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4n π Electrons but Stable: *N*,*N*-Dihydrodiazapentacenes

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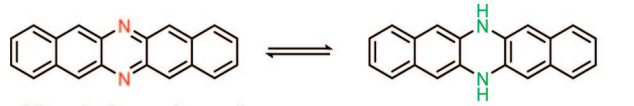
Received April 3, 2009



Despite having 4n π electrons, dihydrodiazapentacenes are more viable than their 4n+2 π azapentacene counterparts. *Ab inito* valence bond block-localized wave funtion (BLW) computations reveal that despite having 4n π electrons, dihydrodiazapentacenes are stabilized and benefit substantially from four dihydropyrazine ethenamine (enamine) conjugations. Almost all of these dihydrodiazapentacenes have large negative overall nucleus independent chemical shifts NICS(0)$_{\pi zz}$ values even though their dihydropyrazine rings (e.g., for **6**-H$_2$) are modestly antiaromatic, as their paratropic contributions are attenuated by delocalization throughout the system.

Introduction

Polycyclic six membered ring molecules with 4n π electrons elicit attention, especially when their 4n+2 π electron counterparts are unstable. Remarkably, the 4n π electron dihydrodiazapentacenes (**5b**-H$_2$, **5c**-H$_2$, **6**-H$_2$ and **7**-H$_2$) have been known since the late 19th century,[1−7] but attempts to synthesize their aromatic 4n+2 π electron counterparts (**5b**, **5c**, **6** and **7**) have not succeeded (see Scheme 1).[8,9] Although **4b** and **4b**-H$_2$ (Scheme 2) were redox-interconvertable, Hinsberg noted that **6**-H$_2$ could not be oxidized to **6** (Scheme 1).[4] The 4n+2 π azaacenes resemble the parent acenes[10] in being increasingly unstable as the number of rings increase, however very recently a tetraazapentacene derivative has been synthesized by Bunz et al.[9]

How can the peculiar viability of the 4n π electron dihydrodiazapentacenes be rationalized? The larger parent acenes usually have small HOMO−LUMO gaps and are not persistent[11−14] unless protected by bulky substituents at strategic positions.[15−18] Furthermore, Houk and Wudl noted that heptacene and the higher acenes had singlet diradicaloid character.[13] By analogy the azaacenes (**5b**, **5c**, **6** and **7**, Scheme 1) are to show a small band gap and increased reactivity. So why are the 4n π electron dihydrodiazapentacenes so viable and perhaps more stable than their formally aromatic 4n+2 π azapentacene derivatives? The dihydrodiazapentacenes (24 π electrons) have more π electrons than the azapentacenes (22 π electrons) at the cost of incorporating a formally antiaromatic 8π electron dihydropyrazine

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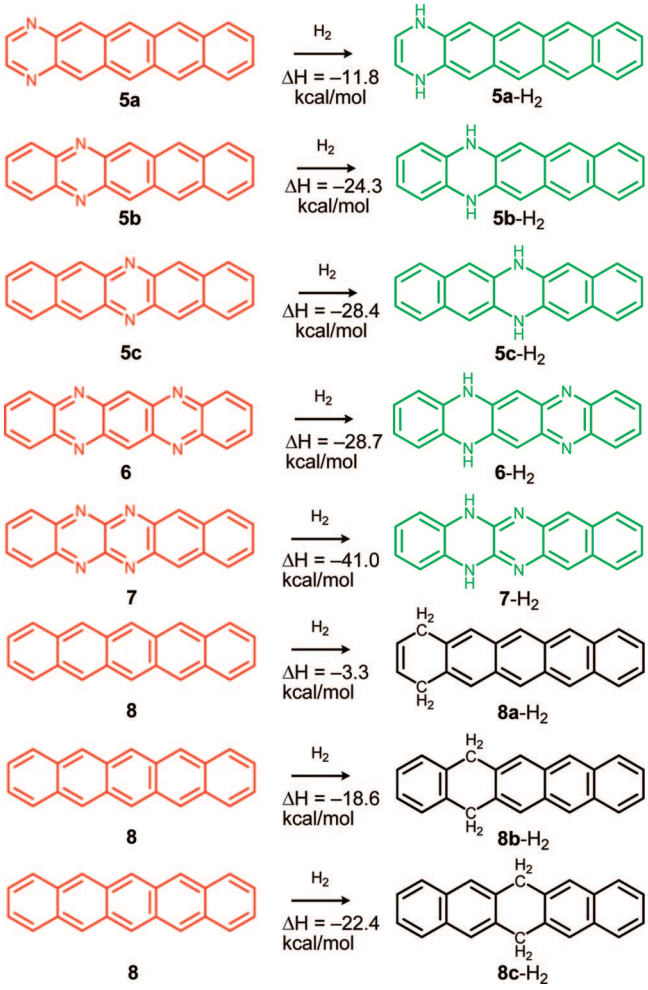
10.1021/jo900684c CCC: $40.75
Published on Web 05/12/2009

