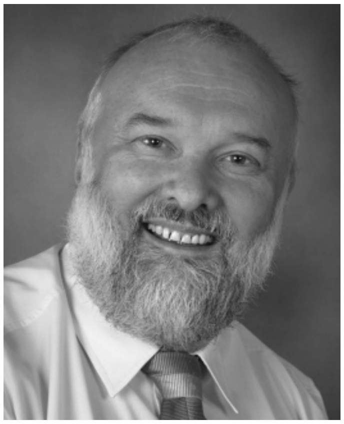

Henry Rzepa received both B.Sc. and Ph.D. degrees from the University of London at Imperial College, the latter in the field of physical organic chemistry studying kinetic isotope effects in reactions of indoles. In 1974, he took up a postdoctoral fellowship in Austin, Texas, with Michael Dewar in an area that thereafter became known as computational chemistry. Since he has moved back to Imperial College London, where he is now Professor of Computational Chemistry, his research has developed in three main areas: the mechanisms of stereospecific reactions and properties of catalytic processes, the exploration of novel forms of aromaticity, and the semantic development of Internet-based publishing. The astute reader may notice aspects of all three interests in the present review; the latter in particular is expressed via the associated electronic supporting information, which the author hopes may provide one glimpse of the future of chemical publishing.

1. Introduction and Scope

The Möbius strip is named after the theoretical astronomer and mathematician August Ferdinand Möbius (1790−1868). In a memoir, presented to the French Academie of Sciences, which came to light only after his death, he discussed his discovery (in September 1858) of the properties of the one-sided surface that bears his name. Möbius is also accredited with some early ideas in the development of group theory. Another German mathematician and physicist, Johann Benedict Listing, had earlier introduced the term *topology* (in 1847) and followed this (in July 1858) by his independent description of Möbius bands. The base form of this object is formally described[1] as a nonorientable (one-sided) surface obtained by cutting a closed band or cylinder into a single strip, giving one of the two ends thus produced a one-half (180°) twist, and then reattaching the two ends. This twist need not be identified with the discrete region of the original cut in the strip, but may be delocalized evenly throughout the resulting band.[1] Listing also investigated the topology of higher-order Möbius bands, also called paradromic rings, produced by imparting additional twists prior to attaching the ends. Other chemically relevant topologies, such as trefoil knots, also have the properties of a Möbius strip. These topologies all have the property of dissymmetry, in that their mirror images are not superimposable with the original.

In this review, molecular instances of conjugated Möbius bands and related systems are reviewed, with a focus on the relationship among their properties, geometries, and associated electronic delocalization. Closed molecular bands can be classified in terms of either the topology of the electronic coordinates (wave function) or of the nuclear coordinate framework alone. A useful further subdivision of the first category is in terms of a wave function derived from purely a p-atomic orbital basis set in which a 180° phase shift is induced by the nuclear framework and a system where the phase shift results from inclusion in the basis set of one or more appropriate d atomic orbitals. A short review of Möbius hydrocarbons has recently appeared.[2]

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2. Electronic Möbius Bands: Background and History

Some 100 years passed after Möbius' and Listing's mathematical explorations before Möbius topology caught the imagination of chemists. For several decades, it was the theoretical aspects that dominated their attention. Only recently has the laboratory synthesis of such molecules been accomplished, the measured properties of which can now provide a test of the theoretical predictions.

The early theoretical studies focused on the implications of Möbius topologies in electronic wave functions and how the essential 180° (π) half-twist might be introduced into a cyclic array of atomic orbital (AO) basis functions. The first such mechanism considered was by Craig[3] in 1959. He analyzed the consequences of d-atomic orbitals (AOs) present in an alternating cyclic array of $p_\pi-d_\pi(d_{xz})$ AOs. This was a model for many known ring systems containing an $(AB)_n$, $n = 3,4$, pattern of alternating first-row atoms A and second-row atoms B (Figure 1). Calculations at the Hückel molecular orbital level revealed that where the AO basis comprises equal numbers of p- and d-functions, the delocalization energies were smooth functions of n, showing no equivalent to the Hückel $4n + 2$ stability rule, and leading in the limit of large rings to the same delocalization energy per π-electron as $p_\pi-p_\pi$ overlaps. No overt connection was made at this stage with Möbius topologies. The first person to do this was Heilbronner[4] in 1964, who considered the implications of replacing all the d-AOs in the above basis by one comprising only p-AOs. The necessary phase shift was instead introduced by twisting the nuclear framework itself such that the AO basis would lie on the surface of a Möbius band (Figure 2). This framework comprised a monocyclic annulene formed from a ring of carbon atoms in which each atom was assumed to be sp^2-hybridized for the σ-framework and to bear a further pure 2p atomic orbital (AO).

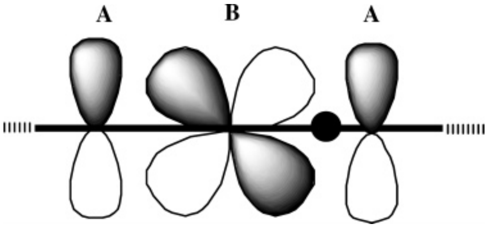


Figure 1. Craig model[3] for an array of $p_\pi-d_\pi-p_\pi$ atomic orbital overlaps. The phase shift occurs at the position marked with a dot. In Craig's model, A and B are repeated within a planar cyclic array.

In conventional planar annulenes, such as benzene, each 2p AO is regarded as overlapping in parallel fashion with its adjacent neighbors, to form what is topologically known as a cylinder. Fundamental to the understanding of aromaticity is that double occupancy by $4n + 2$ electrons of the π-molecular orbitals derived from such a planar cyclic array of p-AOs (Figure 3a, $n = 1$) results in maximizing the resonance energy per electron and hence the associated stability of the system (at least for small- and medium-sized rings).[5] Occupancy instead by [$4n$] electrons in a planar, bond-equalized structure is regarded[6] as resulting in an open shell configuration (Figure 3b, $n = 2$), although the stabilization (resonance energy per electron) is less than that for $4n + 2$ electron occupancy. Only the triplet configuration is considered aromatic in both a geometric and a magnetic sense.[6b] The $4n$ singlet diradical electronic configuration (with two singly occupied MOs) is classically described as "anti-aromatic"[7] and had been assumed to be destabilized as a planar π system. It has been increasingly recognized[8] that even planar D_{8h} cyclo-octatetraene ($4n$, $n = 2$) is in fact only slightly, if at all, destabilized by π-electron effects and that instead angular ring strain at the planar geometry plays the dominant role.

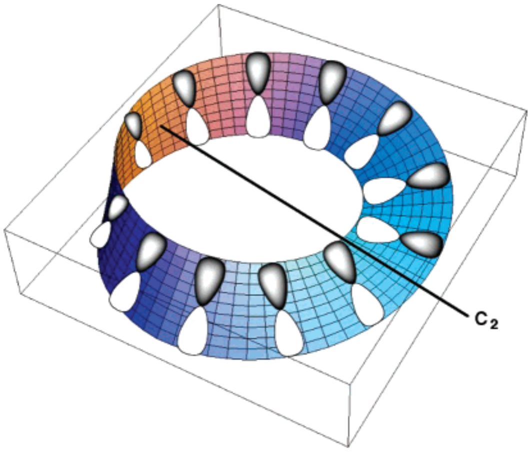


Figure 2. An idealized Möbius strip bearing an evenly distributed p-atomic-orbital basis set, showing a single phase inversion ("knot") located along the C_2 axis (shown as a line) at a point where extension of the local surface would intersect with the strip. The "knot" could also be located at the alternative intersection of the axis with the strip. A rotatable 3D model of a Möbius strip can be viewed via the Supporting Information available for this article or at ref 1.

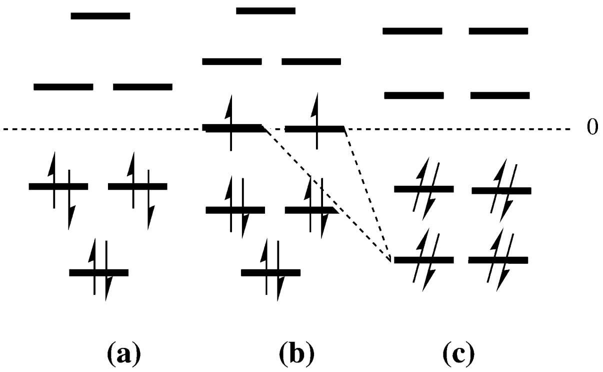


Figure 3. Hückel-MO-derived energy levels for (a) the conventional Hückel $4n + 2$ electron occupancy of an assumed planar cyclic array of p-AOs, (b) $4n$ occupancy, shown as a triplet state, and (c) $4n$ occupancy following a single phase inversion (half-twist) in the AO array, shown as a singlet state.

If the cylinder is half-twisted into a Möbius topology, a single 180° phase shift is introduced into the array of $4n$ 2p AOs (Figure 2). Hückel molecular orbital theory now predicts[4] that for a basis set with an even number of 2p AOs, the resulting energy levels will be degenerate (Figure 3c, $n = 2$) and that occupancy of n pairs of bonding MOs by $4n$ electrons would then result in a closed shell configuration, with each orbital doubly occupied. Each energy level however is rendered less stable than its untwisted counterpart (Figure 3b) due to a reduced $p_\pi - p_\pi$ resonance overlap, as described by the simple expression

$$\beta^{M} = \beta \cos (\pi/(4n)) \tag{1}$$

When this is 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 made several inferences from this result.

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

Although not directly stated by Heilbronner, two other points have been inferred from his work.

4. The outcome of twisting a planar cyclic open-shell $4n$ π-electron array into Möbius topology is more favorable than the same process performed for a closed-shell $4n + 2$ π-electron array.
5. The Möbius-twisted AO basis results in molecular orbitals that if populated with $4n + 2$ electrons will favor open shell configurations.

These results have been more simply presented as stating (for transition states)[9] that a cyclically conjugated closed shell thermal system in which the p-atomic orbital basis contains an odd number of 180° phase shifts distributed evenly along a Möbius band will have lowest π energy if occupied by $4n$ ($n = 1, 2,$ etc.) electrons. An additional corollary reverses these rules for open-shell (singly excited) transition states, that is, a $4n + 2$ electron system with half-twist Möbius topology is preferred to a $4n$ system.[9] In those cases where this results in a system with 2-fold rotation symmetry, it was subsequently shown that the resulting occupied molecular orbitals can be usefully partitioned into the sum of two cyclic $2n$-electron manifolds, one having Hückel and the other having Möbius topology.[10] Various other explorations of the theoretical aspects of such topologies for cyclic π systems have appeared, including a more rigorous proof of Heilbronner's original treatment, a graph-theoretical analysis, and magnetic properties.[11] In comparison, theoretical analysis of the higher-order Möbius (paradromic) rings is a relatively neglected area.

Heilbronner[4] was careful to question whether his derivation of an "electron in a ring" was also acceptable for three-dimensional problems, and he noted that it might simply be an artifact of an essentially two-dimensional Hückel model having no three-dimensional counterpart. Nevertheless his suggestion that simple (Dreiding) models for $(CH)_n$ annulenes ($n \geq 20$) in a Möbius topology showed no apparent bond angle or steric repulsion was remarkably prescient. It would take some 3 decades for this suggestion to be followed up with systematic and quantitative explorations of the conformational surfaces of such annulenes; perhaps their anticipated complexity was too daunting.

