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The aromaticity and Möbius characteristics of carbeno[8]heteroannulenes and triplet state annulenes†

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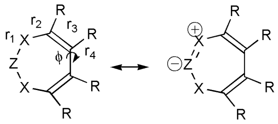
Two types of annulene which may show significant Möbius aromatic character and bond and twist delocalisation are proposed; triplet states with $4n + 2$ occupancy of the p_π array of atomic orbitals and a novel 8-π carbeno[8]heteroannulene ring system 1 where the Hückel highly antiaromatic nature as a planar system can be attenuated or even reversed by the C_2 symmetric Möbius distortion.

The criterion for aromaticity in a cyclically conjugated array of p_π atomic orbitals has long been recognised as requiring occupancy by $4n + 2$ electrons for closed shell ground state singlets (the Hückel rule) and by $4n$ electrons for appropriate triplet and open shell singlet excited electronic states. Numerous stable molecule examplars of the Hückel rule are of course known.[1] A more recent extension derives from the concept of a Möbius array of p_π atomic orbitals, the properties of which were first studied by Heilbronner in 1964.[2] Using Hückel molecular orbital theory he inferred that $4n$ closed shell electron occupancy was required to retain π resonance stabilisation energy. Although not stated by Heilbronner, the corollary that triplet/singlet excited states involving a Möbius array require $4n + 2$ occupancy for aromaticity completes a quartet of aromaticity criteria which taken together have found popular application as selection rules for inferring the aromaticity of transition states[3] of pericyclic reactions. A recent focus has been on identifying closed shell stable molecule (as opposed to transition state) examples relating to the $4n$ p_π electron Möbius criterion. For example, Schleyer first reported[4] that the most stable conformation of the cyclic $C_9H_9^+$ 8_π cation with C_2 symmetry had a calculated diatropic ring current (quantified as a Nucleus Independent Chemical Shift or NICS value[5]) and a geometry which was consistent with significant Möbius aromaticity. We proposed[6] that a high energy Möbius conformation of [16] annulene also with C_2 symmetry was mildly aromatic on the basis of NICS values, and subsequently suggested[7] that replacing a two electron C=C double bond in a planar $4n + 2$ Hückel aromatic ring with the four electron allene unit (C=C=C) could induce modest $4n$ Möbius aromaticity and C_2-derived chirality in a variety of ring conjugated systems. Here we extend these examples with two more types. The first is the novel ring system **1**, in which the transition between $4n$ Hückel anti-aromaticity and $4n$ Möbius aromaticity can be tested in a systematic manner. The second derives from noting that no stable molecule examples relating to the corollary stated above ($4n + 2$ p_π triplet state occupancy implying Möbius-like aromaticity) have hitherto been proposed, and for which we now evaluate various candidates.

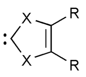
The presence of a Möbius configuration of p_π atomic orbitals is associated with the presence of a chiral symmetry element (*e.g.* C_2 axis) and the absence of a C_s plane of symmetry in those molecules which could have either (or both). Our criteria for judging aromaticity in such species are two fold. Nucleus independent chemical shifts[5] approximately associate overall negative NICS values with a diatropic ring current and aromaticity, and positive values with a paratropic ring current and anti-aromaticity, although the integrated NICS value contains contributions from both types of ring current. We emphasise here not the absolute NICS values, but their trends. The second criterion derives from the original suggestion by Heilbronner that an ideal Möbius aromatic would exhibit neither bond length localisation, nor any localisation of the Möbius twist present in the ring. We have previously noted[6,7] that ring perfluorination enhances such delocalisation in other Möbius systems and reduces the mixing of C–R σ components with the cyclic p_π array, and have also included examples of F-substituted systems. Optimised energies at the RB3LYP/ /6-31G(d) level[8] of a variety of ring systems derived from **1** and of triplet state monocyclic ring systems at the ROB3LYP/ /6-31G(d) level are available *via* the ESI†.

