To What Extent Can Nine-Membered Monocycles Be Aromatic?

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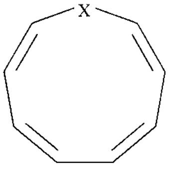
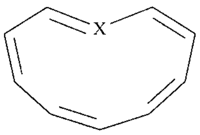
Ab initio and density functional computations have been used to characterize the heteronins. New targets for synthesis are suggested on the basis of the results. The aromaticity of the heteronins was evaluated via numerous criteria such as magnetic properties (NICS and δ_H), geometric indices (Bird, BDSHRT and HOMA), aromatic stabilization energies (ASE), and the barriers to planarity. Along with the experimentally characterized cyclononatetraenyl (**1CH**$^-$) and azonide (**1N**$^-$) anions, the phosphonide ion (**1P**$^-$, which has not been reported before), favors planar (C_{2v}) symmetry. All the other heteronins are nonplanar in order to alleviate ring strain. Comparisons of the neutral planar heteronins (constrained to C_{2v} symmetry) show the extent to which heteroatoms like P and S, as well as N and O (in oxonin, **1O**), can participate in the cyclic electron delocalization. Due to hyperconjugation, the C_{2v}-symmetric 9,9-distannylcyclononatetraene **1C(SnH$_3$)$_2$** is moderately aromatic, in contrast to **1CH$_2$**, which is a nonaromatic, conjugated system. The planar C_{2v}-symmetric **1BH** and **1AlH** and **1CF$_2$** are antiaromatic, like the planar form of **1CH**$^+$. Annelation with three-membered rings resulted in planar heteronins. The sole exception was phosphonin (**8PH**), but the barrier to planarity decreased to 1.8 kcal/mol in **8PR**, due to the bulky **R**: 2,6-di-*tert*-butylphenyl substituent at the phosphorus atom. Among the 8π heteronins, only the previously reported **1CH**$^+$ is Möbius-aromatic; **1BH**, **1AlH** and **1CF$_2$** also have C_2 structures but are nonaromatic due to large torsional angles which preclude cyclic delocalization.

Introduction

Heteronins (**1**) are nine-membered heterocycles, π-isoelectronic with $(CH)_9^-$ (**1CH**$^-$).[1] These potentially aromatic 10π-electron monocyclic systems suffer from less strain than the ten-membered annulenes, e.g. cyclodecapentaene (**2CH**) and azacyclodecapentaene (**2N**) which do not favor planar geometries.[2–4] Indeed, **1CH**$^-$ is a thermodynamically stable, planar D_{9h} species exhibiting a high degree of cyclic electron delocalization (δ_H = 6.72–7.13 ppm, depending on the solvent and the counterion).[5–9] Azonin (**1NH**) and the azonide ion (**1N**$^-$) are, however, the only known, stable 10π heteroaromatic monocycles.[7,10–12] According to Anasstassiou and Reichmanis,[7] the delocalization of the heteroatom lone pair is about 58% in azonin and about 77% in the azonide ion (on the basis of their ^{13}C NMR chemical shifts in the δ position, relative to those of **1CH$_2$** and **1CH**$^-$ as references). Oxonin (**1O**) and **1NR** (where R is an electron-withdrawing group, e.g. ethoxycarbonyl) readily rearrange into more stable bicyclic forms (Scheme 1, X = O, NR) like cyclononatetraene (**1CH$_2$**) itself.[11]



1X (X = BH, AlH, NH, N$^-$, PH, P$^-$, O, S, CH$_2$, CH$^-$, CH$^+$)



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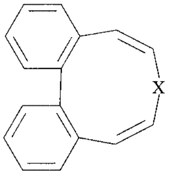

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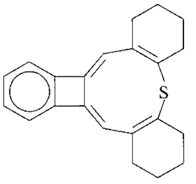

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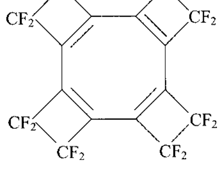

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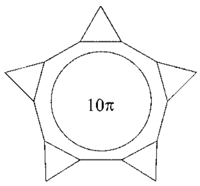

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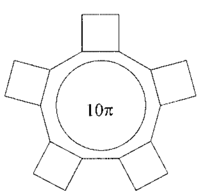

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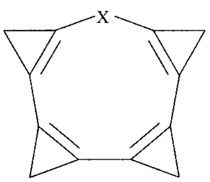

8X (X = CH$_2$, O, S, PH)

The parent thionin (**1S**) has not been synthesized,[10] but derivatives (**3S** and **4**, as well as **3O**) are known. According to their ^{1}H NMR spectra, **1O** and **1NR**, as well as **3O**, **3S**

