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A Hückel Theory Perspective on Möbius Aromaticity

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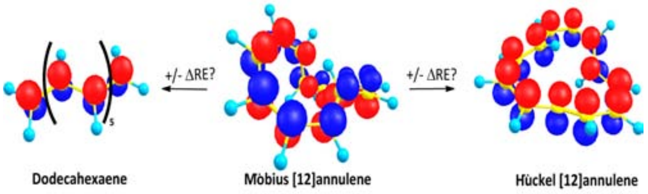
ABSTRACT



Do Mobius 4n-π annulenes have appreciable π resonance energies (RE)?

Heilbronner's Hückel molecular orbital treatment of Möbius 4n−π annulenes is revisited. When uneven twisting in π-systems of small Möbius rings is accounted for, their resonance energies become comparable to iso-π-electronic linear alkenes with the same number of carbon atoms. Larger Möbius rings distribute π-twisting more evenly but exhibit only modest aromatic stabilization. Dissected nucleus independent chemical shifts (NICS), based on the LMO (localized molecular orbital)−NICS(0)$_\pi$ index confirm the magnetic aromaticity of the Möbius annulenes considered.

In 1964, Edgar Heilbronner demonstrated that a model basis for a 4n π-electron annulene, consisting of a planar cyclic array of atomic p orbitals, could accommodate an evenly distributed 180° twist without a loss in π-electron energy.[1a] Remarkably, he found that the normal Hückel rule was reversed for these twisted annulenes, with 4n π-electron species being closed shell and 4n + 2 species open shell. Heilbronner inscribed an unsigned[1b] representation of the twisted p orbital basis onto a Möbius strip and referred to these twisted species as "Möbius-type" annulenes. The term "Möbius aromaticity" was coined shortly afterward,[2] but further interest in the Möbius concept lay mostly dormant until 1998.[3]

Today interest in the Möbius aromaticity of 4n−π annulenes exhibiting a half twist in their π-system widespread.[4,5] Many such species have been characterized computationally,[6,7] but their experimental detection has been problematic. A Möbius conformation of the [9]annulene cation was postulated to exist as a short-lived intermediate upon solvolysis of *exo*-9-chlorobicylco[6.1.0]nona-2,4,6-triene and 9-chlorocyclononatetraene,[3] but recent evidence indicates a Hückel (untwisted) structure is more likely.[8] Herges et al. reported synthesis of the first Möbius annulene in 2006,[9] but its aromaticity has been contested.[10]

Ab initio computations on the neutral 4n−π [12]-, [16]-, and [20]annulenes suggest that their lowest lying Hückel conformers are all more stable than any Möbius topology.[6a]

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[1] (a) Heillbronner, E. *Tetrahedron Lett.* **1964**, 1923–1928. (b) Note, however, that Heilbronner's derivation of the rules for Möbius aromaticity necessarily included signed p AOs.

[2] Zimmerman, H. E. *Acc. Chem. Res.* **1971**, *4*, 272–280.

[3] (a) Mauksch, M.; Gogonea, V.; Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2395–2397. (b) Heilbronner's witty reaction to this paper, including his account of the genesis of the Möbius concept, is given in the Supporting Information.

[4] Rzepa, H. S. *Chem. Rev.* **2005**, *105*, 3697–3715.

[5] Herges, R. *Chem. Rev.* **2006**, *106*, 4820–4842.

[6] (a) Castro, C.; Isborn, C. M.; Karney, W. L.; Mauksch, M.; Schleyer, P.v.R. *Org. Lett.* **2002**, *4*, 3413–3434. (b) Mauksch, M.; Tsogoeva, S. B. *Chem.—Eur. J.* **2010**, *16*, 7843–7851. (c) Zhu, C.; Li, S.; Luo, M.; Zhou, X.; Niu, Y.; Lin, M.; Zhu, J.; Cao, Z.; Lu, X.; Wen, T.; Xie, Z.; Schleyer, P. v. R.; Xia, H. *Nature Chem.* **2013**10.1038/NCHEM.1690.

[7] Mucke, E.-K.; Schönborn, B.; Köhler, F.; Herges, R. *J. Org. Chem.* **2011**, *76*, 35–41.

[8] Bucher, G.; Grimme, S.; Huenerbein, R.; Auer, A. A.; Mucke, E.; Kohler, F.; Siegwarth, J.; Herges, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9971–9974.

[9] Ajami, D.; Hess, K.; Köhler, F.; Nather, C.; Oeckler, O.; Simon, A.; Tamamoto, C.; Okamoto, Y.; Herges, R. *Chem.—Eur. J.* **2006**, *12*, 5434–5445.