The most immediate impact of the "thermal $4n$ Möbius" rule was its application not to equilibrium molecules as such but to the theory of pericyclic reactions. The classification of such reactions by Woodward and Hoffmann, and their own explanation of the derived selection rules by the application of orbital symmetry had an enormous effect on stereoelectronic theories of reaction mechanisms. Zimmerman[9] was the first to combine the Woodward–Hoffmann and Heilbronner approaches in formalizing the correspondence between $4n$ π-electron pericyclic transition states bearing an antarafacial mode and the Heilbronner $4n$ Möbius approach. It is noteworthy that neither Heilbronner nor Zimmerman directly associated Möbius π topology with ring aromaticity, merely referring to Möbius nonplanar π MO ground states as energetically comparable (if angle strain were not present) with planar Hückel forms (i.e., points 1–3 above). This correspondence with aromaticity is nevertheless widely assumed, particularly via the Frost–Musulin mnemonic[7b] for obtaining π-MO energies, as first identified by Zimmerman himself.

2.1. Application of Möbius Topologies to Transition States

In 1993, Jiao and Schleyer elegantly demonstrated that pericyclic transition states[12] proceeding with half-twist Möbius topology would indeed have predicted aromatic properties. They calculated[13] the [1,7] sigmatropic migration of a hydrogen atom in (*Z*,*Z*)-1,3,5-heptatriene, finding the transition state with the expected C_2 symmetry and a characteristic helical motif (Figure 4). The C–C bond lengths (1.395–1.410 Å; $\Delta r_{C-C} = 0.015$ Å) had bond equalization comparable to benzene. The calculations also revealed the presence of a diamagnetic ring current and predicted ^1H NMR chemical shifts for the ring protons attached to the sp^2 carbons to be in the range 6.3–6.9 ppm (relative to TMS, cf. ~7.0 for benzene itself). Interestingly, Dewar, an active proponent of the aromatic transition state approach, had eschewed Möbius aromaticity as a valuable concept in this regard.[14]

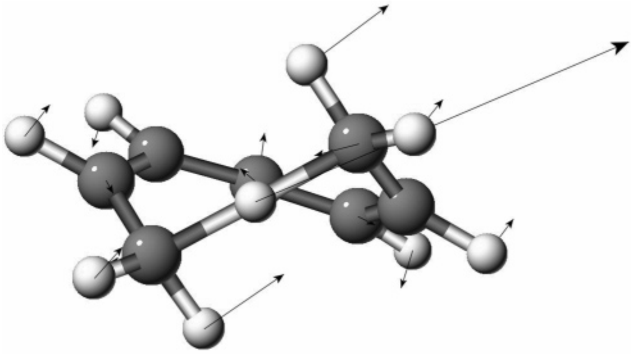


Figure 4. Computed[13] geometry (MP2/6-31G*) for a [1,7] sigmatropic antarafacial hydrogen shift occurring via a half-twist Möbius aromatic transition state.

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 ~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 ~180° for a half-twist system; even one orthogonal dihedral (~90° ± 15°) will interrupt delocalization
aromatic stabilization energy (ASE)[c]	~1.5−3.0 kcal mol^{-1} per ring carbon	not systematically evaluated for highly nonplanar systems
exaltation of diamagnetic susceptibility[d]	−15 to −120 ppm·cgs	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]	7−9 ppm (outer protons)	appears typical of both Hückel and Möbius aromatic rings
induced current densities[j]		little evaluated for nonplanar Möbius systems
π molecular orbitals[k]	Möbius orbital symmetric with respect to (ideal) C_2 axis	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.

Jiao and Schleyer also predicted[13b] Möbius transition state aromaticity for an electrocyclic pericyclic reaction; there appear to be no reports of the analysis in such terms of cycloaddition reactions proceeding via Möbius topology.

During the period 1964−1994, the focus on Möbius systems evolved largely into a rationalization for the stereoselective behavior of pericyclic reactions in terms of an aromatic transition state model. Heilbronner's suggestion that the larger annulenes might be capable existing in conformations exhibiting the Möbius characteristics noted above had not been translated into any reported successful syntheses of stable examples, nor were there any other published suggestions for alternative stable systems that might be subjected to experimental study. In particular, it was desirable that the association between cyclically conjugated Möbius π systems and concepts such as aromaticity and electronic delocalization should be subjected to experimental scrutiny, using criteria such as the equality of the ring bond lengths or magnetic properties.

This validation was essential, since, as Heilbronner was only too aware, the clear σ/π separation possible for planar conjugated systems is blurred when such systems are twisted. Under these circumstances, it becomes more difficult to separate the electronic influence of the σ framework from the conjugated π manifold. It is also apparent that for finitely sized ring systems, there must be a continuum between an entirely planar (Hückel) system, a slightly twisted system (in which perhaps the total distribution of the twist among the basis set of n-functions does not sum to precisely, or even approximately, π), an optimal Möbius system where the effect is potentially maximized, and an unevenly twisted system where one (or more) of the adjacent angles between two 2p AOs approaches an orthogonal value of 90° and across which conjugation is hence largely interrupted. There may even exist overly twisted systems in which the twist is significantly more than π or even the 2π or higher necessary for paradromic rings. It was not immediately obvious however that any realistic and finite ring-sized molecule would necessarily exist where maximum Möbius-derived π stabilization would not be attenuated or even completely lost by even greater destabilization due to angular or steric strain or to σ-electronic effects.

2.2. Quantifying Möbius Aromaticity

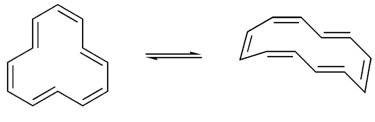
The evaluation by Jiao and Schleyer[13] of quantitative estimates of the aromaticity of transition states with Möbius topology emphasized the importance of having well calibrated criteria for this purpose. Some of the more important of these, both computed and experimental, that have been proposed for quantifying aromaticity are summarized in Table 1. These reference points are included here for convenience with the caveats that not all have been evaluated as necessarily relevant for Möbius conjugated rings and that many are relatively approximate in their nature. Reference to these will be made when specific systems are discussed herein.

3. Delocalized Heilbronner-Type Möbius Systems

With the Heilbronner motif of introducing a phase shift into a cyclic array of purely 2p AOs, the focus is in providing a mechanism for introducing one π phase shift utilizing the geometry of the nuclear framework. Most early investigations centered on systems with strategically located *transoid* double bonds placed at an appropriate location in a medium-sized conjugated ring. The term transoid is used here, since in a truly delocalized twisted system, the alkene may not be constrained to precise periplanarity.

The smallest annulene for which such a strategy might be conceivably accommodated without prohibitive angular strain is transoid [8]annulene, but calculations[15] have revealed little resulting conjugation between the E and neighboring Z double bonds, due to essentially orthogonal overlaps of the adjacent 2p AOs. The result is little evidence of any aromatic character in this molecule. In effect, the rotation between pairs of neighboring p-orbitals was very unevenly distributed around the ring in the fully relaxed geometry. The authors noted that fixing two dihedral angles during geometry optimization to artificially delocalize the rotation had the effect of significantly *increasing* the ring aromaticity (as quantified using the NICS(0) index in Table 1, and described more fully in section 3.3).

Recently, a more spectacular example of this particular effect was identified by Castro, Karney, and co-workers.[16] Intrigued by the low value of the experimental barrier for cis−trans isomerization in a tri-*trans*-[12]annulene, **1**, they proposed a delocalized transition state on a reaction pathway involving single/double bond shifting. This was predicted to exhibit Möbius aromatic properties such as bond-length equalization (Figure 5, $\Delta r_{C-C} = 0.031$ Å) and dihedral twisting (deviating from coplanarity by, for example, 38° in the region of cis−trans isomerization and approximately equating to the $\pi/(4n)$ angle in eq 1). Thus the [12]annulene **1** adopts a conformation in the equilibrium state that contains one or more orthogonal overlaps between adjacent 2p AOs and that must totally inhibit any Möbius aromaticity at this geometry, but rotation of one trans C=C bond increasingly eliminates this orthogonality and enables strong Möbius conjugation when the transition state is reached.



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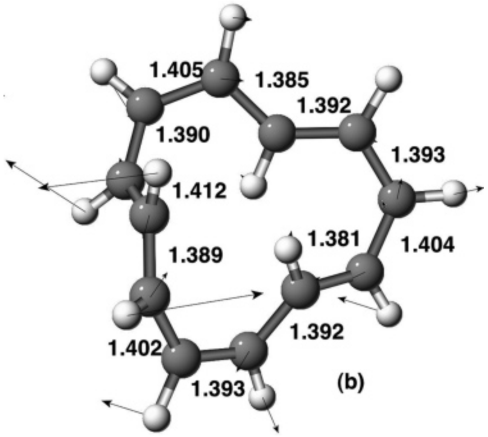
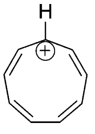


Figure 5. (a) Computed geometry[16] (BH&HLYP/6-311+G(d,p)) for bond shifting/cis−trans isomerization in tri-*trans*-[12]annulene, **1**, occurring via a Möbius aromatic transition state. Displacement vectors correspond to the imaginary transition normal mode. The bond marked with a length of 1.412 Å has a HCCH dihedral angle of 142°.

A nine-membered ring appears to be the first realistically sized system that can accommodate both a *transoid* alkene and the induced ring strain without orthogonalizing the 2p overlaps. In 1972, Anastassiou and Yakali had reported their speculations[17] on why the charged $4n-\pi$ nine-membered ring annulene **2** forms and scrambles ^{2}H so easily with an explanation couched in terms of a nonplanar C_2 symmetric conformation avoiding the *destabilizing* effects of anti-aromaticity. This argument was in 1998[18] replaced by a proposal for a *stabilizing* effect by, as it happens, the original discoverers of this cation. They argued, following Heilbronner, that π delocalization and stabilization is facilitated when the ring adopts a half-twist Möbius conformation. The lowest energy conformation was confirmed (B3LYP/6-311+G(d,p) calculation) as having C_2 (rather than C_s) symmetry. Although the presence of a C_2 axis of symmetry does not, per se, imply Möbius conjugation, convincing evidence of such was obtained from the calculated geometric and magnetic properties of **2**. These are discussed in detail below as exemplars of the basic properties expected of a Möbius system exhibiting aromaticity.



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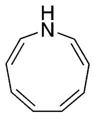

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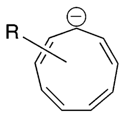

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3.1. Ring Bond Length Variation in 2

The computed[18] geometric features of **2** are shown in Figure 6, which includes a comparison with the geometry of enforced planarity. Some analogy with, for example, Figure 4 is obvious; the migrating hydrogen atom is now replaced by a CH$^+$ unit, and in a transition state, the energy maximum becomes an energy minimum. It is worth noting that although a planar [9]annulene of this type will have some inherent angular ring strain due to deviation from

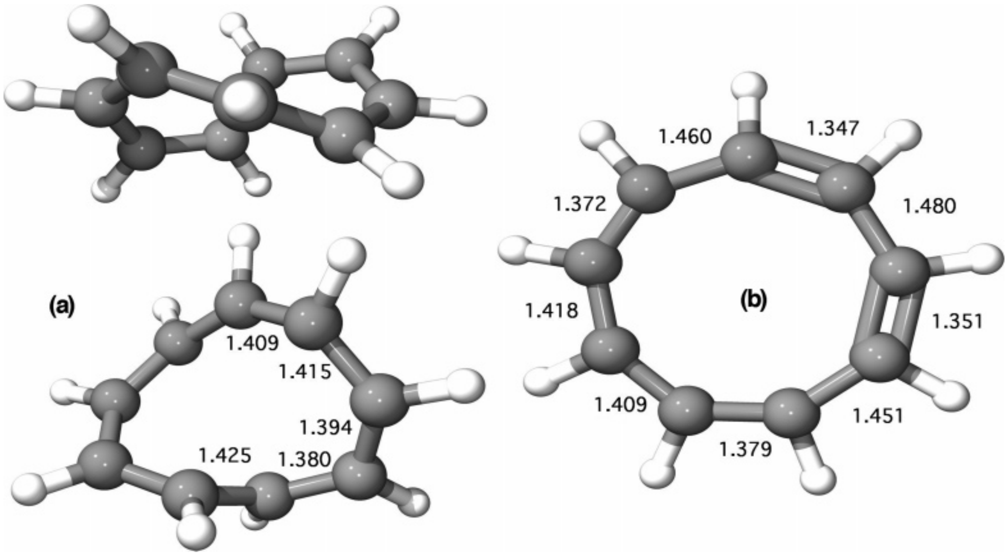


Figure 6. The $C_9H_9^+$ system **2** at (a) the lowest energy [B3LYP/6-311+G(d,p)][18] conformation, including a view along the C_2 axis showing the transoid double bond in the background and (b) the enforced planar geometry.