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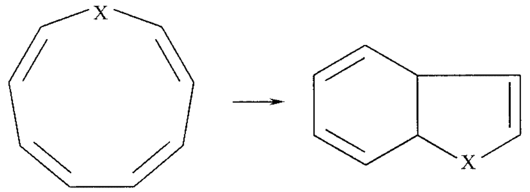
and **4** do not exhibit diatropic ring currents.[11,13–15] This agrees with the olefinic rather than aromatic behavior of these heteronins: hydrogenation,[11,14] rapid decomposition[11,16,17] and Diels–Alder[12,18] reactions. Some heavily substituted derivatives of **1PH** have also been reported.[19–21] They have been characterized as flexible, nonaromatic structures by their NMR data.

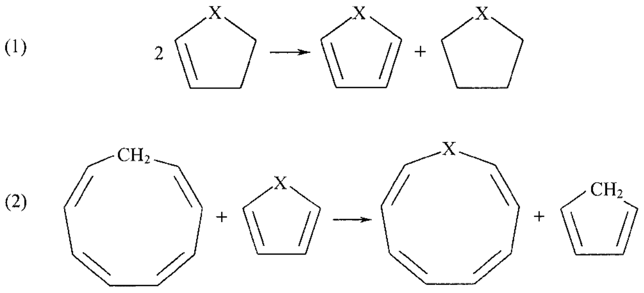


Scheme 1

Some theoretical reports are available for the heteronins **1NH**, **1O** and **1S**.[22] Early semiempirical calculations[22a–22d] (considering planar structures only) and graph-theoretical considerations[22e,22f] suggested that the aromatic character of **1NH** is the largest among the heteronins. The aromaticity of **1S** is close to that of **1NH**, but **1O** is nonaromatic, according to most of these studies, which only considered the planar structures. These were optimized (at the MNDO level) for **1NH**, **1O** and **1S** and the aromaticities of the nonplanar **1S** and **1O** were found to be rather small.[22d] The structure and aromaticity of **1O**, **1NH** and **1S** have been investigated at the B3LYP/6-311G(2d,p) level of theory in a recent paper,[22g] and compared to the corresponding five-membered heterocycles. Both **1NH** and **1S** (in contrast to the MNDO results)[22d] were found to be planar and aromatic, while **1O** is a nonplanar, nonaromatic species. The nonplanar, nonaromatic character of **1O** has been attributed to the high electronegativity of oxygen preventing effective cyclic electron delocalization. Apart from the information obtained experimentally and reviewed by Anastassiou,[10] no broad, comprehensive study of the heteronins, emphasizing their aromaticity, is available; the recent theoretical paper[22g] only considers heteroatoms O, N and S.

Computational chemistry is an ideal method to investigate the relative thermodynamic stability and the aromaticity, not only of the minimum energy forms but also of the planar structures uniformly. We now characterize the heteronins (**1X**; X = NH, N^-, PH, P^-, O, S) and **1CH**$^-$ by a variety of geometric (Bird,[23] BDSHRT[24] and HOMA[25] index), energetic (barrier to planarity and aromatic stabilization energy, ASE, see Scheme 2) and magnetic criteria (^{1}H NMR chemical shifts, nucleus-independent chemical shifts, NICS[26]). For comparison, we investigated the 8π-electron species (X = BH, AlH, CH^+,[27] NH^{2+}) as well. Depending on the geometry and the electronic state, these species have the potential of being singlet antiaromatic, singlet Möbius aromatic,[27] or triplet aromatic.[28]

Effective hyperconjugative participation of the σ-bonds in 6π-electron aromatic cyclic delocalization has recently been demonstrated to stabilize 5,5-distannylcyclopentadiene and 5,5-disilylcyclopentadiene.[29] In contrast, 5,5-difluorocyclopentadiene has the opposite behavior due to the electron withdrawal and is antiaromatic.[29–31] Is it possible to planarize and to stabilize a nine-membered ring by this kind of "hyperconjugative aromaticity"? To investigate this possibility, we also computed **1X**, where X = $C(SiH_3)_2$, $C(SnH_3)_2$, CH_2 and CF_2.



Scheme 2

Although cyclononatetraene, oxonin, thionin and phosphonin are known to be nonplanar species, annulenes can, in general, be planarized by condensed small ring attachment. Such species could be investigated experimentally, as has been reported for the cyclooctatetraene derivative **5**.[32] Like the small ring-fused cyclodecapentaenes **6**, **7**,[33] planar structures **8X** also are predicted computationally here.

