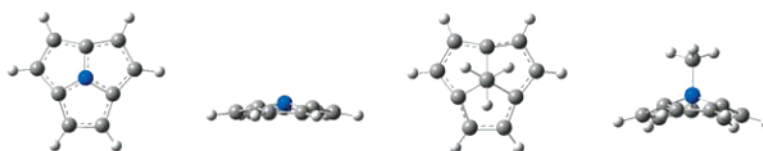# Aromaticity and Curvature in Heteroacepentalenes

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Heteroatom-substituted acepentalene derivatives which are isoelectronic with the known acepentalenediide dianion are nonplanar, fused aromatic tricycles which are hemifullerenes of the corresponding C_{20} heteroanalogue. Depending on the number and position of heteroatoms, they may be anionic, neutral, or cationic. A nucleus-independent chemical shift study indicates that substitution of the central carbon of the acepentalenediide system with N or O results in a substantial increase in aromaticity. Peripheral aza substitution on the other hand tends to increase curvature and decrease aromaticity. Alkylation or protonation at the central position of asymmetrically substituted heteroacepentalenides leads to chiral, bowl-shaped, 10π aromatic species.

Introduction

Aromatic systems which are distorted from planarity have long been objects of theoretical interest. Classic examples include paracyclophanes,[1] peri-substituted acenes,[2] helicenes,[3] cyclacenes,[4] bridged annulenes,[5] and highly substituted porphyrins.[6] The advent of fullerenes and carbon nanotubes has precipitated nothing short of a frenzy in the study of curved aromatics, and molecules such as corannulene and related polycyclics which can be mapped onto the surface of fullerenes have consequently also enjoyed much attention.[7] In this context, the recent observation of the C_{20} fullerene **1** was of particular interest to us.[8] The simplest nonplanar "clipping" of **1** is acepentalene **2**,[9] an unstable, antiaromatic molecule.[10] Adding two electrons to **2** however gives the aromatic acepentalenediide dianion **3**, the dilithium salt of which has been prepared by de Meijere and co-workers by a remarkable superbase-induced dehydrogenation of triquinacene **4**.[11] An X-ray crystal structure showed **3** to possess a gentle curvature, a morphology which represents a compromise between the maximization of π-orbital overlap and the puckering expected from the trefoil fusion of three five-membered rings. Recently, we described an aza analogue of **3**, i.e. the aromatic azaacepentalenide anion **6** (Figure 1), which could be prepared by N-oxidation of aza-triquinacene **5** followed by treatment with base.[12] Anion **6** is a two-electron reduced north-polar clipping from $C_{19}N$, a fullerene so far known only to theorists.[13] Systems such as **3** and **6** are

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(9) The IUPAC name for acepentalene (**2**) is cyclopenta[*cd*]pentalene. Nomenclature conventions for the heterotricyclic systems vary. The trefoil fusion of three aromatic molecules with nitrogen at the center was given the common name [*n,n,n*]cyclazine by Boekelheide in 1959 (Windgassen, R. J., Jr.; Saunders, W. H., Jr.; Boekelheide, V. *J. Am. Chem. Soc.* **1959**, *81*, 1459). The IUPAC name for **6** is pyrrolo[2,1,5-*cd*]pyrrolizinide, whereas **8** is 2a,6b-diazacyclopenta[*cd*]pentalene. For simplicity, the common acepentalene root name is used in this paper, along with the IUPAC numbering scheme shown for structure **2**.