idealized sp^2 angles, 10π-electron nine-membered ring systems are nevertheless thought to be on the edge of existing as planar species.[19] With **2** however, the calculated planar geometry shows strong bond length alternation (maximum $\Delta r_{C-C} \approx 0.131$ Å), normally taken to indicate lack of aromatic delocalizing stability and being more characteristic of non- or anti-aromatic systems. The force constants calculated for the planar stationary point show two negative values, the more negative of which (ν 179 cm^{-1}) reveals vectors corresponding to deplanarization toward a C_2 symmetric species (some 20 kcal mol^{-1} lower in energy). The less negative force constant (corresponding to $\nu = 66$ cm^{-1}) has vectors distorting toward a geometry having only a C_s plane of symmetry. The C_2 symmetrization is accompanied by a substantial *decrease* in the degree of bond length alternation ($\Delta r_{C-C} \approx 0.043$ Å, Figure 6), again suggestive of increased delocalization and hence increased aromaticity. The Julg and HOMA normalized values (Table 1) for these geometric effects were not reported for this particular system.[18]

That these effects are associated specifically with $4n$ π electrons is demonstrated by comparison with the molecule **3**. This nine-membered ring system differs from **2** only in replacing a formal zero π-electron CH$^+$ unit with a two-electron NH unit, becoming in the process a closed shell $4n + 2$ electron system. Here a CCSD/6-31G(d) ab initio calculation[19c] shows the planar nine-membered ring to also suffer a deplanarizing, C_2 symmetrizing distortion but now attributed entirely to relief of angular ring strain. In direct contrast to **2**, this is accompanied by a substantial *increase* in the degree of bond length alternation and hence a *decrease* in delocalization and aromaticity due to loss of planarity. Clearly, the $4n$ electron system appears to have delocalization increased by twisting, while for the $4n + 2$ system this is reduced by twisting, a concept in accord with the simple interpretation presented by Heilbronner. Although recent results[20] raise the probability that aromaticity deduced from geometric criteria such as bond alternation/delocalization alone for larger rings ($\geq 14\pi$) may not be a reliable indicator of aromaticity, the correspondence between aromaticity and bond length equality remains true for smaller rings, such as **2** and **3**. It had also been shown[21] that the B3LYP density functional method (used to calculate the geometry of **2**) tends to overemphasize the degree of delocalization of aromatic $4n + 2$ annulene systems, an observation also confirmed[19c] by CCSD(T) calculations for the 10π system **3**. To reduce such uncertainties, it was suggested that the preferred metrics should be based on magnetic rather than geometric criteria alone.[20]

3.2. Ring Dihedral Twisting in 2

An alternative geometric measure of delocalization, which is not available for planar Hückel-like aromatics, is how even the twist distribution might be in a putative half-twist Möbius system. With the caveat that in small rings, effects such as angular strain, nonplanarity at individual atom centers, "bond bending", and further relief of strain via cis/trans isomerization may distort the results, the HCCH dihedral angles calculated for **2** are 129°, 24°, 23°, 10°, and 18°. The first of these corresponds to the (approximately) transoid configuration present to reduce angular strain and hence deviating from 180° by 51°. The degree of twist sums to 183°, with an average of 20°, and while individual values can differ significantly from this mean, it is nevertheless apparent that the twist is not localized in any single region of the ring, conforming at least qualitatively the interpretation of delocalized Möbius aromaticity previously inferred from the equalization of bond lengths. What remains to be established is whether this form of delocalization is as susceptible as are the bond lengths to the nature of the electron correlation treatment in the computational procedures used.[20]

3.3. Magnetic Properties of 2

An extensive volume of research has shown that the most meaningful measures of aromaticity derive from the ability to sustain a diatropic ring current (with anti-aromatic molecules sustaining a paratropic current). Schleyer originally proposed NICS(0) (nucleus independent chemical shift),[22] being the absolute magnetic shielding computed at ring centers, as an approximate but particularly convenient criterion for estimating ring aromaticity and antiaromaticity. This was later refined to also include NICS(1)[23a] (being the value 1 Å above the ring plane) as more usefully, but also approximately, separating out the effects of the diamagnetic contribution to the ring current (due to π circulation above and below the plane) from the paratropic contributions (due to in-plane σ circulation and local shielding effects which drop off rapidly from the ring center). A further elaboration[23b] introduced the NICS tensors, with the NICS_{zz} component perpendicular to the ring plane being regarded as the best metric for the characterization of the π system of the ring, comparable with ring current densities (cf. Table 1). From the preceding introduction, it can be seen that the NICS concept is somewhat less useful when applied to systems that (by definition) do not have a reference plane and hence where the π/σ separation is only approximate (and largely defined by lack of mixing between the lower energy σ manifold and the higher energy π system). Despite these misgivings, NICS(0) metrics have proved semiquantitatively useful in investigating the aromaticity of Möbius systems. Moreover for large rings, where the σ-contribution to the total NICS tends toward zero, NICS(0) tends toward NICS(π).

For **2**, a NICS(0) value of $\delta = -13.4$ ppm was calculated[18] (typical of aromatic systems, Table 1). This compared with the NICS(0) value of -9.7 ppm for benzene at the same theoretical level and with $+42$ ppm for **2** computed at a planar (anti-aromatic) geometry. Pertinent to this comparison is the observation that NICS(0) shows only a modest dependence on ring size (although it may become less useful for both larger rings and also very small rings where local shielding effects become important).

Other magnetic measures of aromaticity, particularly the exaltation Λ in diamagnetic susceptibility χ_{tot} of -18.8 ppm·cgs (compared to that estimated from fragment increment schemes)[24] agree with NICS(0) in predicting aromaticity for **2** (Table 1), although comparisons among molecules with different shapes and sizes are known to be less reliable for this metric. Also less certain are the appropriate fragment increment schemes to be used, for e.g. a *transoid* C−C as opposed to a cis or trans alkene. Finally in this regard, it is noteworthy that although e.g. ^{1}H NMR chemical shifts have also been used as approximate indicators of diatropic ring currents for planar aromatic systems, such criteria have been much less explored for the Möbius system.[13,25]

3.4. Molecular Orbitals for 2

Heilbronner's simple derivation of Möbius stability (using Hückel MO theory) predicated pairs of degenerate π energy levels. In reality, this degeneracy is broken for a C_2 symmetric molecule, and for **2**, the four highest occupied orbital eigenvalues are $-11.7/-12.1$ and $-13.5/-14.1$ eV.[18] Although these orbitals are contaminated by some mixing with the C−H σ manifold, the topology reveals each pair to comprise a symmetric (a) and an antisymmetric (b) combination with respect to the C_2 axis, corresponding to the Möbius and Hückel partitioning originally suggested[10] (Figure 7). The higher energy Möbius orbital shows a characteristic "needle and thread" pattern (also describable as a rotaxane-like motif). The more stable Möbius orbital tends toward two intersecting rings, separated by a single node following the locus of the nuclear ring. In this, it follows the similar single-node model for the most stable π orbital in benzene in which the nuclear plane lies at the node. These basic orbital motifs can be easily perturbed by other effects (i.e., CH interactions), but they do appear loosely characteristic of many half-twist Möbius aromatic systems. This picture also serves to emphasize that the canonical phase shift is not necessarily localized at any one center but can run continuously along the nuclear circle for the lowest energy orbital.

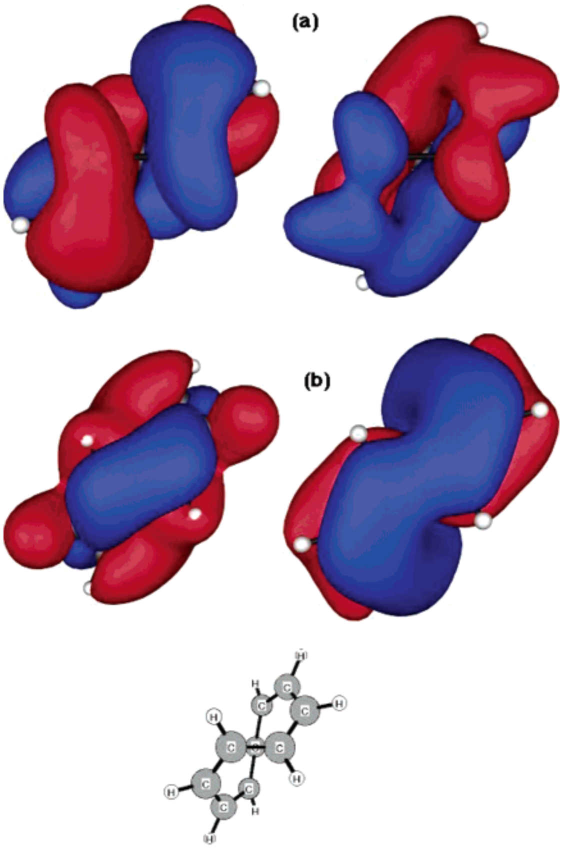


Figure 7. Molecular orbitals [B3LYP/6-311+G(d,p)] contoured at an isosurface value of 0.02 au[30] for **2** showing (a) the Hückel orbitals of b symmetry, -11.7 (31b), -14.1 (28b) eV and (b) the Möbius orbitals of a symmetry, -12.1 (30a), -13.5 (29a) eV. Orbital pairs 31 and 30 and 29 and 28 would be formally degenerate in Heilbronner Hückel-MO theory. Rotatable 3D models of all orbitals are available via the Supporting Information.

A similar insight can be obtained by inspecting the wave function for the related nine-membered ring anionic species **4**. This was reported[26] as a triplet, which as a 10-electron $4n + 2$ system is inferred to prefer a stable half-twist Möbius conformation. This

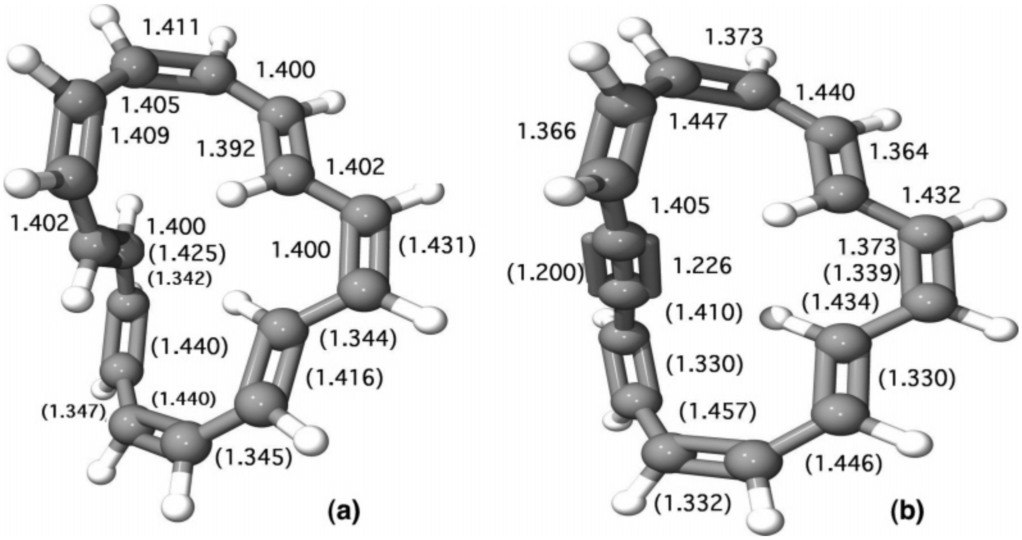


Figure 8. Calculated B3LYP//6-31G(d)[28] (KMLYP//6-31G(d)[29,30] values shown in parentheses) geometries for (a) [16]-annulene showing the Möbius conformation with the C_2 axis oriented horizontally and (b) dehydro[16]annulene,[30] one *trans*-alkene lying in the C_2 axis having been replaced by a linear alkyne.