Methods

Final geometries were optimized at the B3LYP/6-311+G(d,p) level of theory. Vibrational frequencies were computed at B3LYP/6-31G(d)//B3LYP/6-31G(d), also using the Gaussian-98 program package.[34] Relative energies and heats of reaction are ZPE-corrected. When small energy differences were obtained, single-point CCSD(T)/cc-pVDZ computations were performed on the B3LYP/6-311+G(d,p) geometries. For the tin-containing compounds, the LANL2DZ effective core potential was used, as implemented in the Gaussian-98 package, with polarization functions on all carbon and tin atoms (of d type with preexponential coefficients of 0.800 and 0.183, respectively). Magnetic properties (dissected NICS and δ_H relative to TMS) were computed by using the deMon Master program[35a] at the IGLO-III A5/PW91//B3LYP/6-311+G(d,p) level of theory.[35b] In some cases, in order to save computational time, HF-GIAO/6-311+G(d,p) NICS values were computed for the same geometries.

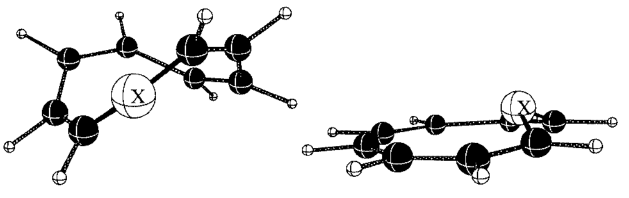
Results and Discussion

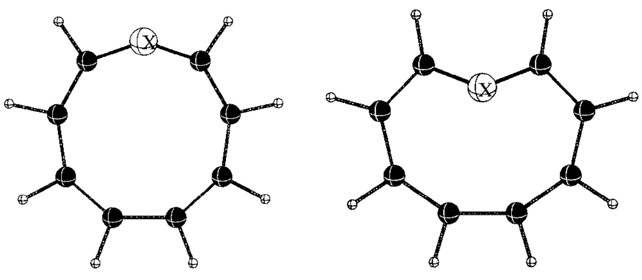
The paper is organized as follows. First we discuss the relative energies of the different possible conformations of the heteronins. Next, aromaticity, as a possible stabilizing effect of the planar C_{2v} structures will be analyzed, and compared on the basis of geometric, magnetic and energetic aromaticity criteria. The difference in the aromaticity ordering of the C_{2v} structures and their relative stability with respect to the nonplanar conformers will be discussed, considering other destabilizing (ring strain) and stabilizing (Möbius aromaticity of the 8π systems) effects, as well as triplet excited states. Finally, we consider substituent effects, which can stabilize the planar structures, resulting in potentially synthesizeable aromatic heteronins.

Conformations

The conformations considered for the heteronins, **1X**, are shown in Figure 1. Apart from the D_{9h} conformation of the cyclononatetraenyl anion and the potentially aromatic C_{2v} "*out*" structures of the heteronins, **1CH**$^-$ also is known to have a C_s "*in*" conformer which can rearrange to the D_{9h} form via an energy barrier of at least 30 kcal/mol (depending on the experimental conditions).[9a] The C_2 (twisted), C_s and C_1 geometries − where ring strain can be released at the cost of reduced aromaticity − were also considered in the present work.

Planar structures were computed to be minima only for **1CH**$^-$ (D_{9h} "*out*"), **1NH** (C_{2v} "*out*"), **1N**$^-$ ("*out*" and "*in*" both C_{2v}) and **1P**$^-$ (C_{2v} "*out*"). For **1CH**$^-$, the D_{9h} "*out*" is more stable than the C_s "*in*" structure by 15.7 kcal/mol [7.0 kcal/mol at the CCSD(T)/cc-pVDZ level] in agreement with the experimentally observed relative stabilities.[9] For **1C(SnH$_3$)$_2$**, **1O**, **1S** and **1C(SiH$_3$)$_2$**, the C_{2v} "*out*" structures are 3.5, 4.2, 4.2 and 8.6 kcal/mol higher in energy, respectively, than the most stable geometries.[36] [Note that we find **1S** to be *nonplanar*, contradicting the recent statement of Salcedo et al.[22g] Consequently, we repeated their computations at the level reported,[22g] but the results confirmed our nonplanar preference. Like our B3LYP/6-311+G(d,p) results, the planar C_{2v} structure of **1S** is a transition state 4.0 kcal/mol higher in energy than the nonsymmetric minimum at the B3LYP/6-311G(2d,p) level of theory used by Salcedo et al.[22g]] The planarization energies of **1PH**, **1CH$_2$**, **1AlH**, **1BH**, **1CF$_2$** and **1CH**$^+$ exceed 10 kcal/mol (10.7, 14.3, 21.9, 22.0, 22.1 and 26.2[37] kcal/mol, respectively). Is the preference of the planar structures of **1CH**$^-$, **1N**$^-$, **1NH** and **1P**$^-$ due to their greater aromaticity than the other isoelectronic species?


