Möbius aromatics arising from a C=C=C ring component†

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Replacement of one planar C=C unit in Hückel $4n + 2$ aromatic rings by a twisted C=C=C results in chiral $4n$ π Möbius aromatic rings.

The history of aromatic chemistry is dominated by the concept of planar ring systems containing $4n + 2$ conjugated π electrons, the so-called Hückel rule of aromaticity. Heilbronner[1] in 1964 was the first to suggest that applying a Möbius twist to the ring would create an aromatic species if $4n$ π electrons were conjugated. The Möbius concept has been widely applied to considering the aromaticity of pericyclic transition[2] states, but only recently have candidates for stable Möbius aromatics been suggested. Schleyer and coworkers have reported that a Möbius twisted conformation of the $4n$ π system $C_9H_9^+$ is aromatic[3] on the basis of calculated nucleus independent chemical shifts (NICS),[2] a technique which appears reliable and useful at quantifying aromaticity. We recently reported calculations on two conformations of [16]annulene,[4] one being conventionally antiaromatic, but the other having a pronounced Möbius-like twist not associated with any particular region of the ring. This isomer exhibited a NICS value consistent with mild aromaticity rather than antiaromaticity. Here we suggest further candidates for consideration as Möbius aromatics.
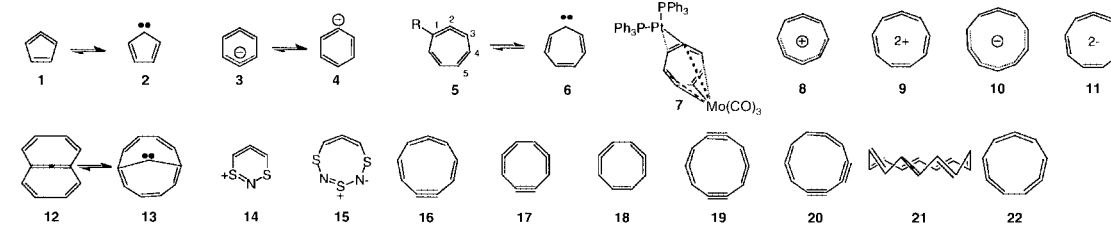
Our initial focus was on the chiral species cycloheptatetraene **5**. The presence of a C=C=C substructure in the 7-membered ring reduces the dihedral angle between the 1,3 allene substituents from 90 to 47–50°, which has the effect of breaking the degeneracy of the two highest occupied allene orbitals (Fig. 1; see ESI†). Interaction of both resulting orbitals with the remaining ring π orbitals would create a similar Möbius topology to that envisaged by Heilbronner, the specific case of **5** resulting in what could be termed a [7]Möbius annulene. A NICS calculation (−6.5 ppm, Table 1) establishes that this orbital interaction results in a mildly aromatic system, being rather less so than benzene itself (NICS −10 ppm). NICS calculations on benzannulated derivatives of **5** were reported[5] but the aromaticity of the allene-derived ring was not discussed. The ~40° distortion at the allene unit in **5** is clearly destabilising, since the species is isolable only at low temperatures, dimerising at higher temperatures *via* a π² + π² cycloaddition (a process known to be inhibited by bulky groups at the 1,3 positions[6]). The calculated bond lengths for **5** also show some alternation, indicative of a reactive species (Fig. 2). The HOMO and HOMO − 1 AM1 orbits computed for **5** are both symmetric with respect to C_2 axis and derive from the twisted allene system, but are now delocalised over the entire ring, and show Möbius topology (Fig. 2). Heilbronner predicted the HOMO for a pure Möbius aromatic would exhibit degeneracy,[1] but purely in a Hückel MO context. No degenerate representations in C_2 symmetry are necessary in **5**, although we do note that the energy difference between HOMO and HOMO − 1 (1.6eV/AM1) is less than that for allene at this twist angle (2.2 eV, Fig. 1†).