system was studied as the perfluorinated analogue, primarily to reduce contamination of the wave function by replacing relatively high-energy C−H units with the lower-energy C−F equivalents and in the process reducing σ/p_π mixing. As with **2**, there is little predicted bond alternation (1.377−1.411 Å; Δr_{C-C} = 0.034 Å), the FCCF twist (180°−131° = 49°, 36°, 33°, 8°, 25°) is fairly evenly distributed around the ring, and the NICS(0) value (−13.0 ppm) is typical of aromatic character (Table 1). Commensurate with these geometric and magnetic criteria, the lowest-energy Möbius orbital again shows an intersecting ring nodal pattern.[26]

4. Other Möbius Cycloalkene Systems

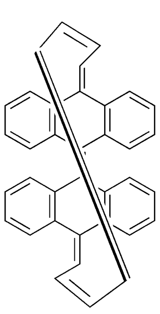
Shortly after the report of the cationic 8π **2** appeared, a Möbius C_2 symmetric conformation of neutral 16π [16]annulene was proposed.[27] Heilbronner's original assertion (that only [20] or higher annulenes were likely to exhibit such conformational folding) still held, since this reported conformation was calculated to be significantly higher in energy than Hückel-folded forms. In 2002, further lower-energy Möbius conformations of [12]-, [16]-, and [20]-annulenes were reported,[28] although these were still higher than the Hückel forms (albeit by only 6.2 kcal mol^{-1} for the [20]annulene). The Möbius [12]annulene contains two transoid motifs and reveals relatively prominent bond length alternation (Δr_{C-C} = 0.078 Å, HOMA = 0.69), but this variation is almost eliminated for a Möbius, C_2-symmetric isomer of [16]-annulene containing three transoid bonds (Figure 8, Δr_{C-C} = 0.019 Å, HOMA = 0.93, Julg = 0.997) and is only slightly greater for a [20]annulene containing five transoid bonds (Δr_{C-C} = 0.049 Å, HOMA = 0.85, Julg = 0.95). The NICS(0) values for these three annulenes (−14.6, −14.5, and −10.2 ppm, respectively) also fall typically into the aromatic region, as do the magnetic susceptibility exaltations (−36.5, a particularly notable −112.9, and −95.2 cgs·ppm, respectively, see Table 1).

For larger rings, bond length alternation (or lack of it) may not always be directly related to aromaticity. KMLYP is a density functional rehybridization[29] that predicts, apparently correctly,[20b] that Hückel aromatic [18]annulene itself has alternating bond lengths in a manner that reduces the overall molecular symmetry from D_{6h} to the less symmetric C_3 point group. The difference between the calculated shortest and longest C−C bonds, Δr_{C-C} is 0.099 Å (KMLYP) compared with 0.017 Å (B3LYP). If KMLYP is applied[30] to the [12], [16], and [20] Möbius annulenes described above, Δr_{C-C} increases from 0.078, 0.019, and 0.045 Å (B3LYP) to 0.131, 0.087, and 0.108 Å, respectively (KMLYP). While the B3LYP density functional hybrid has been shown to overemphasize bond length equality for planar aromatic rings,[21] the hitherto lack of such experimental data for Möbius rings means its behavior for these systems remains unestablished.

A perturbation that becomes possible in larger annulene rings is to replace one transoid alkene in, for example, [16]annulene with an alkyne (Figure 8b) at a position that retains the C_2 symmetry. The effects upon Möbius character of alkyne groups present in the ring system have not been reported;[28b] on dehydro[16]annulene, the consequence appears to be increased bond alternation (Figure 8b) and reduced aromaticity (NICS(0) = −7.9 ppm).[30] The triple-bond motif adds the possibility of either extending the phase shift in the orbital basis (tending toward a 2π-twisted system) or augmenting the 4n π-electron count, either of which on its own would tend to reduce the association between half-twist Möbius character and the 4n electron selection rule. The phenomenon certainly deserves further exploration.

4.1. Synthesis and Properties of a Möbius Cycloalkene

All the above studies were predominantly theoretical, and no direct test against experimental structure data was available for comparison. The first synthesis of a putative Möbius annulene, which would enable the predictions to be subjected to experimental scrutiny, was accomplished in 2003.[31] Herges' strategy was to construct a system based on transoid-alkene-induced twisting of a benzo-substituted [16]-annulene, **5**. The challenge faced was immense; [16]annulene itself in solution is thought to be an equilibrium mixture of many conformations,[32] which are known to rapidly interconvert at temperatures as low as −150 °C. It was also desirable, if possible, to achieve concomitant isolation of a non-Möbius form, for example, **6**, to define a reference point for subsequent comparison of the measured and calculated properties.



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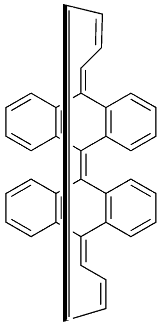

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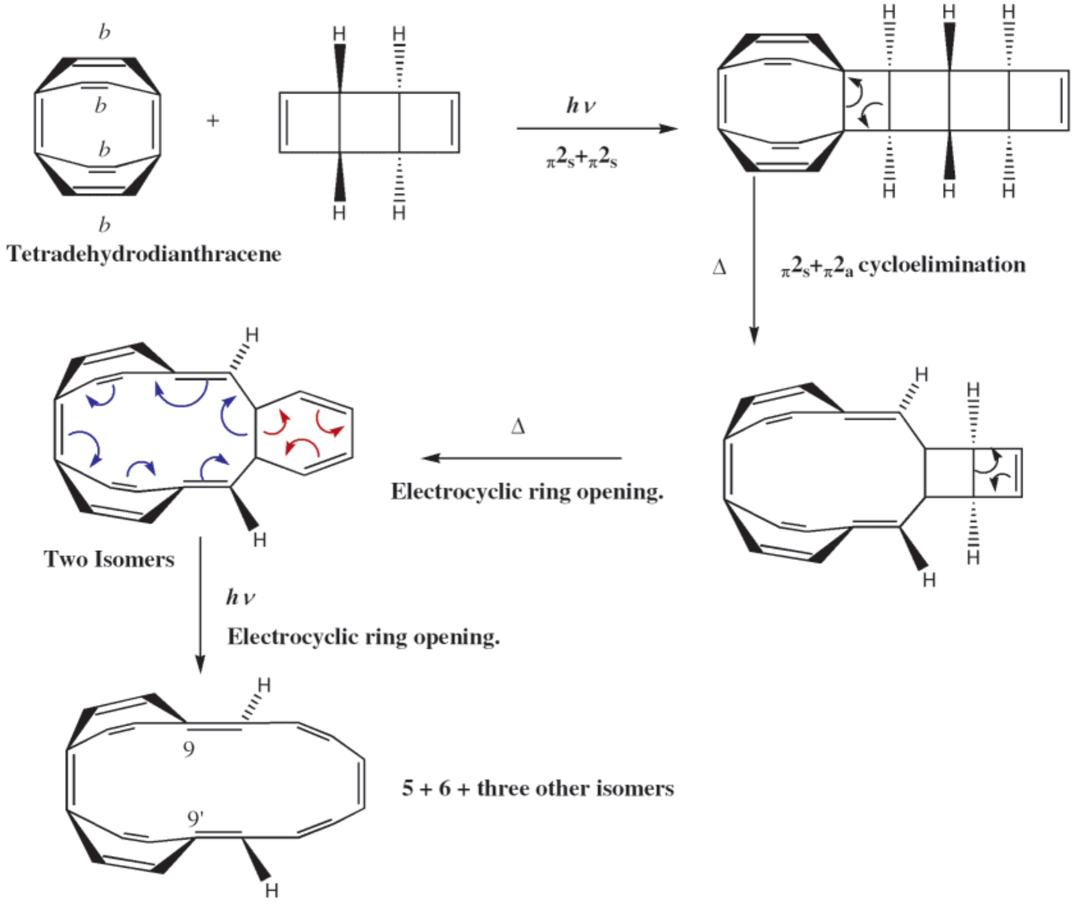
The solution was a synthetic strategy that involved introducing ring strain early via a tetrahydrodianthancene ring and then expanding this ring with a sequence of pericyclic ring metatheses and ring opening reactions (Scheme 1).

With the availability of crystal structure data for both **5** and **6**, the challenge was now one of disentangling those features arising from Möbius character from those due to, for example, ring strain or the perturbing influence of the four benzo substituents present.[34] It is worth noting at the outset that both **5** and **6** appear to be singlet (diatropic) closed shell species and that the discussion can be couched in terms of the thermal rather than the excited-state selection rules for electronic stability. The following arguments were presented by Herges et al.[31] in discussing the C_2 chiral isomer **5**.

1. The crystal structure allows one to determine whether the twist angles allow a significant degree of $p_\pi - p_\pi$ overlap (cf. ref 16). The CCCC dihedral angles in **5** (measured from the published X-ray structure and starting at C9 carbon, Scheme 1) were 4°, 168°, 0°, −35°, 2°, −35°, 0°, 168°, 131°, −5°, −108°, −4°, 108°, 4°, and −131°. While the twist is clearly not evenly distributed around the ring, the closest to π-orthogonality is 108°, a value that, it was argued, still allows "considerable" cyclic conjugation (in the Heilbronner sense). This approach however is only meaningful when sp^2 hybridization is adopted by all the atoms, and several of the atom centers in **5** are nevertheless significantly pyramidalized.

Scheme 1. The Synthetic Strategy[31] for the Synthesis of a Möbius Annulene[a]



[a] Bonds marked with a *b* bear benzo groups, omitted for clarity. Reaction arrows shown in either blue or red represent two electron counting alternatives.

2. The aromatic stabilization energy (ASE) computed by the indene/isoindene approach[8c] is based on retaining or disrupting conjugation in an aromatic system by fusing five-membered ring appendages in one of two distinct ways to afford an indene-like or an isoindene-like system. This method gave an uncorrected stabilization energy due to conjugation (ISE_{Π}) of 4.04 kcal mol^{-1} for **5** (20% of the value obtained for benzene) but a destabilization energy of -2.22 kcal $^{-1}$ for **6** commensurate with its anticipated Hückel antiaromaticity. This was taken to indicate that more efficient conjugation makes the former more stable, despite the latter having a slightly smaller ring strain.

3. HOMA (harmonic oscillator measure of aromaticity)[33] is a method of normalizing variation in bond lengths in terms of aromaticity. The availability of experimental structural parameters for the Hückel as well as the Möbius isomer enables HOMA indices (taken over all bonds, including the four benzo groups) for each system to be directly compared. The values of 0.35, 0.17, and 0.98 for **5**, **6**, and benzene, respectively, were taken by Herges et al.[31] as indications of a greater degree of aromaticity in **5** compared to **6**. Since it was recognized that the presence of four benzene rings may exert a significant perturbation on this index, HOMA values for just the nine bonds in the polyene bridge were also computed[31] for comparison. Values of 0.50 and 0.05 for **5** and **6**, respectively, appear to give a more distinct indication of the aromaticity of **5**.