C_2 (twist) C_s


C_{2v} "out" (all-cis, CNT-like) C_{2v} "in" (heart)

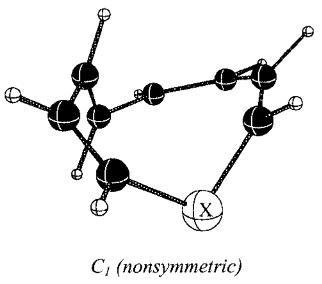

C_1 (nonsymmetric)

Figure 1. Possible heteronin conformers

Aromaticity Criteria

Various aromaticity criteria for the C_{2v} "*out*" conformers of the heteronins are compiled in Table 1. The Bird aromaticity index, which is a measure of the bond length equalization, shows small values for the 8π-electron systems (**1BH**, **1AlH** and **1CH**$^+$) and for **1CF$_2$**, in agreement with their expected antiaromaticity. The anionic species (**1CH**$^-$, **1N**$^-$ and **1P**$^-$) have the largest Bird indices. Quite large Bird aromaticity values are obtained for the C_{2v}-symmetric **1PH**, **1S** and **1NH**, while those for **1O**, **1C(SiH$_3$)$_2$** and **1C(SnH$_3$)$_2$** are intermediate.

Aromaticity, as a manifestation of the ring current arising from the cyclic electron delocalization, can be described by the chemical shift of the ring protons, or better, by the nucleus-independent chemical shifts (NICS).[26] The NICS values are a composite of contributions from the σ-skeleton (which diminishes rapidly above the ring)[26b] and from the π-system, which exerts a longer-range diamagnetic effect for aromatics. Good aromaticity characterizations are NICS$_\pi$(0), the π contribution at the ring center (which can be obtained from the IGLO program)[26b,35] and NICS(1), the total value 1 Å above the center (which can be obtained by most magnetic property programs). NICS(1) often is quite close to the NICS$_\pi$(1) value due to the reduction and the cancellation of the σ contribution (cf. Table 1). The behavior of NICS data of the C_{2v} "*out*" heteronins resembles that of the geometric aromaticity indices. The 8π-electron **1BH** and **1CH**$^+$ are clearly antiaromatic; **1AlH** and **1CF$_2$** also have some antiaromatic character (NICS $>$ 0), whereas the anions and **1NH** are the most aromatic systems. The NICS values of the hyperconjugated **1C(SiH$_3$)$_2$** and **1C(SnH$_3$)$_2$** are like those of oxonin, **1O**. Note that **1CH$_2$** exhibits small negative NICS values due to the local shielding effects of the four double bonds. NICS values for the C_{2v}-symmetric **1CH**$^-$, **1CH$_2$** and **1CH**$^+$ can serve as references for the evaluation both of the "aromatic" and the "antiaromatic" NICS data.

The aromatic stabilization energies of the planar structures have been estimated by comparing the heteronins to the corresponding five-membered heterocycles (see Scheme 2), by employing the C_{2v} "*out*" structures of the heteronins and the cyclononatetraene, **1CH$_2$**. The ASEs of the five-membered ring systems were evaluated by using Equation (1) in Scheme 2. The aromatic stabilization ener-