SCHEME 1. Heats of Hydrogenation for the Diazapentacenes 5−7 and Pentacene 8 Reduced to the Dihydroazaacenes 5(a−c)-H_2-7-H_2 and Dihydropentacenes 8(a−c)-H_2[a]

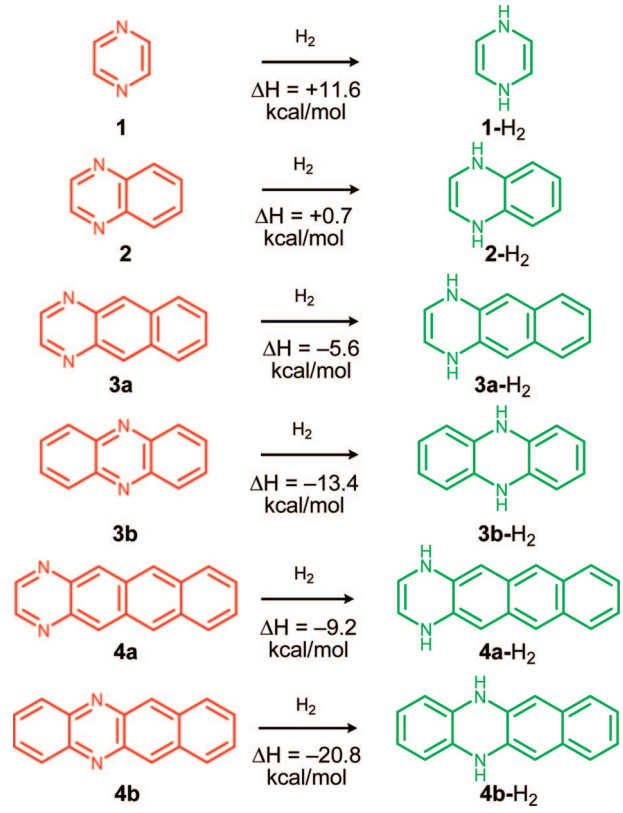


[a] All data are computed at the B3LYP/6-311+G** level including ZPE correction. Compounds with a 4n+2 π perimeter are traditionally aromatic (in red); formally antiaromatic compounds have a 4n π perimeter (in green).

moiety. But rather than having three butadiene-like conjugations, each of the dihydropyrazine rings have four ethenamine (enamine) conjugations instead. How large are these ethenamine stabilizations? Are they sufficient to overcome the energetic penalty of the unfavorable 4n π electron count? The planarity of the dihydrodiazapentacenes suggests that they are not very antiaromatic. Thus, Nuckolls postulated that the unusual stability of both **5b**-H_2 and **5c**-H_2 was related to breaching the π conjugation of the pentacene framework into smaller aromatic subunits.[6] While both **5b**-H_2 and **5c**-H_2 can have two Clar rings,[19] but **5b** and **5c** only one, is this explanation adequate to resolve the unusual stability of the 4n π dihydrodiazapentacenes?

Current interest in these nitrogen-containing heteroacenes[20−23] arises from their potential applications as organic thin film transistors.[24] Nevertheless, there have not been any systematic studies explaining the unexpected existence of the 4n π electron dihydrodiazapentacenes. The questions we wish to answer in this paper are: What is responsible for the viability of the formally antiaromatic 4n π dihydrodiazapentacenes? To what extent do the ethenamine moieties confer energetic stabilization? Despite having 4n π electrons, do the dihydrodiazapentacenes still benefit from aromaticity?

SCHEME 2. Heats of Hydrogenation for the Smaller Azaacenes 1−4 Reduced to Dihydroazaacenes 1-H_2-4(a−b)-H_2[a]



[a] All data are computed at the B3LYP/6-311+G** level including ZPE correction. Compounds with a 4n+2 π perimeter are traditionally aromatic (in red); formally antiaromatic compounds have a 4n π perimeter (in green).