The issue of the degree of aromaticity in **5** was then taken up by Castro, Karney, Schleyer, and co-workers from several viewpoints.[35] In essence, the question is whether the benzannelation of the [16]annulene dominates the structural effects, deriving from Clar's view[34] that the aromatic sextet in a benzene ring should not be viewed as being easily shared with adjacent rings or as contributing to the aromaticity of those rings. Thus the dominant valence-bond structure shown in **5** reflects the bond lengths obtained from the crystal structure and reveals the presence of four Clar aromatic sextets. This concept is reflected in the HOMA values for the nine-bond polyene bridge noted above, which, Castro et al. argue, suggests that the stabilization of **5** relative to **6** is confined just to that region and is not intrinsic to the delocalized π circuit (i.e., indicative of true cyclic electronic delocalization). The major conclusion from this analysis is that benzannelation will destroy the aromaticity of a Möbius aromatic system, just as it does for a Hückel aromatic system.

Castro et al. also presented a reinterpretation of several of the other points made by Herges et al. They noted that several of the dihedral angles in **5**, particularly the values of 108° and 131°, deviate by 50°−70° from maximum $p_\pi - p_\pi$ overlap, being substantially more than the rotations of around 30° they had themselves computed for a Möbius conformation of [16]annulene itself[28] (see also Figure 8). It is worth reiterating Heilbronner's assumption that maximum electronic stability will be achieved in a Möbius annulene only if the loss of overlap due to the phase shift is evenly distributed (delocalized) around the ring. However, as Schleyer and co-workers have demonstrated for [18]annulene,[20] some degree of bond length alternation along the σ framework of the molecule ($\Delta r_{\mathrm{C-C}} \leq 0.1$ Å) does not necessarily preclude strong aromaticity within the π cycle.

The HOMA analysis presented by Herges et al is also not entirely free of ambiguity. Castro et al.[35] computed a bond path following just the 16-bond annulene core, which specifically excluded the additional bonds in the benzo (Clar) groups, and found a value (-0.02), which they suggest cannot support delocalization of the annulene core of **5**, given that a HOMA value equal to 0 represents a nonaromatic, Kekulé-type structure.

In regard to the ISE_π values, Castro et al. noted that this method had been developed based on specifically planar systems and that extension to significantly pyramidalized or indeed Möbius systems was as yet untested. Normalized per carbon, they argued that an aromatic stabilization energy (ASE) derived using the ISE_{Π} approach of 0.25 kcal mol^{-1} per π electron for **5** was in fact insignificant compared to the value for benzene of 5 kcal mol^{-1} and further that the computed value for **5** was due to effects confined to the polyene bridge rather than to that of the entire ring. Further corrections for an S-cis/s-trans effect were found to reduce the total ASE for **5** to 0.6 kcal mol^{-1}, indicating that the molecule is neither stabilized nor destabilized by delocalization.

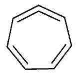
Castro et al.[35] also carefully evaluated several magnetic criteria. The exaltation Λ in diamagnetic susceptibility χ_{tot} calculated using the incremental approach[24] gave a value of -30.0 cgs·ppm for **5** (which is comparable to that of, for example, naphthalene). Arguing that this value is dominated by the four benzene (Clar) rings, a more realistic value corrected for this effect of $+19.6$ cgs·ppm was obtained for the [16]annulene constituent. Such a positive value is normally considered more typical of an anti-aromatic species (Table 1). Acknowledging the difficulty in evaluating Λ for molecules with this degree of complexity, they argued that this result provided no evidence of delocalization of the central annulene ring. The NICS(0) value computed for **5** (-3.4 ppm) is also not typical of strong aromaticity, which they suggested had been significantly attenuated by the "Clar aromatic hextet effect"[34] of localizing the aromaticity into predominantly the four benzo groups.

It is apparent from the above discussion that separating the effects due to pure Möbius-derived aromaticity from the overall properties of **5** is nontrivial. What is clearly evident from the above discussion is the importance of having available further synthetically sourced and characterized molecules where the interplay between experiment and theory can be explored.

4.2. Möbius Systems Derived from Allenes

Introduction of a four-electron allene unit as an alternative to a trans alkene for inducing a phase shift into the p orbital basis has been proposed.[36] In an unstrained environment, the two $p_\pi - p_\pi$ interactions in allene are of course perfectly orthogonal.

Spliced into, for example, benzene to replace a single C=C unit, the resulting seven-membered ring allene, **7**, is twisted, and the orthogonality between the two double bonds is removed, potentially allowing formation of an eight-electron ($4n$) system with some measure of Möbius character.[36] An orbital diagram correlating **7** with the planar $4n + 2$ π-aromatic carbene **8** revealed the origin of the Möbius orbitals, as well as highlighting artifacts introduced from mixing with the undesirable CH σ-manifold.[37] This contamination was projected out using perfluorination, and the result was a computed increase in the (FCCF) twisting around the ring, small bond alternation (Δr_{C-C} = 0.051 Å), and (by reducing the σ paratropic contributions to the ring current) a strongly negative (diatropic) NICS(0) value of -13.2 ppm. Such injection of a C=C=C unit into a variety of carbo and heterocyclic systems failed to identify any more prominently Möbius aromatic systems, as judged from the computed NICS(0) values.



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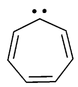

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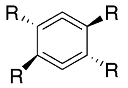

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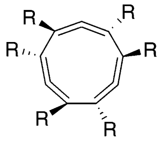

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The allene unit can also be used multiple times in the same ring. The system constructed from two such units in which the twists reinforce (**9**) shows a strongly paratropic NICS(0) value (+23.3 ppm) and highly localized bond lengths (Δr_{C-C} = 0.178 Å) indicative of what could be regarded as Möbius antiaromatic character.[37] The Möbius characteristics are nevertheless revealed by the HOMO and LUMO (Figure 9), both of which have a clear intersecting ring motif but have opposing chirality with respect to the nuclei. One possible reconciliation of these properties is that **9** is in fact a paradromic Möbius ring with a double twist in the orbital topology, but which as a $4n$ π closed shell system may be predicted as having anti-aromatic rather than aromatic character.

In contrast to **9**, the D_3-symmetric ring formed from three C=C=C units (**10**) bears a modestly diatropic ring current (NICS(0) = -9.9 ppm) and the (degenerate) HOMO manifests Möbius topology (Figure 9). The figure also shows the lowest energy unoccupied orbital for **10** showing the higher nodal properties of Möbius orbitals. Although not discussed in the original report,[37] it is presently suggested that the analogy with **7** and **9** implies that **10** might be regarded as a paradromic ring with a triple twist in the orbital topology, inferred again to be aromatic as a $4n$ electron system. Species **10** is also of interest in regard to its interaction with transition metals,[38] reportedly being predicted to result in a molecule in which the Möbius character evolves into an aromatic unit in which the metal center plays a key role. A return to this theme will be made in section 8.

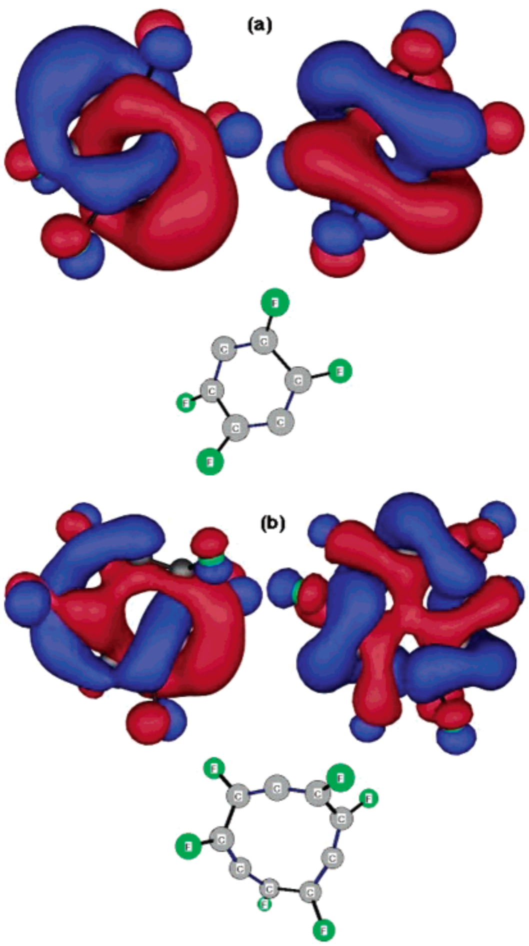
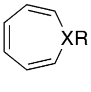


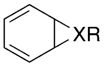
Figure 9. Calculated[37] molecular orbitals (B3LYP/6-31G-(d)) contoured at an isosurface value of 0.02 au for (a) **9**, R = F, showing the HOMO and LUMO and (b) **10**, R = F, showing the (degenerate) HOMO and the LUMO + 3.

5. Heterocyclic Möbius Annulenes

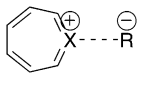
The preceding discussion centered around the grail-like hunt for a Heilbronner $4n$ annulene in which various subterfuges are used to induce a single phase shift in the conjugated AO basis and which was focused on the necessarily medium and larger ring sizes. An alternative approach is to look at smaller rings, for which a trans alkene bond may not be geometrically possible but where the Möbius effect may be manifested not so much in aromatic properties and delocalization but in more subtle and smaller geometric distortions. Thus the seven-ring heteropines **11** are a well-known class of $4n$ π electron heterocycles, existing in equilibrium with ring-closed isomers **12**. If **11**, X = N is constrained to planarity, the calculated bond lengths show considerable localization (Δr_{C-C} = 0.14 Å) and the NICS(0) value (+17.5 ppm) indicates paratropicity.[39] From this geometry, by following a distortion retaining only a C_2 axis of symmetry, a new lower energy valence-bond isomer was located. This form revealed a more delocalized pattern with a smaller degree of bond alternation (Δr_{C-C} = 0.10 Å) corresponding approximately to valence isomer **13**, which sustains a



11,



12, X=N,O,S,P



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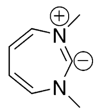

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modestly aromatic NICS(0) value of −6.6 ppm. As noted earlier for cation **2**, the C_2 distortion upon **11** has the effect of inverting the anti-aromaticity (paratropicity) into aromaticity (diatropicity).

If R is a halogen (F, Cl, etc.), then remarkably, the X−R bond ionizes as the twist is induced and the cationic residue now resembles a C=N=C allene-like component (cf. **13**), reminiscent of **7**. Changing the heteroatom from X = N to X = P in **13** enables the atom X to both sustain a covalent X−R bond and retain a degree of Möbius character, a property that appears *not* to be due[39] to any significant d-orbital participation from the phosphorus, which would have had the effect of localizing the phase shift to the node at X = P. As discussed in section 8, such localization would inhibit any C_2 nonplanar distortion of the ring. The moderate diatropicity (NICS(0) = −10.9 ppm) with X = P suggests a new Möbius initiator, the C=PX=C fragment, which is further explored below. The systems **13** were however predicted[39] to be relatively high in energy compared to **11** or **12**, and are hence unlikely to be easily detectable experimentally.

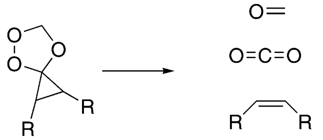
Possibly more viable synthetic targets are the diheterocyclic rings such as **14**.[26] Like **11**, they are [4*n*]heteroannulenes but with the additional functionality of being regarded as a C/carbene, to which, for example, metal coordination might be attempted. As with the planar forms of **2** and **11**, the planar form of **14** is calculated as being substantially paratropic with NICS(0) = +23.6 ppm and $\Delta r_{C-C} = 0.135$ Å. This planar geometry is a transition state, having a single negative calculated force constant, the vectors of which correspond specifically to a C_2 symmetric distortion. Following this mode results in a decrease in both the energy and the NICS(0). Ring substitution with F increases this trend, resulting in a twisted geometry associated with a noticeable *decrease* in the bond length alternation ($\Delta r_{C-C} = 0.134$ (H)/0.114 (F); NICS(0) = +1.2 ppm (F)). This particular system captures about halfway the evolution from a Hückel anti-aromatic ring to a more aromatic Möbius ring. To describe it merely as nonaromatic is to lose the subtle effects induced by the ring twist. The resulting asymmetric (chiral) ring was explored as an novel monodentate chiral C-ligand for metals such as palladium.[40]

6. Multicyclic Möbius Rings

Herges[41] introduced the concept of coarctate aromaticity in his transition state models for concerted peri-bicyclic reactions sustaining four forming/cleaving bonds at a single atom or group (e.g., **15**). He enumerated selection rules for such reactions in which 4*n* electron participation was presumed to proceed via a Möbius transition state involving tetrahedral geometry with a phase shift presumed localized at the coarctate atom.