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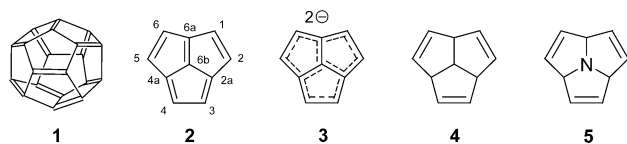
fused aromatics consisting of 6π-electron five-membered aromatic rings, 10π-electron pentalenediide-based aromatic rings, and a 10π-electron nine-membered peripheral aromatic ring. In this work, we examine the aromaticity and curvature of the acepentalene, acepentalenide, and acepentalenium species which result from heteroatom substitution into the acepentalenediide system, as well as the effect of increasing electron withdrawal on the protonation energy of the aromatic anions. We also isolate the 10π perimeter of the tricycle by substitution at the *centro* atom, which leads to chiral, bowl-shaped aromatic molecules.
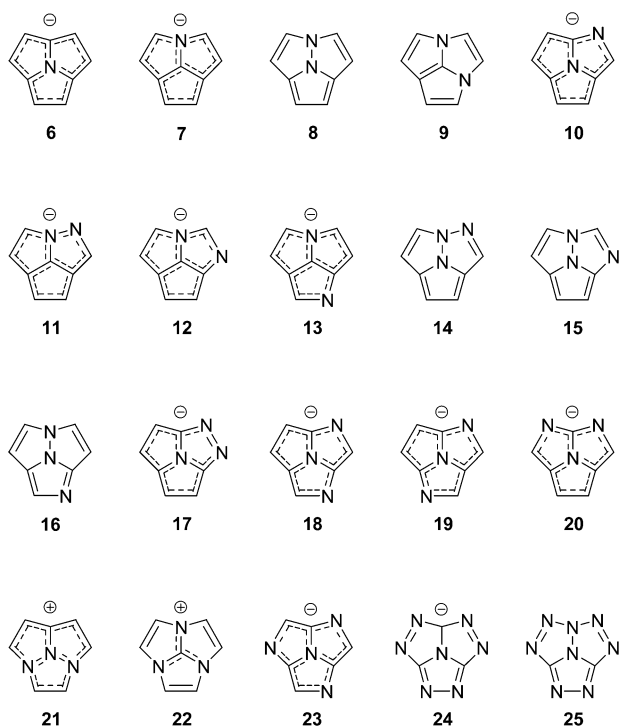

FIGURE 1. Structures of azaacepentalenes **6−25**.

Methods

Geometry optimizations were performed at the B3LYP density functional level of theory[14] using the 6-311++G(d,p) basis set. Symmetry was used where possible to simplify calculations after it was verified that test optimizations performed in the absence of symmetry resulted in virtually identical structures. Vibrational frequencies were calculated in order to characterize stationary points as either minima or transition states on the potential energy surface and to apply zero-point energy corrections where relevant. NMR magnetic shielding tensors were calculated using the gauge-independent atomic orbital (GIAO) method[15] applying the same

Results and Discussion

Taking the known 10-azaacepentalenide **6**[12] as the starting point, there is only one other monoaza isomer of the acepentalene ring system which can be aromatic without invoking a dianionic state, i.e., 2a-azaacepentalene **7**. Problems associated with the modeling of acepentalenediide **3** and aza congeners thereof will be discussed later in the paper. Two neutral diazaacepentalenes **8** and **9** and four diazaacepentalenides **10−13** are possible by systematic variation of the position of the two nitrogens around the tricycle. There are 25 possible triazaacepentalenes, of which 6 are neutral, 13 are monoanionic, 4 are dianionic, and 2 are cationic. This study is limited to neutral, monoanionic, or cationic isomers with a central nitrogen (**14−21**), except in the case of cation **22**. Finally, the symmetric tetra- (**23**), hepta- (**24**), and octaaza- (**25**) species were also examined.

The chemistry of these nonbenzenoid aromatics is largely uncharted. A literature search beyond compounds **3** and **6** reveals that none of the other parent ring systems is known, although in a few cases substituted versions thereof have been described. Thus, a diazaacepentalene **8** with a phenyl group at the 2-position was synthesized as early as 1966 but only characterized by combustion analysis.[17] A series of more highly substituted derivatives of **8** have since been prepared.[18] Benzannulated and otherwise polysubstituted diazaacepentalenes **9** were reported in 1995,[19] and multiply annulated derivatives of **13** appear in a recent Japanese patent.[20] Finally, alkyl bis-(carboxylic ester)-substituted versions of **14** are also known.[21] Only in the cases of the substituted analogues of **8** and **14** is the aromaticity of the system remarked upon, and in no case is their nonplanar character noted. Partially or completely saturated versions of **7**,[22] **10**,[23] **15**,[24] and **22**[25] have also been reported.