The diaza system **1, X = NH, R = H, Z = C:** is the $4n$ homologue of the carbene **2, X = NMe**, a ligand of current interest as a phosphine mimic in metal coordination chemistry.[9] Initial calculations at a planar geometry reveal it to be strongly anti-aromatic, with a NICS value (23.6) quite similar to that calculated for cyclobutadiene **3**. The two C–N bond lengths (1.35 Å) are equal and their value indicates that a closed shell ylid representation (*i.e.* **1a**) is better than the carbene. Unlike **3** however, no first order Jahn-Teller distortion to the bond-alternating form represented by **1a** occurs, because the presence of the two nitrogen heteroatoms increases the energy separation of the otherwise degenerate orbitals. Given the presence of two nitrogen lone pairs, we were quite surprised to find that only one, small negative root was calculated for the Hessian matrix at the planar geometry, the vectors of which do not correspond to pyramidalisation of the lone pairs, but instead represent a twist to create a chiral species with C_2 symmetry. The energy lowering resulting from following this small geometric distortion is an inconsequential 0.15 kcal mol^{-1}, but this is accompanied by a relatively large reduction in the calculated NICS value to 19.4 ppm. The angular ring strain is the factor that prevents more Möbius distortion, and hence it appears that these systems are finely balanced between planar Hückel anti-aromaticity and Möbius aromaticity; in this specific case the former still imparting the dominant character. We also contrast this distortion with that found experimentally and theoretically for the 8-π azepine, oxepine and thiepine rings (**4**), for which a



1, Z=C,Si,HC$^+$; R=H,F; X=HC$^-$,NH,O,PH,S

1a



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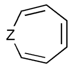
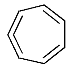


4, Z=NH,O,S



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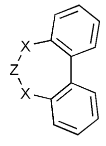

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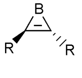

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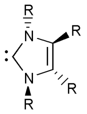

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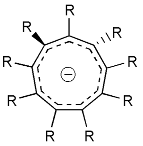

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† Electronic supplementary information (ESI) available: due to the two printed page length restriction on this communication, energies and coordinates for all the systems studied can be viewed *via* the ESI. See http://www.rsc.org/suppdata/cc/b1/b110626k/

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C_s distortion is of lower energy than a C_2 mode.[10] A closer analogy can be drawn to the 8-π system **5**.[7] Another stabilising mode exhibited by anti-aromatic systems is aromatisation by π–π* excitation to a lower energy triplet state, as occurs for *e.g.* **3**. This mode is not adopted by **1**, the triplet π–π* state being 28.3 kcal mol^{-1} higher in energy than the singlet, in agreement with its ylid (**1a**) rather than carbene-like characteristics. The aromatic NICS value of the triplet (−8.3) is appropriate for a 4*n* p_π triplet.[11] The perfluoro system **1, X = NF, R = F, Z = C:** which is significantly more twisted, as indicated by the dihedral angle *ϕ*, and is less anti-aromatic, as measured by the NICS value and reduced bond alternation. The chiral system derived from biphenyl (**6**) is likewise only mildly anti-aromatic (NICS 8.9), and a viable candidate for synthesis.