[10] Castro, C.; Chen, Z.; Wannere, C. S.; Jiao, H.; Karney, W. L.; Mauksch, M.; Puchta, R.; Hommes, N. J. R. v. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2005**, *127*, 2425–2432.

10.1021/ol401491s

Moreover, these species exhibit small barriers to *cis*−*trans* isomerization;[11] hence, experimental isolation of neutral Möbius annulenes seems unlikely. Möbius conformations of a few annulene cations are believed to exist as global minima, but most undergo fast exothermic electrocyclization,[7] and none have been observed experimentally.

The difficulties in detecting Möbius aromatic annulenes may seem surprising since aromaticity is often associated with stability. Literature evaluations of Möbius annulene aromaticities have been based mainly on geometric and magnetic criteria, and the thermal and kinetic instability of these systems attributed to ring strain. But do "medium sized" Möbius [*n*]annulenes with 8, 12, 16, and 20 carbons benefit from aromatic stabilization? According to Heilbronner's simple Hückel molecular orbital (HMO) treatment, Hückel and Möbius conformations of $4n-\pi$ annulenes have the same resonance energy (RE). Zimmerman's[2] qualitative explanation of this result is that the π-electrons in $4n-\pi$ annulenes experience the same total number of phase shifts in their MOs, irrespective of whether the p orbital basis has Hückel or Möbius topology. For example, the four lowest energy π-electrons in both Hückel and Möbius cyclooctatetraene experience a sum total of four nodes between them and the next four a total of 12 (See Figure 1). Hence, as the REs of medium-sized Hückel $4n-\pi$ annulenes exceed those of a linear polyene reference with the same number of carbon atoms and π electrons,[12] it seems closed shell Möbius conformations should be stabilized energetically by aromaticity.

Of course, Heilbronner's HMO treatment was very simplistic. In reality, Möbius annulenes are not planar, and their bending distortion into three dimensions, characterized by writhe (W_r), results in unequal twist angles between adjacent p orbitals, which need not sum to π. Instead, it is the linking number (L_k) that must sum to π for half-twisted Möbius systems,[13] where $L_k = T_w + W_r$, and T_w is the sum of local p AO torsional angles. Importantly, depending on the value of W_r, T_w may be either less or greater than π, which can significantly impact computed HMO REs of Möbius annulenes. Other important consequences of nonplanarity include $\sigma-\pi$ mixing (which results in $\sigma \rightarrow \pi^*$ hyperconjugation)[14] and varying degrees of bond length alternation.[15]

In addition, the highest symmetry that a Möbius annulene can attain is C_2,[5] which has no degenerate representations. Hence, the quasi-π MOs of Möbius annulenes do not occur in degenerate pairs. The 2-fold MO degeneracy given by Heilbronner's treatment is an artifact of assuming that the HMO resonance integrals (β), which represent the interaction energy between two adjacent p AOs, are equal for all pairs of p orbitals. In reality, two βs will generally only be equal if they are symmetry equivalent.[16] Moreover, Janneskens et al. have shown that interactions between nonadjacent p AOs, which are neglected in HMO theory, are also unequal for Möbius annulenes.[16] Hence, MO degeneracies are absent at the SCF level.

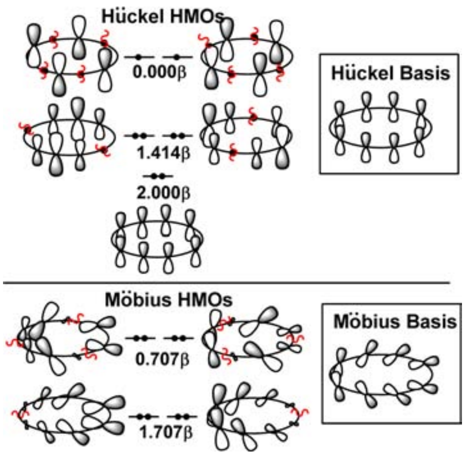

Figure 1. HMO bases and occupied symmetry orbitals for Hückel (top) and Möbius (bottom) cyclooctatetraene. Phase shifts are marked as red lines.

Despite its inherent simplicity, HMO theory's success in predicting the reversed rules for aromaticity in twisted $4n-\pi$ annulenes indicates its qualitative usefulness. Hence, an improved HMO treatment which takes explicit account for the nonuniform twist angles between each pair of adjacent p AOs may help explain the apparent lack of aromatic stabilization in medium sized Möbius annulenes.