The aromaticity of **6−25** was evaluated by the nucleus independent chemical shift (NICS) criterion described by Schleyer and co-workers.[26] The ghost atoms used in this procedure were placed 1 Å above and below the centroid of each unique five-membered ring. Although chemical shift values on both the exo and endo faces of the bowls are given (Table 1), those measured on the endo face are strongly influenced by the degree of curvature of the bowl. For this reason, the corresponding NICS values of the planar transition structures for bowl-to-bowl interconversion were also calculated

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TABLE 1. Symmetry, Deviation from Planarity (dp, Å), NICS Values (ppm), Bowl Conformer Inversion Energies (kcal mol^{-1}), and Protonation Energies (kcal mol^{-1})

	symmetry	dp^a	NICS$_{(exo)}$ ^{b}	NICS$_{(planar)}$ ^{b}	NICS$_{(endo)}$ ^{b}	$E_{(inv)}$	$E_{(prot)}$
6	C_{3v}	0.390	−9.64	−11.45	−13.85	0.59	−333.5
7	C_s	0.705	−6.23	−7.86	−12.57	6.47	−
8	C_s	0.535	−9.25	−11.59	−13.96	2.08	−
9	C_s	0.716	−5.96	−8.04	−11.37	7.24	−
10	C_1	0.507	−9.28	−11.18	−14.46	1.55	−329.4
11	C_1	0.754	−6.00	−7.75	−12.70	7.93	−
12	C_1	0.780	−6.09	−7.77	−12.97	9.18	−
13	C_1	0.775	−6.01	−7.78	−12.73	9.06	−
14	C_1	0.603	−8.78	−11.62	−14.26	3.12	−
15	C_1	0.629	−8.78	−11.42	−14.18	3.87	−
16	C_1	0.619	−8.55	−11.36	−13.84	3.63	−
17	C_s	0.591	−9.09	−11.20	−15.07	2.82	−317.6
18	C_1	0.598	−8.87	−11.14	−14.88	2.93	−325.5
19	C_s	0.607	−8.93	−11.13	−15.19	3.23	−326.5
20	C_s	0.603	−8.84	−11.10	−14.83	2.98	−324.2
21	C_s	0.628	−8.40	−11.12	−13.17	4.26	−
22	C_{3v}	0.670	−5.96	−8.01	−10.85	6.05	−
23	C_3	0.678	−8.48	−10.94	−15.16	4.71	−318.2
24	C_{3v}	0.886	−8.02	−	−17.21	−	−293.7
25	C_s	0.912	−6.19	−	−14.04	−	−
26	C_{3v}	0.538	−9.42	−11.26	−13.71	2.56	−306.5
27	C_{3v}	0.252	−9.86	−10.65	−11.96	0.10	−253.7
28	C_3	0.666	−8.54	−10.60	−14.49	4.28	−273.6
36	C_{3v}	0.481	−11.73	−14.09	−16.13	1.51	−
37	C_{3v}	1.403	−6.90	−11.81	−12.27	81.07	−
benzene	D_{6h}	0	−	−10.22	−	−	−
pyrrole	C_{2v}	0	−	−10.13	−	−	−

^{a} dp is defined as the distance from the central ring atom to the centroid of the six peripheral ring atoms. ^{b} Averaged value over all three rings (**6**−**37**).

and are presented along with the inversion barriers.[27] One thing that immediately stands out among data for the mono- and diaza species is the greater aromaticity shown by the isomers which possess a central nitrogen. Thus, monoaza isomer **6** and diaza isomers **8** and **10** have NICS$_{(exo)}$ and NICS$_{(planar)}$ values >3 ppm upfield of **7**, **9**, and **11**−**13**. The deviation from planarity (dp) of the *centro*-N species is also substantially less than those with apical carbon. Even the NICS$_{(endo)}$ values for **6**, **8**, and **10** are lower than those of **7**, **9**, and **11**−**13**, notwithstanding the greater curvature of the latter systems. Interestingly, significant C−C bond length alternation is also seen in the *centro*-C species. Whereas compound **6** for example has C−C bond lengths of 1.42−1.43 Å, the same C−C bonds in compound **7** range from 1.39 to 1.46 Å.