The question arises: can such coarctate systems be identified for stable equilibrium species rather than just as transition states? To answer this, several apparently unrelated observations have to be united.

1. Schleyer and Wang[42] have proposed that a level of aromaticity and delocalization can be sustained across a P(V) atom in systems such as **16**.



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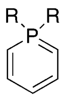

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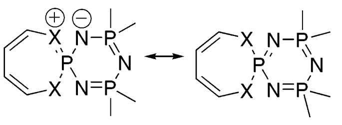
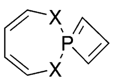


17, X=NR, O



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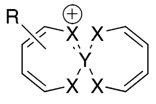
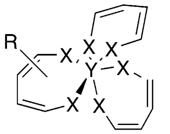
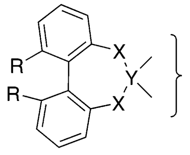


19, X=NR', O,S; Y=Ga, P, etc



20, X=NR',O,S; Y=Group III-V



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2. The suggestion noted above[39] that P(V) can sustain Möbius aromaticity in, for example, **13**, X−R = P−F, is reiterated.

3. The atom shown as C^- in **14** can be regarded as valence-isoelectronic with P.

Drawing these threads together led to the speculation[43] that systems such as **17** might sustain some measure of delocalization and hence Möbius aromaticity within one or more spiro-fused rings connected not as usual by a bond, but by a single atom. Such systems would be related to the coarctate transition states.[41]

Analogues of such systems turn out to be well characterized experimentally,[44] being related to the species **17** and **19**. Crystal structures[44] indicate that the seven-membered ring exhibits only C_2 symmetric deviation from planarity for both X = O and X = NR. The six-membered ring in **17** is however essentially entirely planar, and it apparently supports the conventional 4*n* + 2 Hückel mode of delocalization. From this, an inference might be drawn that the two ring systems are not cross-conjugated. The NICS(0) values for the seven-membered ring (**17**, X = O,NH) show significantly decreased paratropic values than those computed for **14**, one interpretation being that the Möbius distortion more strongly counteracts the Hückel 4*n* anti-aromaticity. Again, F-substitution reduces the paratropic σ magnetic contributions to this ring, and such substituted systems are distinctly diatropic with reduced bond length alternation (Δr_{C-C} = 0.087 Å). Species **18** is a variation on this theme, where two nominally 4*n* π electron rings are spiro-fused. In this example,[45] *both* rings reveal a prominent C_2 distortion and the NICS(0) values (−8.3 seven-ring/−16.2 four-ring, although the latter might be dominated by local magnetic effects) suggest each ring individually has some significant Möbius aromatic character. If this interpretation is sustained, then it implies that Möbius character might be exhibited even within ring sizes as small as four.

The spiro rings in these systems can also be homogeneous (**19**), and crystal structures for tris-spiro analogues (**20**) are also known.[44] These were calculated as for example, X = NF, Y = P, As, etc.,[45] and were described as exhibiting at least some degree of Möbius character. The form of the highest occupied MOs (Figure 9), in revealing eye/thread−thread/eye or eye/thread−eye/thread nodal motifs spanning the two or three rings is characteristic.[45]

Replacing the central main group V element (P, As) with the corresponding transition group V element (**20**, Y = V) is calculated[30] to produce a system in which the ring bond lengths show reduced alternation in all three C_2-twisted rings (Δr_{C-C} = 0.044 Å). The molecular orbitals indicate cross-conjugation across the rings (Figure 10), and the NICS(0) value at each separate ring centroid of −9.1 ppm is characteristic of aromaticity. With this last system, we have reached a point where there may be crossover and indeed mixing between the Heilbronner-like Möbius mode and one where the Craig motif plays a role (Figure 1 and section 8). Examples of mono, bi, and even tri-spirocyclic rings are known for various transition group IV and V metals with X = NR, O, or S,[46] but all these derive from diphenyl or naphthyl ligands as in **21**. Here the steric interactions between the R groups produce dihedral angles tending toward orthogonal at the Ar−Ar bond, resulting in relatively localized bonds. It may be that reducing this steric inhibition of conjugation could result in interesting new candidates for Möbius character.

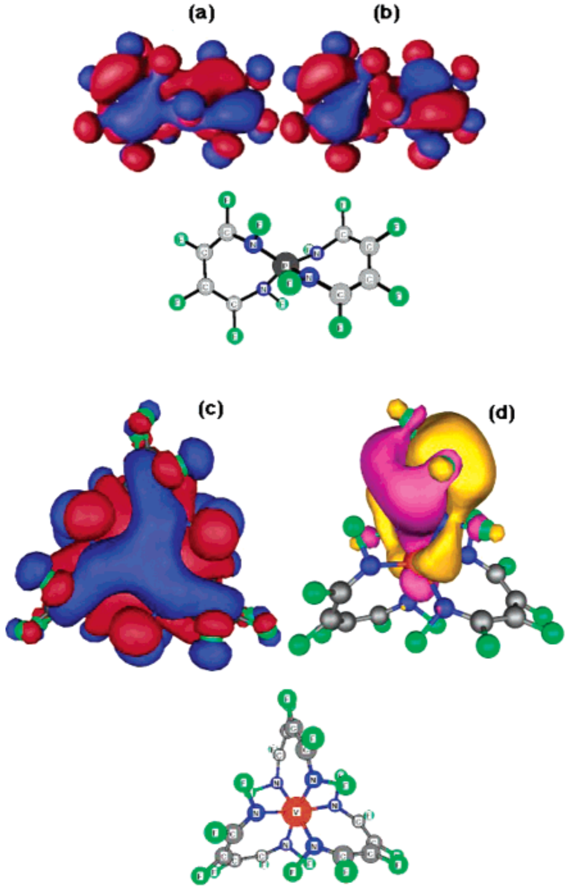
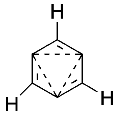


Figure 10. Calculated (6-31G(d))[45] molecular orbitals contoured at an isosurface value of 0.02 au for (a) HOMO of **19**, Y = P^+, X = NF, (b) HOMO − 1 of **19**, Y = P^+, X = NF, (c) HOMO − 8 for **20**, Y = V, X = NF, and (d) localized (Edmiston−Ruedenburg)[53] orbital for **20**, Y = V, X = NF.

7. Multiply/Doubly Aromatic Systems

Schleyer and co-workers introduced the concept of double aromaticity[47] deriving from additive contributions of orthogonal π and σ planes. The examples cited include the 3,5-dehydrophenyl cation **22**, cyclo[6]carbon, and the trefoil molecule **23** in which a 10π-aromatic is orthogonal to a 3-center 2σ in-plane aromatic[38,48] (and which happens to be isomeric with **10**). The same logic allows inference of double π/σ anti-aromaticity for, for example, singlet cyclo[12]carbon and of double π/σ *aromaticity* for a quintet state of the same species.[49] It was argued in this latter article that an orbital phase shift introduced into the double π/σ anti-aromatic unit of cyclo[12]carbon could in principle reduce the π/σ orthogonality by coupling the two 4n electron manifolds. Achieving this by introducing an allene π-Möbius “vector” (**25**) into cyclo[12]carbon and then computing the NICS(0) value appears to indicate elimination of the π anti-aromaticity, while leaving the σ anti-aromaticity more or less intact.[49] This now results in opposing aromatic and anti-aromatic character. These combine to give a system that by the NICS(0) measure (Table 1) is described as nonaromatic. No clear-cut examples have been reported of systems where π-Möbius and σ-Hückel aromaticities cooperate rather than oppose.



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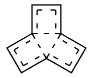

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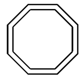

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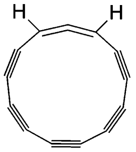

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Cyclo[8]carbon **24** itself is also noteworthy, because it illuminates the interpretation presented by Heilbronner (Figure 3). Thus as a planar singlet, **24** is first classically π anti-aromatic with double electron occupancy of one of the degenerate HOMO pairs, resulting in the expected Jahn−Teller induced alternation of bond length (Figure 11a). Despite this geometric distortion, this second-order stationary point still exhibits two further energy-lowering normal modes, as evidenced by the calculated force constants.[30] The first mode (Figure 11b) is an angular distortion in the σ framework[50] (ν = 762i cm^{-1}) reducing the energy by 27.4 kcal mol^{-1} but leaving the C−C bond length alternation still prominent (Δr_{C-C} from 0.195 to 0.122 Å). The second alternative distortion for **24** is an out-of-plane ring twist (cf.

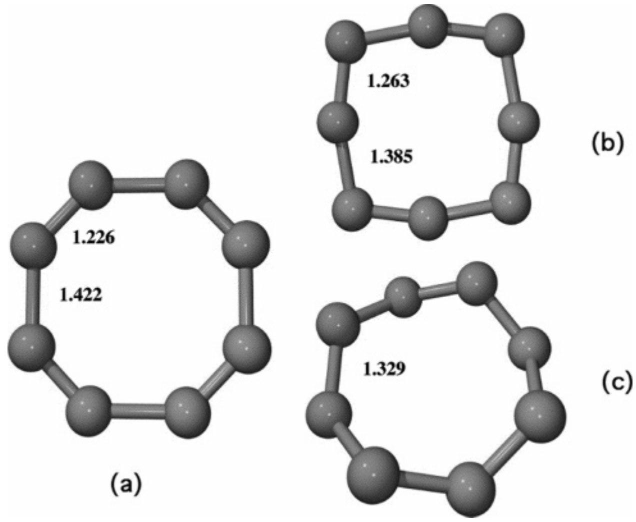


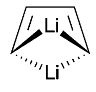
Figure 11. B3LYP/6-31G(d) geometry (Å)[30] for (a) planar cyclo[8]carbon, for which force constants predict an angular distortion to either (b) a planar form with angular distortions or (c) a π-ring-twist nonplanar form in which no bond length alternation occurs.

Figure 11c) occurring in the π framework ($\nu = 477i$ cm^{-1}), reducing the energy by 26.7 kcal mol^{-1} but now also equalizing the bond lengths ($\Delta r_{C-C} = 0.0$). This too leads to an energy minimum and is the result implied by Heilbronner. The NICS(0) value for this latter minimum is +11.0 ppm, a reduction from +42.6 for the planar system (Figure 11a). Because paratropic in-plane local effects can severely perturb the NICS(0) value, NICS(1) and NICS(2) values (being 1 and 2 Å above the plane of the ring) were also computed, having values of 7.3 and 3.3, respectively, again compared to 29.6 and 13.2 for the planar system. This appears to indicate that this particular distortion of the π-framework may result in induction of a degree of Möbius π-aromaticity, counterbalanced by retaining significant σ in-plane anti-aromaticity.

It becomes apparent from this brief discussion of systems exhibiting multiple forms of aromaticity that much remains to be discovered and understood about such hybrid systems.

8. Atom-Centered Möbius–Craig Systems

In this section, a return is made to Craig's suggestion[3] that introduction of a d-orbital into the p-orbital basis can provide a mechanism for introducing a phase shift. Kos and Schleyer[51] had proposed a molecule, **26**, in which the presence of a single Möbius-like phase shift might result in the stabilization of an otherwise Hückel anti-aromatic $4n-\pi$ system. Cyclic conjugation across dilithio-butadiene was assumed to be completed by formation of a metallacycle involving two bridging lithium atoms with the phase shift introduced via a d-orbital-like arrangement of the two unoccupied 2p lithium AOs as in **27** (cf. Figure 1). Such an arrangement of course results in localization of the phase shift at a specific center (with a resulting π antibonding interaction between the two Li atoms), rather than its delocalization throughout the ring as assumed in the Heilbronner model. Calculations[30] [B3LYP/6-31G(d)] in fact reveal that the Li–Li antibonding interaction, and by implication the cyclic Möbius interaction, is small with only a small (<1%) 2p AO contribution from the Li atoms to the carbon-centered π-HOMO, and no ring bond length equalization (predicted C–C lengths of 1.37 and 1.51 Å).