To determine the twist angles between adjacent p orbitals in annulenes at the SCF level, we employ p-type natural hybrid orbitals (NHOs)[17] as our basis (see the Abstract Graphic for pictorial representations). NHOs are "natural" in the sense that they exhibit the maximum occupancy possible for an orthonormal set of localized sp^n and p-type hybrid basis orbitals. Hence, p NHOs conform as closely as possible to the HMO assumption that each carbon atom in a neutral annulene contributes one electron to the π-system via its p AO.[18a]

In a minimal basis, a twisted p NHO can be written as a linear combination of $2p_x$, $2p_y$, and $2p_z$ natural atomic orbitals (NAOs) as[18b]

$$\mathbf{h}_p = c_1 p_x + c_2 p_y + c_3 p_z \qquad (1)$$

where $\mathbf{h}_p$ is a twisted p orbital and c_{1-3} are its expansion coefficients in terms of untwisted $2p_x$, $2p_y$, and $2p_z$ NAOs. Since the "direction" of a Cartesian p NAO is that of a unit

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(11) Castro, C.; Karney, W. L. *J. Phys. Org. Chem.* **2012**, *25*, 612–619.

(12) Kutzelnigg, W. *J. Comput. Chem.* **2006**, *28*, 25–34.

(13) (a) Rappaport, S. M.; Rzepa, H. S. *J. Am. Chem. Soc.* **2008**, *130*, 7613–7619. (b) Wannere, C. S.; Rzepa, H. S.; Rinderspacher, C.; Ankan, P.; Allan, C. S. M.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Phys. Chem. A*. **2009**, *113*, 11619–11629.

(14) McKee, W. C.; Wu, J. I.; Hofmann, M.; Berndt, A.; Schleyer, P. v. R. *Org. Lett.* **2012**, *14*, 5712–5715.

(15) (a) Wannere, C. S.; Moran, D.; Allinger, N. L.; Hess, B. A., Jr.; Schaad, L. J.; Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 2983–2986. (b) Wannere, C. S.; Sattelmeyer, K. W.; Schaefer, H. F., III; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 4200–4206.

(16) Havenith, R. W. A.; Lenthe, J. H. v.; Janneskens, L. W. *Int. J. Quantum Chem.* **2001**, *85*, 52–60.

(17) Weinhold, F.; Landis, C. *Valency and Bonding, A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: Cambridge, 2005.

Table 1. Twist (T_w), Writhe (W_r), and HMO, NBO, and LMO−NICS$(0)_\pi$ π-Electron Delocalization Data for Selected Linear (*l*) and Cyclic Hückel (*h*) and Möbius (*m*) Polyenes

	C_8H_{10}	[8]annulene		$C_{12}H_{14}$	[12]annulene		$C_{16}H_{18}$	[16]annulene		$C_{20}H_{22}$	[20]annulene	
	l	*h*	*m*	*l*	*h*	*m*	*l*	*h*	*m*	*l*	*h*	*m*
HMO RE_1[a]	1.518β	1.657β	1.657β	2.592β	2.928β	2.928β	3.676β	4.109β	4.109β	4.763β	5.255β	5.255β
HMO RR_1[b]	1	1.092	1.092	1	1.130	1.130	1	1.118	1.118	1	1.103	1.103
HMO RE_2[c]	1.518β	1.125β	1.434β	2.592β	1.944β	2.495β	3.676β	3.497β	4.084β	4.763β	4.960β	5.103β
HMO RR_2[d]	1	0.741	0.945	1	0.750	0.963	1	0.951	1.111	1	1.041	1.071
avg θ[e]	0	18.41	17.33	0	19.18	15.88	0	9.97	9.73	0	6.31	8.29
std dev θ[f]	0	18.41	22.08	0	18.55	14.56	0	10.53	6.49	0	7.40	7.59
T_w[g]		0.000	−0.863		0.104	−1.462		0.000	−0.244		−0.007	−0.725
W_r[g]		0.000	−0.137		−0.104	0.462		0.000	−0.756		0.007	−0.275
NBO RR[h]	1	0.625	0.944	1	0.678	1.062	1	0.925	1.917	1	0.992	1.143
rel *E*[i]		0.00	+21.37		0.00	+4.16		0.00	+15.12		0.00	+6.75
NICS$(0)_\pi$[j]		−3.80	−9.87		+4.44	−11.08		+10.10	−11.73		+12.49	−9.00