Results and Discussion

We computed the heats of hydrogenation for both the 4n+2 π electron azaacenes and their parent acenes (number of rings $N = 1-5$) by evaluating the cross ring 1,4-hydrogenation reaction energies for each of the different rings of the various compounds. The resonance energies (REs) and aromatic stabilization energies of the 4n π dihydrodiazapentacenes and 4n+2 π azapentacenes were evaluated based on Mo's *ab initio* block-localized wave function (BLW)[25] procedure (see Methods). Nucleus Independent Chemical Shift (NICS)[26] computations (see Methods) characterized the magnetic aromaticity of these 4n and 4n+2 π species.

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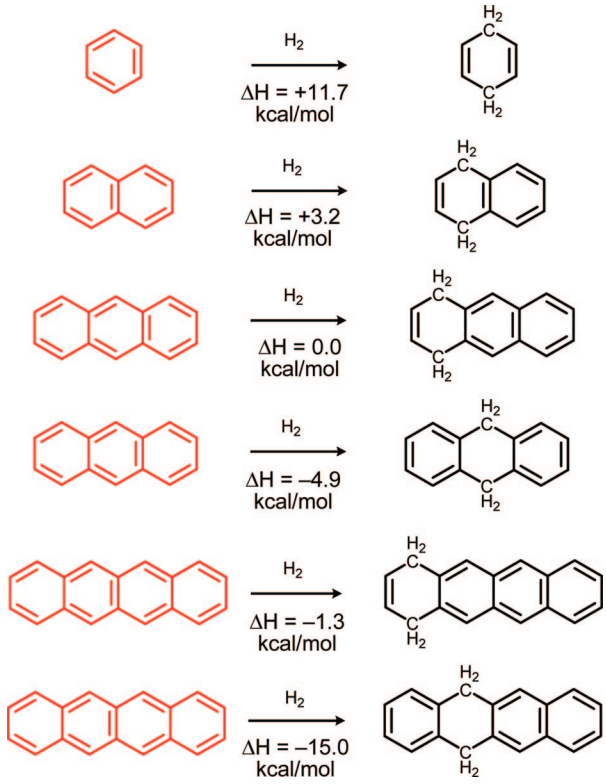
SCHEME 3. Heats of Hydrogenation for the Smaller Acenes Reduced to Dihydroacenes[a]



[a] All data are computed at the B3LYP/6-311+G** level including ZPE correction.

Heats of Hydrogenation ($\Delta H(H_2)$). As expected from the instability of the larger acenes, the computed $\Delta H(H_2)$ for the azaacenes and their parent acenes become increasingly exothermic as the number of rings increase (Schemes 1, 2 and 3). The $\Delta H(H_2)$ for pyrazine **1** and benzene are endothermic, due to the loss of aromaticity in dihydropyrazine and 1,4-cyclohexadiene (Scheme 2 and 3). Although dihydropyrazine **1**-H_2 is destabilized by antiaromaticity (eight π electrons), it is stabilized by four ethenamine conjugations involving the N lone pairs, while 1,4-cyclohexadiene is nonaromatic, and it is stabilized by four hyperconjugations instead. Thus, the $\Delta H(H_2)$ values for pyrazine and benzene are essentially the same.

In contrast, the $\Delta H(H_2)$ for the larger azaacenes ($N = 3$ to 5) are more exothermic than their acene parents (by 5 to 8 kcal/mol, Scheme 1). Unlike **1**-H_2, the ring π electrons of the dihydropyrazine moieties of the dihydrodiazaacenes are not confined to a single six-memberd ring, but can delocalize to adjacent benzenoid rings. For this reason, the dihydropyrazine rings of the 4n π dihydrodiazaacenes are expected to be less antiaromatic (see also ECRE section, below). Hence, the fully conjugated dihydrodiazaacenes are stabilized to a greater extent compared to their corresponding dihydroacenes, involving hyperconjugation.

Note that the $\Delta H(H_2)$ for various azaacene and acene isomers differ depending on the position of the hydrogenated ring. Those with a reduced "inner ring" (e.g., **5(b−c)**-H_2 and **8(b−c)**-H_2) have greater $\Delta H(H_2)$'s than those with the "outer ring" hydrogenated (e.g., **5a**-H_2 and **8a**-H_2); as the former results in two Clar rings, but the latter only in one (see Scheme 1). Clar's rule states that isomers with a maximum number of sextet rings are advantageous energetically.[19] Thus, the $\Delta H(H_2)$ of **3b**, **4b**, **5b** and **5c** are twice as exothermic as their 1,4-dihydro isomers, **3a**, **4a** and **5a**. The acenes demonstrate the same trend.