Table 1. Aromaticity criteria for the planar C_{2v} "*out*" heteronins

X[g]	NICS(0)/**NICS$_\pi$(0)**[a]	NICS(1)/**NICS$_\pi$(1)**[a]	Bird[b]	BDSHRT[24]	HOMA[c]	ΔE_{plan} [d]	ASE[e]	$\delta_H(\gamma,\delta)$[f]	No. of imaginary frequencies
	ppm	ppm	–	–	–	kcal/mol	kcal/mol	ppm	–
BH	+21.0/**+14.8**	+16.6/**+14.4**	29.9	47.5	–	22.0	+9.6	3.5, 3.4	2
AlH	+7.2/**+2.2**	+5.3/**+3.2**	41.7	50.3	–	21.9	+1.3	5.3, 5.2	2
CH$^+$	[h]	[h]	56.9	57.2	+0.37	26.2	+18.9	[h]	2
CH$_2$	−4.8/**−9.6**	−5.1/**−6.2**	49.1	54.1	+0.09	14.3	−2.8	7.1, 7.1	1
CH$^-$	−14.3/**−19.0**	−12.7/**−14.0**	100	58.9	+0.95	0	−55.6	7.1, 7.1	0
NH	−12.9/**−18.2**	−11.5/**−12.7**	78.3	59.7	+0.91	0	−24.6	7.8, 7.9	0
N$^-$	−14.0/**−19.0**	−12.5/**−13.0**	94.8	59.8	+0.96	0	−41.7	7.1, 7.0	0
PH	−14.4/**−18.7**	−12.8/**−13.7**	83.3	66.0	+0.97	10.7	−2.0	8.1, 8.2	1
P$^-$	−13.8/**−18.0**	−12.4/**−13.4**	96.4	59.2	+0.91	0	−34.3	7.4, 7.3	0
O	−10.8/**−16.2**	−9.9/**−11.2**	65.6	58.1	+0.67	4.2	−13.0	7.5, 7.8	1
S	−12.4/**−17.3**	−11.2/**−12.7**	79.8	61.4	+0.88	4.2	−10.8	8.1, 8.2	1
CF$_2$	+5.6/**−0.4**	+3.8/**+1.6**	31.0	51.1	−0.28	22.1	+8.4	5.5, 5.7	2
C(SiH$_3$)$_2$	−9.1/**−13.0**	−8.8/**−9.2**	66.1	56.5	+0.42	8.6	−5.4	7.7, 7.7	1
C(SnH$_3$)$_2$	−10.4/**−16.2**	−9.9/**−11.9**	75.4	53.6	+0.51	3.5	−9.8	7.9, 8.0	1

[a] NICS(0) denotes nucleus-independent chemical shift at the geometrical center of the ring and NICS(1) stands for NICS at 1 Å above the center. [b] Bird indices[23] are calculated on the basis of the H_3C-X single and $H_2C=X$ double bond lengths at the B3LYP/6-311+G(d,p) level of theory. [c] HOMA values are computed via the "virtual CC bond length" approach. [d] The barrier to planarity was obtained as the difference of the B3LYP/6-31G(d) ZPE corrected B3LYP/6-311+G(d,p) total energy of the most stable and the C_{2v} conformers. [e] Aromatic stabilization energies were computed as the sum of the heats of the homodesmotic reactions (1) and (2), shown in Scheme 2. [f] ^{1}H chemical shifts of the γ and δ protons were computed at the same level as NICS. [g] According to **1X**. [h] Due to wavefunction instability, these values (although indicating strong paramagnetic ring currents) are not reliable.

gies in Table 1 are the sum of the energies of reactions (1) and (2).[38]

The anions are stabilized most, due to the greater charge distribution than in the corresponding anions of the five-membered heterocycles. Note that the widened CCC bond angle in the allyl anion (132°)[39] corresponds more closely to the average angle in the nine-, rather than in the five-membered rings. Hence, the negatively charged rings should be less strained in the planar **1CH$^-$**, **1N$^-$** and **1P$^-$** conformations, compared to the planar forms of **1CH$_2$**, **1NH** and **1PH**. The predicted stabilization energy is also high for **1NH**, moderate for **1O**, **1S** and **1C(SnH$_3$)$_2$**, and smaller for **1C(SiH$_3$)$_2$**. For **1CH$_2$** and **1PH** (see below) the stabilization is near zero. Among the unfavorable C_{2v}-symmetric 8π-electron heteronins, the destabilization is slight for **1AlH**, moderate for **1BH** and **1CF$_2$**, and largest for **1CH$^+$**.

Note that hyperconjugation can be effective in the heteronins. As the different aromaticity measures for C_9H_8X systems [X = CH^+, CF_2, CH_2, $C(SiH_3)_2$, $C(SnH_3)_2$, and CH^-] compared in Figure 2 show, **1CF$_2$** has significant antiaromatic character but **1C(SiH$_3$)$_2$** and **1C(SnH$_3$)$_2$** are moderately aromatic (like **1O**). This behavior is similar to our previous results for five-membered rings.[29]

The different aromaticity criteria of the planar C_{2v} structures correlate well with each other with the exception of **1PH**. The stabilization energy is low, as computed by the isodesmic reactions (1) and (2), while high aromaticity can be concluded on the basis of geometric and magnetic measures. The energies from reactions (1) and (2) are misleading, since the five-membered phosphole and the fully and partially saturated reference structures in reaction (2) involve tricoordinate phosphorus and have nonplanar PH groups. All of these forms are more stable than the corresponding planar structures due to the high inversion barrier at the tricoordinate phosphorus atom.[40–42] The stabilization given by reaction (1) becomes −14 kcal/mol when planar phosphole and planar reference molecules are used. The stabilization given by reaction (2) is −26.7 kcal/mol, when all phosphorus environments are planar.