[a] HMO RE_1 = HMO resonance energy (RE) for an evenly twisted (Heilbronner) p orbital basis. [b] HMO RR_1 = RE ratio, quotient of the RE of a species the RE a linear alkene with the same number of π-electrons and carbon atoms (using an evenly twisted p basis). [c] HMO RE_2 = HMO RE for an unevenly twisted p NHO basis (HF/6-31G*//B3LYP/6-311+G**). [d] HMO RR_2 = RE ratio for an unevenly twisted p NHO basis. [e] Avg θ = average of the unsigned p NHO twist angles (deg). [f] Standard deviation of the unsigned p NHO twist angles (deg). [g] Twist and writhe values (in units of π) are based on p NHO directional vectors and B3LYP/6-311+G** geometries. [h] NBO RR_2 = NBO π-electron RE ratio. [i] Rel *E* = relative electronic energy (kcal/mol) at B3LYP/6-311+G**. [j] LMO-NICS$(0)_\pi$ chemical shifts (ppm) (PW91/IGLOIII//B3LYP/6-311+G**).

vector pointing in its Cartesian direction (i.e., a p_z orbital is directed along the *z*-axis) the same coefficients in (1) also define the direction of a twisted p NHO as[17]

$$D(\mathbf{h}_p) = c_1x + c_2y + c_3z \qquad (2)$$

where $D(\mathbf{h}_p)$ is the direction of the p orbital and c_{1-3} its *x*, *y*, and *z* components. Once the directional vectors of all p NHOs are known, they can be placed on their respective carbon atoms, and the $D(\mathbf{h}_p)_i$-C_i-C_j-$D(\mathbf{h}_p)_j$ dihedral angle gives the twist angle (θ_{ij}) between the p orbitals on adjacent carbon atoms C_i and C_j. Substituting each θ_{ij} into the expression $\beta_{ij} = \cos(\theta_{ij})$ gives the resonance integrals between all adjacent p NHOs in a system, and the HMO REs of twisted annulenes can then be computed in the normal way.

We evaluated the p NHO twist angles T_w and W_r for Möbius and Hückel conformations of [8]-, [12]-, [16]-, and [20]annulene at the HF/6-31G*//B3LYP/6-311+G** level. The Möbius and Hückel geometries of [12]-, [16]-, and [20]annulene correspond to compounds **1**, **5**, **7**, **11**, **13**, and **14** in ref 6a. The Hückel structure of [8]annulene was taken to be tub-shaped D_{2d} cyclooctatetraene, and the Möbius conformer C_2 *cis*,*cis*,*cis*,*trans*-cyclooctatetraene from ref 16. All geometries were optimized at the B3LYP/6-311+G** level and are provided in the Supporting Information. We also computed the LMO−NICS$(0)_\pi$ magnetic metric of aromaticity[21] for each annulene at the PW91/IGLOIII // B3LYP/6-311+G**) level.

The HMO REs for an idealized Heilbronner basis (i.e., no p twisting for Hückel conformers and a constant 180°/*n* p orbital twist for Möbius [*n*]annulenes) and the unevenly twisted p NHO basis are tabulated in Table 1 as HMO RE_1 and HMO RE_2, respectively. The HMO REs of iso-π-electronic linear C_nH_{n+2} alkenes are also provided for comparison. For a neutral polyene with an even number of π-electrons, HMO REs are obtained by summing the energy of each π-electron to give the total π-electron energy of the system (Tπ-e) and then subtracting from this value *m* times the Tπ-e of ethylene, where *m* is the number of double bonds in the polyene. For example, the Tπ-e of benzene and ethylene are 8.00β and 2.00β, respectively, and the HMO RE of benzene is $8.00\beta - 3(2.00\beta) = 2.00\beta$.

The HMO parameter β carries units of energy; hence, in principle HMO REs in terms of β can be converted to more familiar energy units (e.g., kcal/mol). For example, if the RE of benzene is taken to be 60.0 kcal/mol, then $\beta = -30.0$ kcal/mol. In practice, however, the value of β depends on the theoretical method or thermodynamic equation used to evaluate the RE of a given system. Thus, in order to remove indeterminacies associated in the value of β, we define an HMO RE ratio (HMO RR) as the quotient of the HMO RE of a polyene with that of an iso-π-electronic linear polyalkene with the same number of carbon atoms. For example, the HMO RR of benzene is: (HMO RE[benzene])/(HMO RE [hexatriene]) = 2.02. It is evident from the definition of HMO RR that values greater than 1 indicate aromatic stabilization (i.e., energetic aromaticity), and values less than 1 antiaromatic destabilization.