The $\Delta H(H_2)$ for the tetraazapentacenes (**6** and **7**) are especially exothermic. Both **6**-H_2 and **7**-H_2 enjoy an internal stabilization between the dihydropyrazine and pyrazine ring, as the NH group lone pair of the dihydropyrazine rings alleviates the sigma electron withdrawing effect of the electron deficient pyrazine ring. This synergistic stabilization is smaller for **6** (−3.1 kcal/mol, eq 1) but quite large for **7** (−12.3 kcal/mol, eq 2).

$$\mathbf{5b}\text{-}H_2 + \mathbf{5b} \rightarrow \mathbf{6}\text{-}H_2 + \mathbf{8}\Delta H = -3.1 \text{ kcal/mol} \quad (1)$$

$$\mathbf{5b}\text{-}H_2 + \mathbf{5c} \rightarrow \mathbf{7}\text{-}H_2 + \mathbf{8}\Delta H = -12.3 \text{ kcal/mol} \quad (2)$$

In agreement with the absent experimental reports of 4n+2 π electron diazapentacenes, their heats of hydrogention leading to the 4n π electron dihydrodiazapentacenes are highly exothermic. Pentacene also behaves similarly, but has less exothermic heats of hydrogention compared to that of the corresponding diazapentacenes. Dihydrodiazapentacenes are stabilized by conjugation and leave the dihydropyrazine moieties less antiaromatic than **1**-H_2.

Resonance Energy (RE). The resonance energies (RE) of the dihydrodiazapentacenes and diazapentacenes were evaluated, based on the Pauling−Wheland definition,[27] by the total energy difference between the fully conjugated compound and its most stable resonance contributor, employing the BLW procedure (see Methods). Remarkably, 4n π dihydrodiazapentacenes (**5a**-H_2, **5b**-H_2, **5c**-H_2, **6**-H_2 and **7**-H_2) have significantly greater PWREs (30 to 55 kcal/mol, see Table 1) than their corresponding 4n+2 π derivatives (**5a**, **5b**, **5c**, **6** and **7**) (Table 1), as they benefit from the conjugated ethenamine (**9**)-like subunits of their dihydropyrazine rings. Each 4π electron ethenamine moiety has a conjugated CC double bond and an N lone pair. Note that there are four ethenamine subunits in each dihydropyrazine ring, but none for the pyrazine rings of the 4n+2 π diazapentacenes (as their N lone pairs are in the ring plane). On the basis of the BLW computed RE for ethenamine **9**, each of these conjugations is worth 20 kcal/mol; this value is remarkably large compared to the PWRE of butadiene **10** (12.2 kcal/mol) (see Table S1, Supporting Information). Thus, the RE of aniline (80.3 kcal/mol, C_{2v}) also is greater than styrene (71.5 kcal/mol). Since this feature is present four times for each dihydropyrazine ring, the ethenamine stabilization for each dihydrodiazapentacene might approach 80 kcal/mol. This could account for 25−30% of the total RE of the dihydrodiazapentacenes and is comparable to

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TABLE 1. RE and ECREs of the Azaacenes (1−7) and Dihydroazaacenes (1-H_2 to 7)[a]

compd	PWRE (kcal/mol)	ECRE (kcal/mol)
1	59.8	+30.0
1-H_2	50.3	−1.1
planar-**1**-H_2	56.9	−11.7
2	110.7	+48.8
planar-**2**-H_2	123.8	+20.2
3a	156.5	+58.5
planar-**3a**-H_2	178.8	+38.7
3b	154.4	+59.2
planar-**3b**-H_2	190.9	+52.3
4a	202.1	+67.8
planar-**4a**-H_2	227.2	+52.0
4b	200.4	+70.1
planar-**4b**-H_2	243.5	+68.4
5a	245.8	+70.5
5a-H_2	274.2	+65.3
5b	242.5	+70.1
5b-H_2	291.3	+82.5
5c	242.1	+76.7
5c-H_2	296.1	+84.5

[a] All BLW data are computed at the B3LYP/6-31G* level.