The substitution of C for N in the periphery of the acepentalene ring system results in an increase in the curvature of the bowl. Thus, while **6** has a dp of 0.390 Å and a negligible inversion barrier of 0.59 kcal mol^{-1}, compounds **8** and **10** have dp values of 0.535 and 0.507 Å and inversion barriers of 2.08 and 1.55 kcal mol^{-1}, respectively. The dp of the triaza species **14**−**21** increases to a mean of 0.610 Å, while inversion energies range from 2.82 to 4.26 kcal mol^{-1}. The NICS$_{(exo)}$ shifts of **14**−**21** fall between −8.4 and −9.1 ppm. This, along with the greater curvature, suggests a weakening of aromaticity with increasing N substitution, although the NICS$_{(planar)}$ values are little different from those of **6**, **8**, and **10**. The cationic triaza species **22** lacks a central nitrogen and, like the related **7**, **9**, and **11**−**13**, shows aromaticity inferior to **14**−**21**. Further N substitution in **23**−**25** sees a continuation of the trend toward greater curvature, to the point where the central atoms of **24** and **25** are essentially tetrahedral. Attempts to minimize **24** in a planar conformation

failed, and geometry optimization starting from a planar structure for **25** led to a new, monocyclic energy minimum via 1-6a and 6-6a N−N bond cleavages, bonds that were already elongated in the bowl conformer of **25**.

It would be informative to compare the aromaticity and curvature of these azaacepentalenes with the known acepentalenediide dianion **3**. As discussed above, the indications are that when carbon occupies the apical postion of the tricycle, as it does in **3**, the aromaticity is diminished relative to the *centro*-N species. However, the *ab initio* modeling of polyanions is known to be problematic,[28] and the electron repulsion they experience in the gas phase renders direct comparisons to monoanionic or neutral species of limited usefulness. The optimization of **3** using the same method as for **6** gives a species whose five highest occupied orbitals have positive eigenvalues. The structure of **3** in the gas phase (dp = 0.715 Å) does not correlate well with that in the crystal structure of the dilithium bis(1,2-dimethoxyethane) complex (dp = 0.580 Å), suggesting that any NICS determination on the bare dianion would not be meaningful. Reoptimization of the structure at the MP2/6-311++G(d,p) level of theory does nothing to resolve the autoionization problem and actually increases the depth of the bowl to 0.756 Å. Performing an energy minimization of **3** as it appears in the crystal structure, i.e., including the lithium counterions and solvate molecules, reduces the curvature of the bowl to 0.524 Å and gives a negative HOMO energy, but this action rules out a determination of the NICS aromaticity. However, the presence of lithium in Li$_2$(DME)$_2$**3** affords an opportunity to compare the ^{7}Li chemical shift to that of the hypothetical complex Li(DME)**6**, the lithiated exo faces of which turn out

(27) All planar transition structures were characterized by the observation of one imaginary frequency in the calculated vibrational spectrum.

(28) For recent discussions of this issue, see: (a) Trindle, C.; Yumak, A. *J. Chem. Theory Comput.* **2005**, *1*, 433. (b) Trindle, C.; Yumak, A. *J. Chem. Theory Comput.* **2005**, *1*, 1038. (c) Sommerfeld, T. *J. Am. Chem. Soc.* **2002**, *124*, 1119.
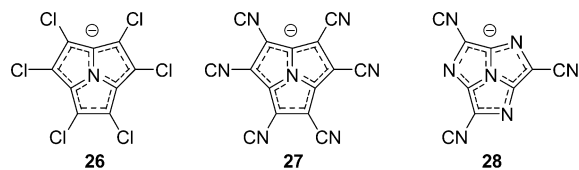
FIGURE 2. Structures of azaacepentalenides **26**–**28**.

to be essentially isostructural. The *exo*-lithium ion in Li$_2$-(DME)$_2$**3** (δ −5.6) is found downfield of that in Li(DME)**6** (δ −7.0),[29] and thus the former appears to be more weakly aromatic, consistent with the above NICS data for azaacepentalenides lacking a central nitrogen.

Substitution at the periphery of azaacepentalenides **6** and **23** with electron-withdrawing cyano groups gives **27** and **28** (Figure 2), resulting in reduction of the dp and a slight upfield shift the NICS$_{(exo)}$ values, although the NICS$_{(planar)}$ values are actually somewhat downfield of those of the parent compounds. The known hexacloroazaacepentalenide **26**[12] was also modeled and found to have slightly greater curvature and comparable aromaticity to **6**. The main reason for including these species in this study is to consider their protonation energies. We had previously observed that while the lithium salt of **6** could only be handled in dry THF solution, the hexachloro analogue **26** was stable in the absence of acids and could even be chromatographed as its tetrabutylammonium salt.[12] The *centro*-N aromatic anions in this study were protonated at a carbon α to the central nitrogen, and the structures were optimized. The protonation energy was determined by subtracting the electronic and zero-point energies of the anions from those of the neutral "acids." The data are given in Table 1. As expected, the protonation energy of the azaacepentalenides decreases with increasing nitrogen content, such that **24** is even less basic than **26**. Substitution with cyano groups dramatically reduces the basicity of the anions. Indeed, **27** has been modeled independently by Maksić et al. and reported to have a protonation energy of 255 kcal mol^{-1} ((B3LYP/ 6-311+G(2d,p)// B3LYP/6-31G(d)) corresponding to a record low pK_a value of −26.5 in DMSO.[30] We conclude from this and our own work that, unlike **6**, anions **23**, **24**, **27**, and **28** should, like **26**, be isolable species which are air- and moisture-stable.