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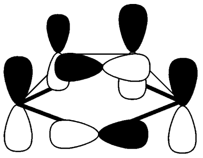

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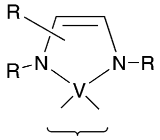

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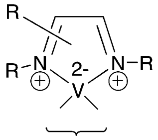

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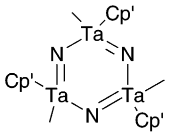

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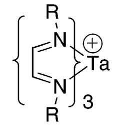

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Craig in his theoretical analysis[3] had focused on main group elements (S, P, etc.) for potential $p_\pi-d_\pi$ ring overlaps. However, the equivalent transition series elements (groups IV, V) in which the valence shell electronic configuration is (e.g., for V) $3d^3$,$4s^2$ are in practice more realistic candidates for such behavior. Indeed, it transpires that a series of group V (vanadium or tantalum) derivatives have been crystallographically characterized[52] that can provide valuable insight into this mode of bonding. Three of these systems are analyzed in more detail here.

The monometallacycle (**28/29**) appears to have the feature sought by Kos and Schleyer.[51] Such metallacycles are common to many important catalytic systems. One vanadium atom with a 3d AO of appropriate form replaces the two Li 2p AOs present in **26**. The authors of the original report of this species had in fact noted[52a] the near equality of the C–N and C–C ring bond lengths (1.375, 1.382 Å; $\Delta r = 0.007$ Å), although their explanation was that the effect originates from two equally probable valence-bond contributions differing in oxidation state of the metal (**28**, **29**). An explanation couched in terms of aromaticity is perhaps less familiar to inorganic chemists. The experimental bond length equality is supported by a model calculation (B3LYP density functional using the 6-31G(d) basis set), which predicts values of 1.370 and 1.372 Å, respectively.[30] Analysis of the bonding (Figure 12) reveals three doubly occupied $p_\pi-d_\pi$ orbitals, of which the most stable has the same nodal pattern as that found for **26**. Metallacycle **28/29** could therefore be regarded as a 6π delocalized system with 2π-occupancy of a $p_\pi-d_\pi$ Craig/Möbius orbital bearing a localized d_π phase shift at the metal atom. Unlike Heilbronner systems, such rings can fully retain planarity of the ring nuclei.

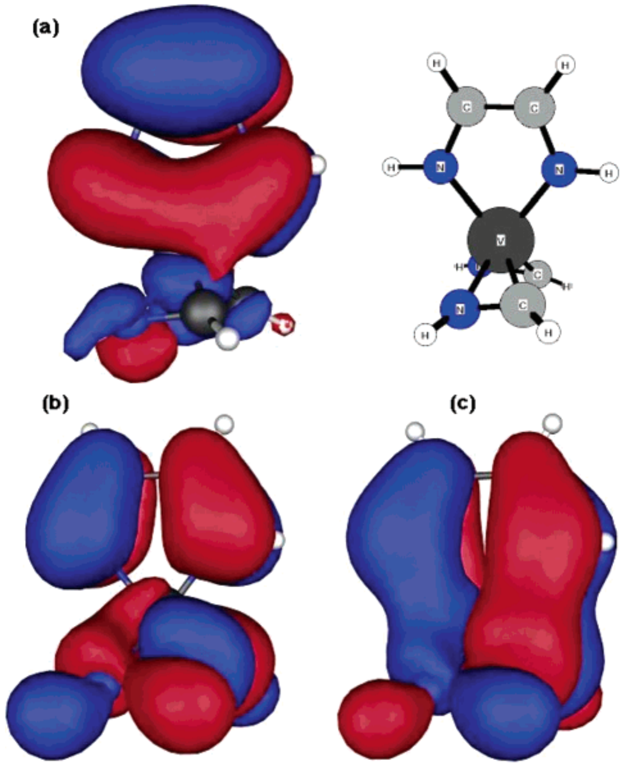


Figure 12. Calculated (B3LYP/6-31G(d)) molecular orbitals for reduced model for **28/29** contoured at an isosurface value of 0.02 au for the three π-like doubly occupied orbitals shown: (a) HOMO (orbital 41), (b) orbital 40, and (c) orbital 38.

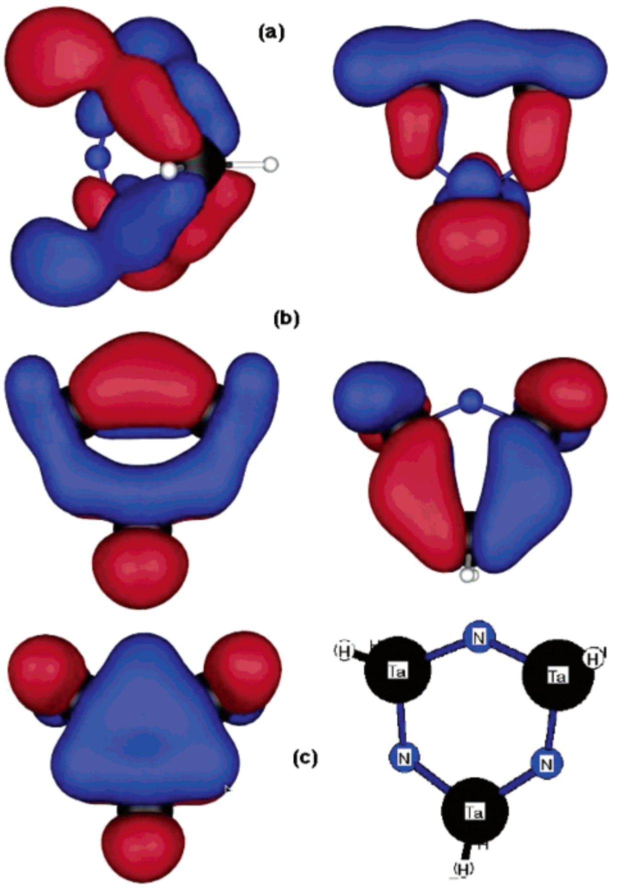


Figure 13. Calculated (B3LYP density functional and Stuttgart/Dresden SDD effective-core-potential basis set from Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta*, **1990**, *77*, 123−141 and represented as B3LYP/SDD[30]) $p_\pi - d_\pi$ molecular orbitals for reduced model of **30** for (a) the e-degenerate HOMO − 3, (b) the e-degenerate HOMO − 8, and (c) the HOMO − 10.

The known tantalum trimetallacycle **30**[52c] is more formally equivalent to the original Craig (AB)$_3$ pattern (Figure 1), and all six Ta−N bond lengths are approximately equal (1.885 Å). B3LYP/SDD calculation (of a model stripped of the Cp′ rings) reveals six equal ring bonds (1.899 Å) and five occupied $p_\pi - d_\pi$ MOs as a $1a + 2e + 2e$ pattern, Figure 13. Formally at least, this constitutes a rare example of a 10π aromatic cycle in a six-membered ring with 4π-occupancy of $p_\pi - d_\pi$ Craig/Möbius orbitals (and 6π-occupancy of Hückel orbitals).

Finally in this series, the related tantalum-centered metallatricycle **31** is considered. This too has been structurally characterized[52b] revealing similar bond lengths indicative of significant electronic delocalization, manifesting across all three rings (averaged C−C 1.37, C−N 1.34 Å; calculated at the B3LYP/SDD level C−C 1.398, C−N 1.372 Å). The rings themselves are twisted with respect to the metal axis to form a chiral propeller-like species with approximate D_3 symmetry. A total of 16 electrons occupy 8 orbitals with $d_\pi - p_\pi$ or $p_\pi - p_\pi$ character. The corresponding eigenvalues bear a $1a + 2e + 1a + 2e + 2e$ pattern. The degenerate HOMO-2 and the HOMO-4 (Figure 14) reveal delocalization over all three rings with an orbital phase shift radiating from the metal atom and including contributions from the twisting of each individual five-membered ring. Localized orbitals[53] reveal a grouping of 12 electrons in the N−C−C regions of the three rings (four per ring) with the four remaining electrons occupying two orbitals, which remain delocalized across two or more rings and the metal atom. Such “delocalization” of localized orbitals was also a reported characteristic for a metallocomplex originating from **10**,[38] being another metal-centered system bearing a 16e aromatic core.

With **31**, therefore, the Craig/Möbius molecular orbitals reveal delocalization encompassing three ring systems and the metal center and passing continuously from the top surface of one ring to the bottom surface of the next ring in a conjoined manner. Such a “Siamese” (or it could be termed a “trinacrian”) twist was noted previously for the molecular orbitals of **20**, which is actually the higher ring homologue of **31** extended with one additional C═C bond. Combining as it does Heilbronner, Craig, and Herges[41] motifs for introducing a phase shift into the orbital basis, **31** appears to be an unusual example of a delocalized, chiral, and unconventional aromatic species. Change in the degree of relative ring inclination (using perhaps steric effects induced by large substituents) might provide a mechanism for varying the degree of overall phase shift in the AO basis and hence a mechanism for tuning Möbius character.

9. Nuclear and Magnetic Möbius Bands

On the macro/mesoscopic scale, the inorganic conductor $NbSe_3$ has been reported[54] as forming tiny

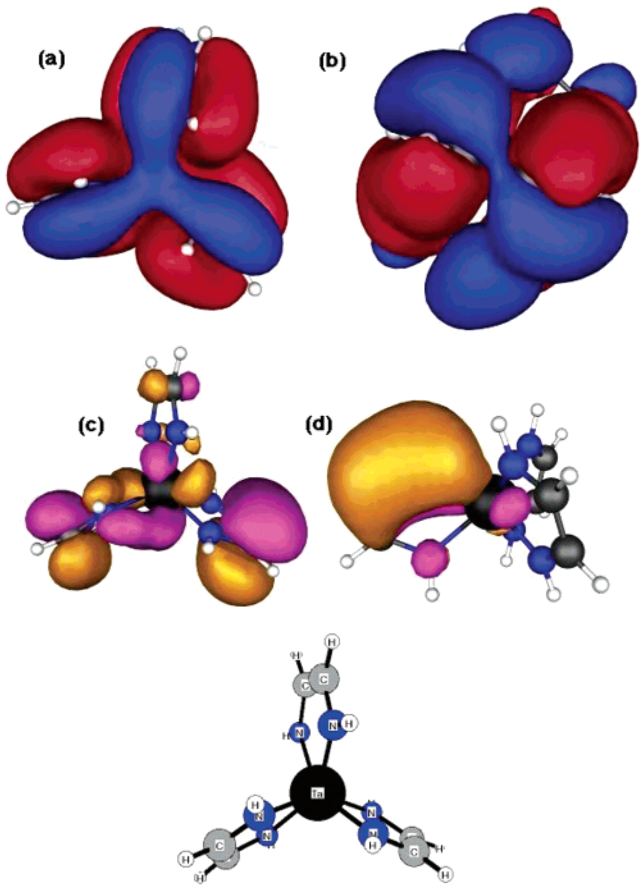


Figure 14. Calculated (B3LYP/SDD[30]) Möbius molecular and localized (Edmiston−Ruedenberg[53]) orbitals for model of **31** for (a) HOMO − 2 (e-degenerate), (b) HOMO − 4, (c) one of two localized orbitals spanning two rings and the metal, and (d) one of six localized orbitals spanning the N−C−C regions.

crystals that take the form of both single and double-twist Möbius strips. It is suggested that "our crystal forms offer a new route to exploring topological effects in quantum mechanics as well as to the construction of new devices". Another mesoscopic model, comprising the well-defined molecular unit $[(C_6H_{11})_2NH_2][Cr_7(VO)_2F_9(O_2CCMe_3)_{17}]$, was described[55] as a nanonuclear wheel of Cr atoms containing a diamagnetic ground state (Figure 15). The odd number of spins present in this species makes it impossible for all spins to align antiparallel to their nearest neighbor. Not all the antiferromagnetic interactions can be simultaneously satisfied, resulting in spin-frustration. The region where the neighboring spins are alternately up and down corresponds to the flat region of a Möbius strip, while a knot occurs between the nearest neighbors where the frustrated spins cannot be arranged antiparallel. The knot is very much analogous to the arrangement of p-AOs shown in Figure 2 and hence constitutes a magnetic equivalent to the Heilbronner model.