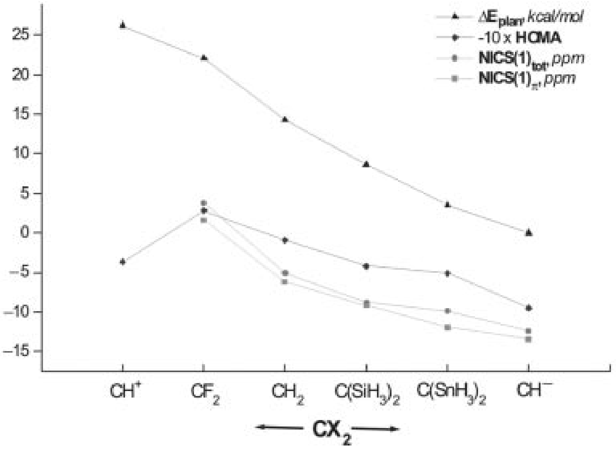


Figure 2. Comparison of various aromaticity criteria for the hyperconjugated $(CH)_8CX_2$ species (C_{2v} "*out*" conformation)

The conjugative ability of a *planar* tricoordinate phosphorus atom is known to be excellent.[42,43] The sum of the energies from reactions (1) and (2) is about 40 kcal/mol, being among the highest stabilization energies in Table 1 (cf. **1CH$^-$**, **1N$^-$**, **1P$^-$**) This agrees with the other high aromaticity indexes obtained for C_{2v}-symmetric **1PH**. Phosphole behaves similarly; the planar structure, which is also a saddle point rather than a minimum, is highly aromatic.[40−42] The inversion barrier of the tricoordinate phosphorus atom in phosphole is low, only 18.0 kcal/mol,[41] but it is even lower, 10.7 kcal/mol, in **1PH**. Since its inversion barrier is decreased by opening one of its valence angles,[42] the planar tricoordinate phosphorus atom is accomodated better in a nine- than in the five-membered ring. Thus, note the 14 kcal/mol stabilization energy given by reaction (1) when the phosphorus environments are planar in both the nine- and the five-membered rings; this is mainly attributable to the alleviation of the angle strain at the planar tricoordinate phosphorus atom in the planar nine-membered ring.

This alleviation of the ring strain helps to planarize the tricoordinate phosphorus atom in **1PH**. However, in the minimum energy structure of **1PH** both the tricoordinate phosphorus atom and the entire ring are nonplanar. Similarly, **1S**, in agreement with the observations of Salcedo et al.,[22g] exhibits rather high aromaticity in its C_{2v} form (see Table 1) but is nonplanar. Ring strain, which should be rather high in both **1PH** and **1S**, is responsible for this behavior. The smaller bond angles (93−95° in H_3P and H_2S) favored by second-row elements are difficult to accommodate in planar nine-membered rings, where the bond angles average 140°. Whereas the nonplanarity of **1O** can be attributed (in agreement with Salcedo et al.[22g]) to a reduction in aromaticity due to the strong electron-localizing effect of oxygen, the nonplanarity of **1S** is attributable mainly to angle strain.

The geometric and magnetic criteria essentially agree on the following aromaticity order of the C_{2v} heteronins: **1CH$^-$** > **1N$^-$** > **1PH** > **1P$^-$** > **1NH** > **1S** > **1O** > **1C(SnH$_3$)$_2$** > **1C(SiH$_3$)$_2$** > **1CH$_2$** > **1CF$_2$** >**1AlH** > **1BH** > **1CH$^+$**. This aromaticity ordering agrees nicely with the π-donor ability of the heteroatom lone pair, similarly to the case of the five-membered heteroaromatic systems. On the other hand, the ASE order parallels the planarization energy more closely; the C_{2v} forms of **1PH** and **1S** are rather high in energy (Figure 3).