As a ligand, **5** is unusual in binding metals to both 'faces' concurrently (*e.g.* **7**),[7] but this is perhaps not unexpected if one considers it having only a single π-face! We also estimate one consequence of **5** (and its metal complexes) being chiral. Thus a typical model chiral auxilliary (*e.g.* R = CHClI or R = camphorsultamil[8]) results in diastereoisomers differing in energy by about 0.4–0.6 kcal mol⁻¹ (AM1), a relatively small discrimination, but possibly one capable of being increased by suitable design. **5** interconverts with its mirror image *via* the Hückel $4n + 2$ π aromatic **6** (cycloheptatrienylidene),[9] which at the correlated level (CASPT2) has recently been shown to be the transition state for this process (barrier ~ 20 kcal mol⁻¹).

Elaborating the theme of substituting C=C=C for C=C (Table 1) we noted that the small ring systems **1** and **2** would be classified as antiaromatic; **2** as a conventional 4π antiaromatic Hückel system with a triplet ground state and **1** as a $4n + 2$ 6π Möbius antiaromatic system. **1** appears not to exist as a minimum at the *ab initio* RHF level, whilst singlet **2** reveals an antiaromatic (positive) NICS value. No minimum for the anion **3** could be located for this putative 8π Möbius aromatic, all optimisations resulting in the aromatic Hückel valence bond isomer **4**, probably because twisting the allene component in **3** to accommodate a 6-membered ring requires too much energy. This is a lesser problem in the larger ring monocation **8**, which appears to be a C_2 symmetric 8π Möbius system exhibiting NICS aromaticity, as is the 8π dication **9**. The singlet neutral form of **9/11** as an antiaromatic $4n + 2$ 10π annulene distorts to remove all symmetry and localise the bonds, whereas the triplet neutral **9/10** retains C_2 symmetry as might be expected of a $4n + 2$ excited state Möbius aromatic, although the NICS value shows only slight aromaticity (−1.3 ppm).[10] Chiral 12π monoanion **10** and the dianion **11** also show aromatic NICS values and have non-planar twisted geometries (Table 1). Each ring of the chiral bicyclic analogue of naphthelene **12** shows only modestly aromatic NICS values. In this instance, the carbene valence bond isomer **13**, a bridged [10] $4n + 2$ Hückel aromatic annulene, is substantially lower in energy, making it unlikely that **12** is a viable synthetic target. System **14** is derived from the novel Hückel-aromatic S/N systems discovered by Rees and Surtees.[11] As an 8π Möbius, **14** has an aromatic NICS value (Table 1). The 12π system **15** has a much smaller NICS value, which might be related to the larger dihedral angle at the allene termini (75°, Table 1) reducing the Möbius like orbital mixing (*c.f.* Fig. 1†). Our results do imply that optimum Möbius aromaticity may be achieved at allene twists of ~ 30–60°.

The presence of two or more allene-like chiral Möbius components raises the possibility that these can oppose or cooperate. An even number of the former becomes equivalent to Hückel; but if the latter the topological implications become more complex. For **17** two conformations can indeed be located, one with C_S (Hückel) and the other with C_2 (Möbius) symmetry, the latter being lower in energy and higher in aromaticity (Table 1). In the 10π Hückel aromatic conformation of the alkyne **17**, the triple bond appears to act purely as a two electron contributor whereas in the C_2 form, a possible four-electron alkyne contribution results in 12π Möbius aromaticity. The alkene analogue **18** has smaller NICS aromaticity values and relative energies, due in part to the significant non-planarity of **18**. More intriguingly the higher aromaticity of **17** may be due

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Table 1 Energies [kcal mol⁻¹ for AM1, E_h (Hartree) for RHF/6-31G(d)] and NICS values (ppm) for the ground state structures