The first molecular-scale Möbius band, synthesized in 1982 by Walba and co-workers,[56] was constructed by cyclizing **32**, a system of (unconjugated) polyether chains connected by three alkene bonds. This product was demonstrated to be a racemic mixture of two chiral enantiomers, unlike the non-Möbius isomeric cylinder also produced by this reaction. The choice of three connecting "rungs" in the Möbius ladder was a fortunate one; Flapan[57] has shown that only ladders with an odd number of rungs are topologically chiral, while those with an even number are not. Other nuclear Möbius topologies such as trefoil knots[58] have also been synthesized, and an enzyme containing such a knot has been identified.[59] These examples however do not contain contiguous electronic conjugation around the single edge.

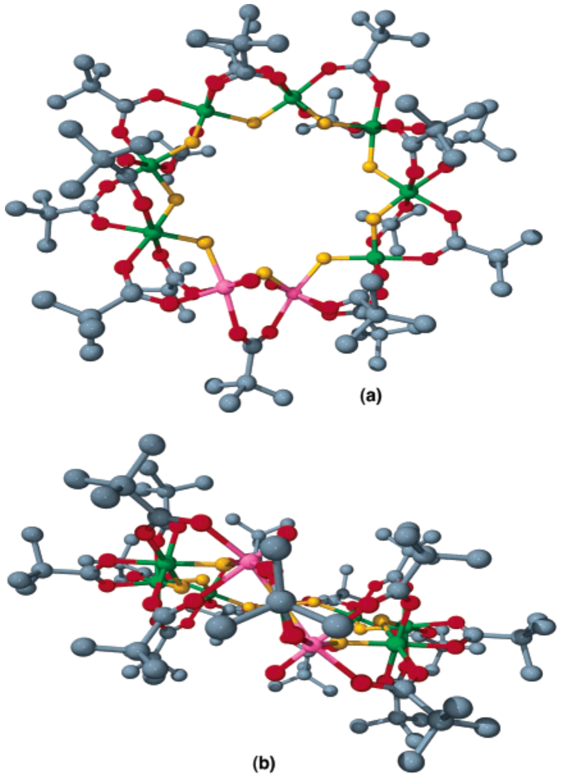
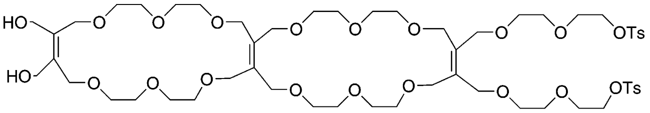


Figure 15. Nanonuclear wheel of Cr and V atoms, in which the anti-ferromagnetic spins comprise a nuclear magnetic Möbius band, shown as two views: (a) top and (b) along the C_2 axis. The hydrogens are omitted for clarity; green = Cr; pink = V; yellow = F; red = O.

Conjugated and delocalized Möbius frameworks could be formed from molecular equivalents to **32**, such as the belt-like cyclacenes **33**. The appropriate larger cyclacenes are as yet unsynthesized, so what follows represents speculation based on quantitative modeling. Connecting the ends of such a strip with one or more prior twists would represent a close molecular analogy to the mathematical definition of a Möbius/paradromic band. Turker[60] was the first to investigate this at a theoretical level using semiempirical molecular orbital methods. The intention was



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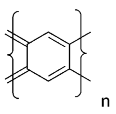

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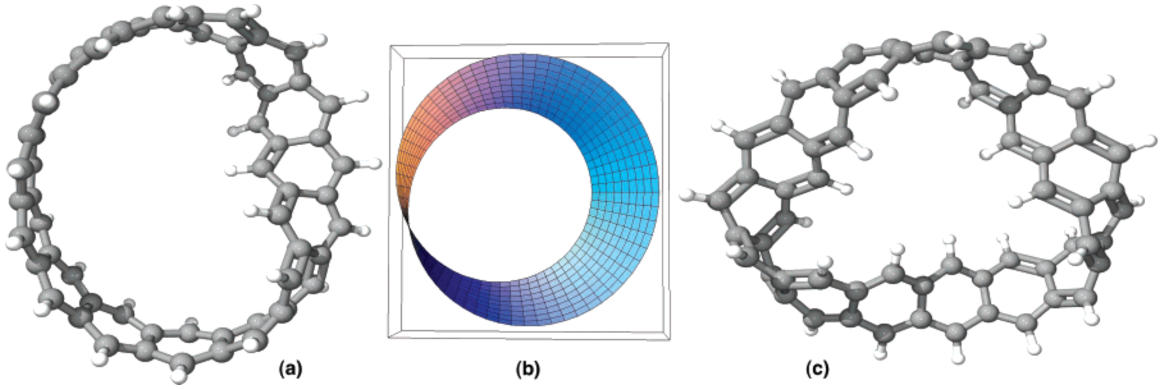

Figure 16. (a) Molecular Möbius band constructed from a cyclacene bearing a single twist compared with (b) a mathematically idealized Möbius band. The two bands have the same absolute configuration (chirality). The C_2 axis is horizontal. Panel c shows the cyclacene bearing a 3-fold twist.

to probe the relationship between the conjugation and delocalization of the edge of such strips and the Hückel $4n + 2$ electron rule.[4] Its relevance to cyclacene bands is that an untwisted system would have two separate edges bound by the $4n + 2$ rule, whereas the introduction of a single twist to form a Möbius band would result in only a single edge. Turker investigated whether any particular stability/instability was associated with the presence of conjugated electrons along the edge of such cyclacene bands. However, to overcome the angular strain induced by taking an intrinsically planar−linear system and closing the band, relatively large cyclacenes have to be chosen. As shown by others (for [18]annulene,[20] for example), the superposition of complex effects such as electron correlation and steric interactions for systems where n is large (≥4) may effectively mask any such effects.

What did become apparent from the calculated geometries of these systems[60] is that the twist was not evenly distributed around the band (Figure 16).[61] Instead, it tended to localize in the region of 3−4 cyclacene benzo units, a result that was not strongly dependent on the ring size or on the particular Hamiltonian used to compute the geometry. This localization was also associated with the C_2 axis of symmetry present in the system, and as with **1**, the molecule is dissymmetric (i.e., capable of existing as enantiomers). For such hydrocarbon-based cyclacenes, the C_2 symmetry axis could potentially travel around the band in a manner reminiscent of a phonon, very probably with a finite energy barrier for doing so, but for which no estimates currently exist. It was even suggested that if the region containing the C_2 axis were to be associated with a different charge distribution compared to less twisted regions, the dynamic rotation of this axis if placed in a magnetic field might represent an interesting molecular variation on nuclear magnetic resonance! Doubly and triply twisted paradromic rings, applied to the same C_{60} cyclacene, revealed unusual regions of both bond localization and delocalization around the (single) C−C cyclacene edge.[61]

Other cyclacene systems have been proposed as being capable of sustaining Möbius isomers. Dobrowolski[62] has taken belts based on nonlinear hexacenes and cut-half-twist-joined them into a variety of Möbius (M) conformations. The M-isomer of coronene, for example, although some 231 kcal mol^{-1} above coronene itself, was proposed as the most likely candidate for future synthesis.

10. Summary

Ample evidence, albeit until recently almost entirely theoretical in origin, has emerged in the past few years to support Heilbronner's prediction of a counterpart to delocalized and planar Hückel aromatic rings, which instead exhibits Möbius topology. The focus in chemistry has been on rings formed by a half-twist. Higher order twisted systems, known as paradromic rings to topologists, but arguably better named as Listing rings, are proposed here as interesting candidates for future study. Molecules sustaining Möbius electronic conjugation are important because of their intrinsically chiral nature; other properties unique to what is now increasingly recognized as a distinct aromatic mode have also emerged. In particular, electronic delocalization in such systems may manifest itself not only in typically "aromatic" bond lengths (Table 1) but also in the degree of delocalization of the 180° phase shift in the orbital topology. The most idealized half-twist Möbius aromatic annulenes include a hypothetical chiral conformation of a $4n\pi$ [16]annulene,[28] a cationic [9]-annulene ($C_9H_9^+$), the $(4n + 2)\pi$ triplet state of an anionic perfluorinated annulene ($C_9F_9^-$),[26] and a [12]-annulene transition state for ring configuration change.[16] The delocalized Möbius π molecular orbitals of selected systems show a characteristic intersecting ring pattern.

The first (of potentially many) Möbius π-systems has now been successfully subjected to a rational synthesis, enabling for the first time direct comparison between experiment and theory. Such analysis shows that the [16]annulene core of this system may not clearly meet the aromaticity criteria outlined in Table 1; it appears as if fusing benzene rings to Möbius aromatic annulenes will greatly diminish their aromaticity. This is in keeping with the Clar concept developed from the analysis of a large body of benzannelated Hückel systems.[63] Thus chemists working to synthesize a Möbius aromatic compound will need to use non-benzenoid systems to anchor the molecule into an appropriate Möbius conformation.

It has also become clear that there must be a geometric continuum between planar Hückel anti-aromatic cycles and half-twisted Möbius cycles, and hence between systems that are clearly dominated by Möbius aromaticity and those where Möbius stabilization merely exerts a distortive perturbation upon the geometry and magnetic properties. Candidates for a separate class of molecule containing a 180° phase shift localized at a metal (more generally a d-orbital) center that do not exhibit chiral symmetry have also been identified. There are tantalizing hints that stabilization via Möbius delocalization may contribute to the conformations of spiro-bicyclic and tricyclic metallacycles and that extension of Möbius conjugation from two to three dimensions across single atom centers might be sustainable. It also seems worth exploring the combination of Möbius aromatic character with σ in-plane forms to produce multiply aromatic molecules.

Because of the chiral nonplanar symmetry of Möbius rings compared to the planar Hückel systems, reliable quantitative measures of their properties and the relative contributions of the π and σ electronic frameworks remain to be developed. In particular, better methodologies for estimating the degree of twist delocalization and the total twist in the electronic topology and for analyzing the molecular orbitals are needed. As yet largely unexplored is whether delocalized Möbius systems are capable of sustaining characteristic patterns of reactivity with selection rules for electrophilic or nucleophilic substitution, for example. For this area to develop, further syntheses and experimental study of stable Möbius molecules will be needed.

11. Supporting Information Available

Molecular coordinates (in CML format and viewed using the Jmol applet), normal mode vibrational coordinates (in XYZ format), and 3D molecular orbital models (in 3DMF format) are available, annotated where appropriate with InChI (International Chemical Identifiers). This material (Copyright 2005 Henry Rzepa) is available free of charge as OpenData via the Internet at http://pubs.acs.org.

12. References

(1) For historical background, see Derbyshire, J. *Prime Obsession: Bernhard Riemann and the Greatest Unsolved Problem in Mathematics*; Penguin: New York, 2004; p 381. Möbius bands are best illustrated as 3D rotatable models. For such, see, for example, http://mathworld.wolfram.com/MoebiusStrip.html and http://mathworld.wolfram.com/TrefoilKnot.html.

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