It is noteworthy that, because of their nonplanar character, the azaacepentalenes lacking an element of symmetry (**10**–**16** and **18**) are chiral. However, the low inversion barriers (Table 1) liken this chirality to that of asymmetrically substituted amines, which is of little consequence until the amine is quaternized and thereby covalently fixed in a single configuration. Similarly, *centro*-alkylation (at N) or protonation (at C) leads to acepentalene derivatives with permanent curvature and, in the case of **31**–**35**, resolvable chirality (Figure 3). These are neutral or zwitterionic molecules with a 10π perimeter, whose high dp values reflect the sp^3 hybridization state of the central atom (Table 2). No measure of the NICS aromaticity of **29**–**35** was undertaken because of the problems associated with the determination of these values in the endo space of bowls of varying curvature which, unlike **6**–**28**, cannot be planarized. However, aromaticity can also be characterized by the geometric criterion of bond length equalization, where a maxiumum carbon−carbon bond length difference (Δr) of about 0.05 Å

(29) The reference used for ^{7}Li chemical shifts was Li(OH$_2$)$_4$.
(30) Vianelloa, R.; Maksić, Z. B. *Tetrahedron Lett.* **2005**, *46*, 3711.
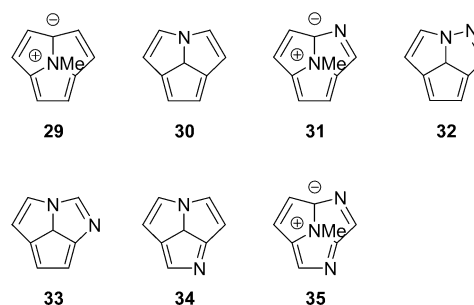
FIGURE 3. Structures of azaacepentalene derivatives possessing a 10π periphery.

TABLE 2. Symmetry, Deviation from Planarity (dp, Å), Maximum C−C Bond Length Difference (Δr, Å), Maximum Pyramidalization Angle ($\theta_{\sigma\pi}$, deg), and Maximum p-Orbital Axis Vector Dihedral (τ_{POAV2}, deg) for Compounds 29−35

	symmetry	dp	Δr	$\theta_{\sigma\pi}$	τ_{POAV2}
29	C_{3v}	0.782	0.024	97.0	14.3
30	C$_s$	0.901	0.072	101.5	17.0
31	C_1	0.841	0.039	98.2	15.5
32	C_1	0.975	0.068	103.1	18.2
33	C_1	0.986	0.091	102.8	18.6
34	C_1	0.979	0.058	103.1	19.0
35	C_1	0.901	0.029	99.6	16.6

would be expected in an electronically delocalized system.[31] Pyrrole, for example, when modeled at the same level of theory as the species described in this work, has a Δr of 0.048 Å, which compares to experimental values between 0.035 and 0.058 Å in the literature.[32] The Δr values for **29**−**35** are included in Table 2 and show that at least **29**, **31**, and **35** should be considered fully aromatic by this criterion. Although **30** and **32**−**34** have Δr > 0.5 Å, comparison to the Δr values of their parent tricylces **7** and **11**−**13** suggests little difference between them in aromaticity; indeed **32** and **34** actually have slightly lower Δr values than **11** and **13**. A typical concern in nonplanar aromatic systems is that extreme torsion angles along the aromatic path will disrupt conjugation. In fact, in **29**−**35** peripheral dihedral angles range as high as 61°. However, a partial pyramidalization of ring atoms occurs in such cases to allow the maximum possible overlap of p-orbitals. The degree of pyramidalization ($\theta_{\sigma\pi}$) and resulting torsion angle between p-orbital axis vectors (τ_{POAV2}) was calculated for **29**−**35** using the POAV method introduced by Haddon.[33] As can be seen in Table 2, in no case is the dihedral angle between neighboring p-orbitals greater than 19°. For comparison, a maximum POAV2 torsion angle of 28.4° can be calculated from the crystal structure of the stable 10π aromatic 1,6-methano^{10}annulene ring system,[34] which has a respectable Δr value of 0.037 Å. Maximum pyramidalization angles for the sp^2 atoms in **29**−**35** vary from 97.0 to 103.1°, which compare to those determined from the crystal structures of **3** (100.8°)[11b] and C$_{60}$ (101.6°).[35] Recently,