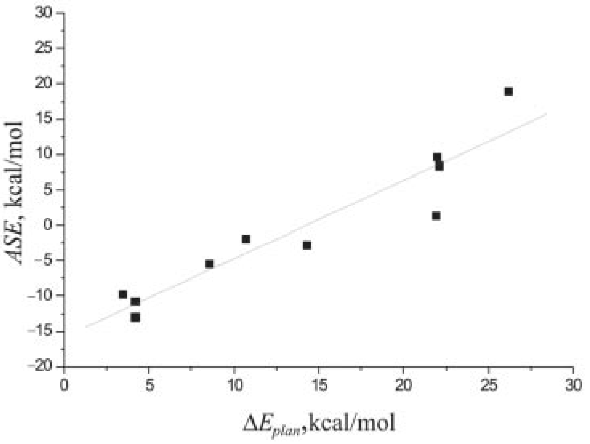


Figure 3. ASE vs. barrier to planarity

8π-Electron Systems

Like the other heteronins investigated here, the 8π-electron systems (**1CH$^+$**, **1BH**, **1AlH** and the hyperconjugated **1CF$_2$**) have singlet electronic ground states. These 8π systems favor C_2 or nonsymmetric structures; the barriers to planarity are large (more than 20 kcal/mol) due to the destabilization of the singlet antiaromatic planar C_{2v} structures. While **1CH$^+$** has the half-twist Möbius-aromatic topology, with dihedral angles between vicinal hydrogen atoms large enough (130°) to allow π overlap,[27a] **1BH**, **1AlH** and **1CF$_2$** have C_2 structures with the conjugation interrupted by the 70−90° dihedral angles between the vicinal hydrogen atoms on the C atoms in the δ positions. The measures of aromaticity collected in Table 2 document the Möbius aromaticity of singlet **1CH$^+$** clearly; **1BH**, **1CF$_2$** and **1AlH** are nonaromatic, with near-zero NICS, and small geometric aromaticity indices. Möbius aromaticity is not restricted to **1CH$^+$**. The optimized structure of the isoelectronic **1NH^{2+}** also adopts a Möbius topology, similar to **1CH$^+$**. Accordingly, the aromaticity measurements in Table 2 indicate its large cyclic electron delocalization.

Table 2. NICS(0) values and Bird indices for the potentially Möbius aromatic species

Species	NICS(0) (ppm)	Bird
1CH$_2$ (C_2)	−0.5	28.8
1CH$^+$ (C_2)	−13.6	85.4
1BH (fully optimized C_2 structur)	+0.9	26.7
1BH (HCCH dihedral is frozen as in **1CH$^+$**)	+0.02	26.0
1BH (forced in the structur of **1CH$^+$**)	−7.8	80.4
1NH^{2+} (C_2)	−14.0	83.6
1AlH (C_2)	+0.4	24.6
1CF$_2$ (C_2)	−0.9	22.1

Is the Möbius aromatic stabilization small in **1BH** and the other two 8π heteronins (**1AlH** and **1CF$_2$**)? An even distribution of the π electrons in the 8π Möbius heteronins requires the C_8H_8 fragment to serve as a net π-electron donor, and the hetero-unit as a π-electron acceptor. The electropositive boron atom is a weaker acceptor than the carbocation (or the amino dication). This situation is similar to the seven-membered ring borepin,[44] which is less aromatic than the isoelectronic tropylium cation (the HF-GIAO/6-311+G** NICS values are −3.7 and −7.4 ppm, respectively). We have calculated a −7.8 ppm NICS(0) value for a boronin (C_8H_9B) structure fixed at the optimized Möbius geometry of **1CH$^+$**. This documents the reduction in aromaticity relative to **1CH$^+$**. Optimizing **1BH** further by relaxing all constraints other than the near 130° dihedral angle of the vicinal hydrogen atoms (in the δ positions), the NICS(0) value dropped to 0.0 ppm, and the alternation of the C−C bond lengths increased significantly, resulting in a small Bird index (26.0, Table 2).

The difference of B vs. C+ conjugation was also shown by comparing the rotational barriers at the terminal C−C bonds of $H_2C^+{-}CH{=}CH{-}CH{=}CH_2$ (21.0 kcal/mol) with

$H_2B-CH=CH-CH=CH_2$ (only 8.3 kcal/mol; both at B3LYP/6-311+G**). The smaller conjugation in **1BH** not only weakens the aromaticity of the Möbius structure, but also alleviates ring strain by decoupling the double bonds and allowing rotation.

Triplet States

The **1CH$^+$** triplet state favors a "shallow-dish" C_s structure with nearly identical (1.401−1.407 Å) bond lengths. The **1BH** triplet is similar, but has a "soup-bowl" geometry and a much larger (1.363−1.442 Å) range of C−C bond lengths. The **1AlH** triplet has a nonsymmetric, deformed minimum. The relative energies of some singlet and triplet 8π heteronins are collected in Table 3. It has been pointed out by Baird,[44] and later fully elaborated by Schleyer and co-workers,[45] that the Hückel aromaticity/antiaromaticity is reversed between the singlet and the triplet systems. **1CH$^+$** has been found to be strongly aromatic in the triplet state, and its C_s structure was found to be more stable than the C_s singlet by 1.2 kcal/mol.[28] Nevertheless, the singlet C_2 (Möbius aromatic − see above) structure of **1CH$^+$** is more stable than the triplet by 24.1 kcal/mol. Among the heteronins, **1BH** and **1AlH** would also be candidates for 8π-electron triplet aromaticity. We have found, however, that these species have a singlet C_2 conformation that is much more stable than both the triplet C_2 and C_{2v} alternatives (see Table 3). The aromaticity in triplet **1BH** and **1AlH** is low even in the C_2 form (e.g. NICS is near to zero). This agrees with our failure to locate Möbius-aromatic singlet **1BH** and **1AlH** forms since the cyclic conjugation energies of these systems must be too low.