The most striking feature of the HMO RR_1 values in Table 1 is that they are all nearly equal to 1. Hence, even under idealized Heilbronner-type assumptions, the REs of medium-sized Möbius and Hückel annulenes are nearly the same as those of their corresponding iso-π-electronic linear polyene. The HMO REs and RRs all decrease when uneven p twisting is accounted for (see HMO RE_2 and

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(18) (a) For our annulene set the average p NHO occupancies are ≥0.996e. (b) In a non-minimal basis p NAOs with higher quantum number *n* (e.g., 3p, etc.) have a negligible effect on the p NHO direction (see ref 17, pp 107−110).

(19) Schleyer, P. v. R.; Manoharan, M.; Wang, Z. X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465–2468.

HMO RR_2 in Table 1). The decreases are most severe for smaller rings and affect Hückel conformers more than their Möbius counterparts. The HMO RE_2 and RR_2 values depend not only on the value of T_w, but also on the magnitude of each individual p orbital twist angle, and how evenly the total amount of p twisting is distributed throughout the ring.[13] These factors can be qualitatively understood in terms of the average and standard deviation of the unsigned p orbital twist angles in each ring system (see Avg. θ and Std. Dev. θ in Table 1

The HMO REs of Hückel 4n-π annulenes are maximized when all p orbital twist angles are equal to zero. Hence their distortion into three dimensions (which relieves open shell instability) lowers their REs more than for Möbius isomers where some p twisting in natural. In general the amount of p twisting decreases, and is distributed more evenly as ring size increases (see avg θ and std dev θ in Table 1). Thus, the smaller Hückel [8]- and [12]annulenes have HMO RR_2 values significantly less than 1, while the values for the 16- and 20-membered rings are nearly equal to 1. This suggests that large 4n$-\pi$ Hückel annulenes should behave like linear polyenes.

The HMO RR_2 values for Möbius conformations are all close to 1 and increase slightly as the rings become larger, allowing their avg θ and std dev θ values to decrease. HMO RR_2 is largest for Möbius [16]annulene, but its HMO RE_2 is only 1.111 times as large as that of linear $C_{16}H_{18}$. These results suggest that medium-sized Möbius annulenes are not stabilized by π-aromaticity to any significant degree.

Our simple HMO treatment takes no account of bond length alternation, the tilting of p orbitals toward or away from one another, and the weak interactions between non-adjacent p orbitals. The computed annulene NBO RR values gauged the importance of these effects. The NBO RR values are defined in the same way as HMO RRs but are based instead on the quotient of NBO π-REs. Table 1 reveals the qualitative agreement of the NBO RR with the HMO RR_2 values. The smaller Hückel annulenes exhibit NBO RRs significantly less than 1, whereas the Möbius NBO RR_2s are generally close to unity. Möbius [16]annulene is an exception. It projects most of its twisting strain into writhe, and its NBO RR, 1.917, is considerably larger than unity. For the reasons stated above, the NBO RR values are probably more accurate than HMO RR_2s. However, the NBO RR of Möbius [16]annulene is still considerably smaller than the corresponding 3.220 benzene value.

Dissected localized molecular orbital (LMO)[19] nucleus-independent chemical shifts (NICS),[20,21] $\mathrm{NICS}(0)_\pi$, computed at the heavy atom center of each of the Möbius/Hückel rings, including contributions only from the "π" LMOs, confirm that Möbius cycles follow the reversed Hückel π electron count rule for aromaticity. As shown in Table 1, the Hückel [4n]annulenes display negligibly small negative to modestly positive $\mathrm{NICS}(0)_\pi$ values, indicative of nonaromaticity to weak antiaromaticity.[22] Conversely, the Möbius conformations exhibit negative $\mathrm{NICS}(0)_\pi$ values ranging from -9.00 to -11.73 ppm, about half of the -23.89 ppm benzene value, indicating modest π aromaticity. Hence, energetic and magnetic aromaticity metrics contrast for 4n$-\pi$ annulenes. Such disparate evaluations for Hückel conformers were noted previously by Wannere et al.,[15a] and our present analysis suggests a similar situation holds for Möbius cycles, which are aromatic by magnetic, but not energetic, criteria. However, even if the REs of Möbius annulenes are not much greater than those of their corresponding linear iso-π-electronic polyene analogues, the notion that the RE of a twisted π system can rival that of an untwisted arrangement is nonetheless remarkable.

Acknowledgment. We dedicate this paper to Prof. Kurt Mislow (Princeton University) on his 90th birthday. NSF Grant No. CHE 105-7466 supported this work.

Supporting Information Available. The geometries and p NHO twist angles for the Möbius and Hückel annulenes in Table 1 are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H. J.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

[21] Chen, Z. F.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842–3888.

[22] An alternative analysis of the ring currents of medium-sized Möbius annulenes is presented in refs 5 and 7.

The authors declare no competing financial interest.