(31) Schleyer and co-workers have called the use of the geometric criterion into question: Schleyer, P. V. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209−218.
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(33) Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243.
(34) Bianchi, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr.* **1980**, *B36*, 3146.
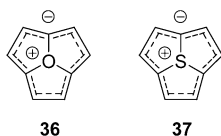(35) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385.

FIGURE 4. Structures of chalcogenoacepentalenides **36** and **37**.

Scott and co-workers have reported a stable corannulene derivative with a $\theta_{\sigma\pi}$ value of 102.6°.[36] These numbers suggest that it is not unreasonable to expect that all of the molecules in Figure 3 possess at least some degree of aromaticity. Interestingly, it is again the *centro*-N representatives of this series which, like their counterparts in Figure 1, display shallower bowl curvature and better evidence of aromaticity than those with carbon centers. Although tricyclic 10π systems like these are unknown in the literature, a paper describing the saturated azatriquinane precursor of **7** is noteworthy,[22] since the authors synthesized the compound to the purpose of oxidizing it to **30**, which ultimately proved unsuccessful.

Finally, aromatic *centro*-chalcogeno (O, S) analogues of acepentalene (Figure 4) were also modeled. These are isoelectronic with **3** and **6** but with no overall charge due to the cationic nature of the central atom. The oxonium species **36** shows somewhat greater curvature than **6** and C−C bond lengths which are likewise equivalent to within 0.01 Å. However, the aromaticity is significantly enhanced, with record NICS$_{(exo)}$ and NICS$_{(planar)}$ values of −11.73 and −14.09 ppm, respectively. The thiaacepentalene **37** shows a far greater dp and inversion barrier than any other species described above because of the length of the C−S bonds, which elevates the sulfur well above the plane described by the four carbon atoms of each five-membered ring. The lack of participation of the central atom in the aromaticity of **37** is more reminiscent of the **29**−**35** series than **6**−**25**, although the Δr value (0.006 Å) is even less than in **29** (0.024 Å).

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(36) Jackson, E. A.; Steinberg, B. D.; Bancu, M.; Wakamiya, A.; Scott, L. T. *J. Am. Chem. Soc.* **2007**, *129*, 484.

Conclusion

In summary, the aromaticity of mono-, di-, and selected tri- and polyazaacepentalene species has been evaluated using the NICS criterion. The molecules in question represent hemispheres of the relevant $C_{20-n}N_n$ fullerene. The NICS method is sensitive to the curvature of the bowl, and the intrinsic aromaticity of the systems may be best evaluated by considering the NICS values of the planarized tricycles, which are low-barrier transition states between bowl invertamers. A key finding is that the presence of N or O at the center of the tricycle is a "sweet spot" in terms of aromaticity, where the NICS$_{(planar)}$ values exceed that of either benzene or pyrrole, while the *centro*-C acepentalenes are substantially less aromatic both by NICS and, in the case of acepentalenediide **3**, ^{7}Li chemical shifts. Further substitution of nitrogen into this system progressively increases bowl curvature and leads to a decrease in aromaticity. In the case of the *centro*-N anions, increasing the nitrogen content at the periphery and/or substitution with electron-withdrawing groups decreases the protonation energy, to the extent that these species are predicted to be stable in aqueous and even acidic media, depending on the degree of substitution. Finally, a novel series of chiral, bowl-shaped, 10π aromatic molecules are proposed which result from either protonation or substitution of the central C or N of asymmetric azaacepentalenides.

Supporting Information Available: Cartesian coordinates, energies, and the number of imaginary frequencies for the optimized structures of **3**, Li$_2$(DME)$_2$**3**, Li(DME)**6**, and **6**−**37**, including both bowl and planar conformations for **6**−**28**, **36**, and **37**. This material is available free of charge via the Internet at http://pubs.acs.org.

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