Table 3. ZPE-corrected relative energies of the 8π-electron heteronins and **1CH$^+$** in their singlet and triplet electronic state (based on the B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) energies and ZPEs)

	Singlet state		Triplet state	
	C_{2v}	C_2	C_{2v}	C_2
$1CH^+$	24.1	0.0	22.7	19.0
1BH	22.0	0.0	35.1	55.8
1AlH	20.9	0.0	43.0	29.4

Experimentally Realizable Planar Heteronins

As pointed out in the introduction, cyclooctatetraene and the strained [10]annulene can be planarized by the attachment of small rings as in **5**,[32] **6** and **7**.[33] Likewise, annelation of the C=C bonds by three-membered rings results in planar nine-membered rings: **8CH$_2$**, **8O** and **8S** have planar minima with well equalized bond lengths. Furthermore, the planarization barrier of **8PH**, 7.6 kcal/mol, is smaller than the 10.7 kcal/mol computed for **1PH** (Table 1). A further reduction of the inversion barrier to only 1.8 kcal/mol (B3LYP/6-31G*) is achieved by attaching a bulky 2,6-di-*tert*-butylphenyl group (known to "flatten" σ^3,λ^3-P atoms).[42,46] The fully optimized structure has a 341° bond angle sum about the phosphorus atom; consequently, the aromaticity of this derivative is high, as shown by its large Bird index of 84.7. Since the computed properties of the planar compounds **8X** are close to those of the C_{2v}-symmetric **1X**, these aromatic heteronins should be experimentally realizable.

Conclusions

Among heteronins, **1X**, only **1N$^-$**, **1NH**, and the experimentally unknown **1P$^-$** are planar, aromatic systems (similar to **1CH$^-$**). The heteroatoms affect the extent of cyclic electron delocalization of the planar C_{2v} structures as in the analogous five-membered rings. **1CH$^-$** and **1CH$^+$** provide the upper and lower bounds for the aromaticity/antiaromaticity of the C_{2v}-symmetric heteronins. While **1CH$_2$** is nonaromatic even when C_{2v} symmetry is imposed, hyperconjugation in **1C(SiH$_3$)$_2$** and **1C(SnH$_3$)$_2$** is effective and their C_{2v} forms are moderately aromatic and resemble the corresponding five-membered rings.[29] Conversely, C_{2v}-symmetric **1CF$_2$** is slightly antiaromatic. The planarity of the heteronins is governed by two opposing factors: the extent of the cyclic electron delocalization and the angle strain. Negative charge delocalization contributes to the planarity of the anions. Despite the considerable aromaticity of planar C_{2v}-symmetric **1PH** and **1S**, they both favor nonplanar structures which alleviate the angle strain induced by the relatively small bond angles at the heteroatoms.

While planarity constraints enhance the aromaticity of the 10π-electron systems, in agreement with the Hückel rule, the opposite is true for the 8π-electron systems. **1NH^{2+}** **1CH$^+$**, **1BH** and **1AlH** avoid the antiaromatic destabilization as well as the ring strain by adopting C_2 (or similar nonsymmetric) conformations. This offers the possibility of stabilization due to 8π Möbius aromaticity,[27] but this only occurs with **1CH$^+$** and **1NH^{2+}**. The other 8π heteronins (**1BH**, **1AlH** and **1CF$_2$**, with weak electron acceptor groups) are simply nonaromatic. Among the planar 8π systems, triplet **1CH$^+$** is aromatic due to its half-filled degenerate π shell.[28,45] However, triplet **1CH$^+$** is 24 kcal/mol less stable than the Möbius aromatic singlet. The aromaticities of the planar **1BH** and **1AlH** triplets are rather low.

Heteronins can be planarized by three-membered ring annelation. The **8X** species (with the exception of **8PH** which has a 7.6 kcal/mol barrier to planarity) were found to be minima. The barrier to inversion can be reduced further; in **8PR** (R: di-*tert*-butylphenyl) it is only 1.8 kcal/mol (B3LYP/6-31G*). Annelation reduces the angle strain of the nine-membered rings. The CC bond lengths of the planar **8X** systems are close to those of the planar-constrained (C_{2v}) **1X** analogs. This shows how monocyclic 10π Hückel aromatic systems with nine-membered rings might be realized.

Supporting Information Available

B3LYP/6-311+G(d,p) total energies and optimized structures in cartesian coordinates (see footnote on the first page of this article).

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