The dioxa system **1, X = O, R = H, Z = C:** as a planar ring also reveals a single imaginary vibrational mode distorting to C_2 symmetry. In this case the reduction in energy is rather greater (1.5 kcal mol^{-1}), the ring twists more, and the NICS value and bond alternation both reduce more than the diaza system (NICS by 7.5 ppm). Perfluorination also induces a negative NICS value corresponding to some mildly aromatic character (NICS −1.3) and the bond alternation reduces even further. Disproportionation to CO_2 and two units of alkyne is only modestly exothermic [−12.4 kcal mol^{-1} at B3LYP/6-311G(3d) level], and perfluorination changes this to an endothermic value [+52.9 kcal mol^{-1} at B3LYP/6-31G(d)]. The latter in particular therefore is most unlikely to easily fragment, and may well therefore be quite stable thermodynamically. The corresponding values for X = NH/NF were an even more emphatic +62.2 and +124.1 kcal mol^{-1} respectively. Of the various other X, R and Z substituents investigated† the following are noteworthy. The combination Z = CH$^+$, X = CH$^-$ corresponds to $C_7H_7^-$, which is reported here in Möbius form. First-order Jahn-Teller induced bond alternation (*i.e.* as with **1a**) breaking the C_2 symmetry can be seen, a feature not present with the more Möbius-aromatic perfluoro form. The lowest energy form of **1, X = PH, R = H, Z = C:** has a Möbius distortion but another higher energy isomer with 'tub' like C_s symmetry can also be located. In contrast, **1, X = S, R = H, Z = C:** reveals neither C_2 nor C_s distortion, the planar C_{2v} form revealing neither any calculated negative roots for the Hessian nor any symmetry-breaking bond alternation. This behaviour is similar to that reported[12] for completely planar cyclic 8 p_π tetrakis(bicyclo-[2.1.1]hexeno) cyclooctatetraene, which also sustains not only a paratropic ring current but also exhibits large bond length alternation (1.33, 1.50 Å). Perfluorination of **1, X = S, R = F, Z = C:** however induces Möbius distortion and a large (−16 ppm) aromatisation of the NICS value. Replacing **Z = C:** with the silylene equivalent (Z = Si**:**) similarly results in C_2 distortions and tends to produce less anti-aromatic species.

Borirene[13] (**7**) is a neutral boron substituted analogue of cyclopropenium cation. As a closed shell singlet, **7** is planar and aromatic, with C_{2v} symmetry.[13] The open shell triplet^3 A state retains only the C_2 axis of symmetry and the NICS value (−9.7) indicates aromaticity rather than anti-aromaticity, as accords a 4*n* + 2 Möbius aromatic. We emphasize that at this stage, we are not claiming that the Möbius triplets are always the most stable triplet possible, merely that in many cases a triplet with such symmetry can be located. The optimised geometry of the all-carbon cyclopropenium^3 A cation also has C_2 symmetry. No NICS value is computed but some bond length alternation does occur (1.412, 1.503 Å), indicating this species is not highly aromatic. Curiously, 6 p_π examples for this type are sparse. A ^{3}A triplet state of furan shows a distortion towards C_2 symmetry, and the NICS value (−3.7) is indicative of mild aromaticity, as are **8, R = F** and the phosphorus analogue. The 6-electron ^{3}A triplet perfluoro tropylium cation optimises to a planar (C_{2v}) non-Möbius form.

Not all the larger ring examples are conspicuously aromatic, probably for a variety of reasons. For example, the NICS probe is placed at a computed ring centroid, and the conformation of some systems ensures that the fluorine ring substituents can also approach this position, thus perturbing the NICS value. Furthermore, boron, introduced to replace C$^+$ in some models, is also known to inhibit aromaticity.[14] The most prominently aromatic triplets were identified for the 10 (**9**) and the 14 p_π systems. Thus triplet **9** exhibits minimal bond alternation†1.408, 1.407, 1.396, 1.377, 1.411 Å, NICS −13.0 and small dihedral angle alternation between adjacent pairs of ring atoms (25.0, 8.0, 33.0, 36.0). The finite size of the ring, and the presence of one pseudo *trans* ring component, precludes a total absence of alternation. Similarly, the 14 electron triplet system $C_{12}F_{12}^{2-}$ manifests only two C–C bond lengths; 1.377 and 1.404 Å and NICS = −12.1 ppm.

We conclude that ring systems such as **1** are predicted to attenuate the Hückel anti-aromaticity expected of a planar 4*n* p_π system with varying degrees of C_2 symmetric distortion towards Möbius aromaticity. We also propose the first formal examples of chiral Möbius conformations of 4*n* + 2 electron triplet aromatic annulenes corresponding to the last of the four aromaticity rules derived from simple Hückel molecular orbital theory, and suggest that these may be of interest in emerging applications such as chiral photochemistry.[15]

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