Species	AM1	AM1 relative energy[a]	RHF/6-31G(d)	RHF/6-31G(d) relative energy[a]	NICS	Dihedral angle[b]/°
1	155.3		c		—	8
2	147.1		−191.4899728		2.1	----
3	d		d		—	----
4	57.3		−230.0200		−9.8	----
5	95.7		−268.4477/−270.2424[e]		−6.5/−5.7[e]	51
6	117.0		−268.4241		−7.0	—
8	279.1		−306.6502		−5.6	65
9	575.9[f]		−344.6697		−3.3	86
10	96.8		−383.7313		−5.1	87
11	173.6		−347.4759[g]		−14.2	41
12	200.7		−420.9538		−4.7	37
13	178.5		−420.9954		−14.9	—
14	273.8		−963.7914		−10.9	27
15	72.9		−1415.9675		−0.4[h]	75
16	140.0		−344.1344		−3.3	67
17	229.2/215.3[i]	−13.9	−304.9658/−304.9946[i]	−18.1	−8.0/−11.1	53/50
18	138.7/134.0[i]	−4.7	−306.2419/−306.2556[i]	−8.6	−2.1/−5.0	50/55
19	259.3/251.4[i]	−7.9	−380.6729/−380.6888[i]	−10.0	+3.3/−1.2	48/45
20	270.0/262.2[i]	−7.8	−380.6627/−380.6755[i]	−8.0	−1.9/+3.3	49/61
21a[i]	182.2		−422.0950		−5.7	65
21b[i]	181.0		−499.0069		+0.3	66
21[i]	183.4		−575.9171		−2.2	71
22	175.4/162.2[k]	−13.2	−344.0594/344.0880[k]	−17.9	+0.3/−6.6	50/50

[a] Relative energy in kcal mol⁻¹. [b] Dihedral angle between the two termini of the allene. [c] Converges to **2** on optimisation. [d] Converges to **4** on optimisation. [e] B3LYP/6-31G(d) level. [f] Triplet state energy of neutral form 133.0 kcal mol⁻¹. [g] B3LYP/6-31G(d) values; RHF/6-31G(d) optimisation converges to a planar geometry. [h] Energy/NICS for 1,3,5,2,4-trithiadiazepine: −1378.1686/−9.3 at the RHF/6-31G(d) level. [i] Hückel/Möbius conformations. [j] **21a**, **21b** and **21** are the 12-π, 14-π and 16-π analogues of [10], [12] and [14]-trannulene. [k] C_2/C_3 conformations.
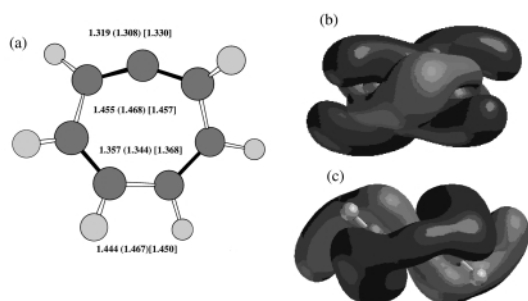
Fig. 2 Calculated geometry (a) (Å, AM1 (RHF/6-31G(d)) [B3LYP/6-31G(d)]) and form of the AM1 HOMO (b) and HOMO − 1 (c) orbitals for **5**.

to in-plane trannulene like aromaticity.[12] The alkyne in **16** appears to act as a Möbius contributor, cooperating with the allene component to give a modestly aromatic 12π system. The isomers **19** and **20** also have two conformations. Hückel **19** as an 8 or 12π 4*n* antiaromatic has the expected positive NICS value, whilst C_2 symmetric **19** is slightly Möbius aromatic. Compared to **19**, isomers **20** show reversed NICS values (Table 1), and may be indicative of more complex topological contributions to the aromaticity. A single Möbius component inserted into *e.g.* [14]trannulene **21** appears much less aromatic than the trannulene itself (Table 1), but it does conform to a 4*n* rather than a 4*n* + 2 rule for aromaticity. Finally we note that C_2 symmetric **22** has three allene contributions and as a 12π system it would be expected to be Möbius aromatic. Two isomers were identified, one with C_2 and a lower energy and more aromatic form with C_3 symmetry in which all three allene units cooperate.

We conclude that a diverse range of Möbius 4*n* π aromatic systems can be constructed by using one or more twisted allene fragments as an initiator. The origins of the Möbius and Hückel contributions to the aromaticity and the nominal electron contributions (4*n* *vs*. 4*n* + 2) of these systems may be quite subtle. A dissection of these origins will be reported in a future article.

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