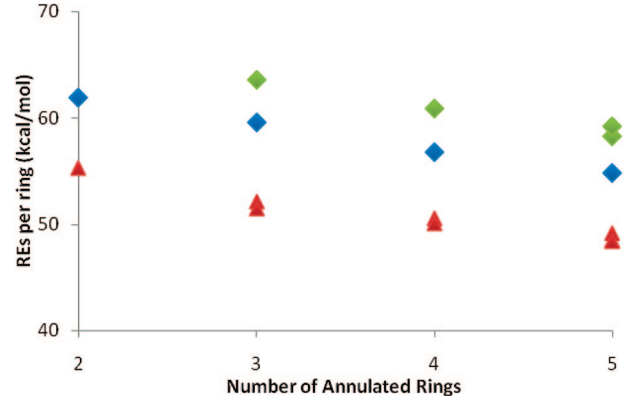

FIGURE 1. Resonance energies (REs) per ring vs the number of annulated rings ($N = 2-5$) for the dihydroazaacenes (**2**-H_2 to **5(a−c)**-H_2; blue and green rhomboids) and diazaacenes (**2** to **5(a−c)**; red triangles). The 1,4-dihydroazaacenes (**2**-H_2, **3a**-H_2, **4a**-H_2 and **5a**-H_2) are in blue; their isomers with reduced inner rings (**3b**-H_2, **4b**-H_2 and **5(b−c)**-H_2 are in green. All BLW data were computed at the B3LYP/6-31G* level.

the PWRE of benzene (61.4 kcal/mol)! For the same reason, the smaller 4n π dihydrodiazaacenes (number of annulated rings: $N = 2-4$) also have REs (10 to 45 kcal/mol) greater than their 4n+2 π cogeners (Table 1).

Note that the PWREs of the dihydrodiazapentacenes depend on the positions of their dihydropyrazine rings, due to the number of Clar rings available. Both **5b**-H_2 (291.3 kcal/mol) and **5c**-H_2 (296.1 kcal/mol) have greater REs than **5a**-H_2 (274.2 kcal/mol). The smaller dihydrodiazaacenes ($N = 2$ to 4) with reduced "inner" dihydropyrazine moieties also have greater REs than their outer 1,4-dihydro isomers. As expected from Clar's rule, isomers with a maximum number of sextet rings energetically more stable.[19] Hence, dihydrodiazaacenes with reduced "inner" dihydropyrazine moieties benefit from having two (instead of one) Clar rings (see the discussion in ECRE section). Both **5b**-H_2 and **5c**-H_2 have two Clar rings, and thus are energetically more favorable than **5a**-H_2, which has only one.

On a per ring basis, the REs of both the diazaacene and dihydrodiazaacene series (number of rings $N = 2-5$) decrease as the number of annulated rings increase (Figure 1),[10] but all of the 4n π dihydrodiazaacenes (Figure 1, green and blue rohmboids) have greater REs *per ring* than their corresponding 4n+2 π azaacenes (Figure 1, red triangles), as they are stabilized by the ethenamine conjugation. The number and positions of the pyrazine rings do not affect the REs of the various azapentacene isomers (e.g., **5a**, **5b** and **5c**), but those of the dihydrodiazapentacenes differ significantly depending on the positions of their dihydropyrazine ring and number of Clar rings available (see above).

Despite their 4n π electrons, dihydrodiazapentacenes have considerably larger REs than the 4n+2 π azapentacenes due to the ethenamine conjugations. Clar's rule rationalizes the different RE values for various dihydrodiazapentacene isomers but is inadequate to explain the 30−55 kcal/mol RE difference between the related 4n π and 4n+2 π species. Thus, the RE difference between phenanthrene (165.2 kcal/mol, two Clar rings) and anthracene (157.5 kcal/mol, one Clar ring) is less than 10 kcal/mol. Like the parent acenes and 4n+2 π electron azaacenes, the larger 4n π electron dihydrodiazaacenes also become increasingly unstable as the number of rings increase[10] but are stabilized substantially by the ethenamine conjugations.

Extra Cyclic Resonance Energy (ECRE). The ECRE[28] measures the aromatic stabilization (destabilization) energy for cyclic conjugated compounds, and is derived from the BLW computed RE of the aromatic (or antiaromtic) compound minus the RE sums of appropriate number and types of acyclic conjugation (including ethenamine) references (see Methods). Thus, all energetic effects other than aromaticity (or antiaromaticity) are canceled out in the ECRE procedure.[28] Positive ECREs indicate aromaticity and negative ECREs indicate antiaromaticity.[28] For example, the ECRE of benzene (+29.3 kcal/mol) is derived from the RE of benzene (61.4 kcal/mol) minus the RE sum of three *syn*-butadienes (10.7 kcal/mol each), as they resemble the three butadiene conjugations of benzene.

Remarkably, all of the 4n π electron dihydrodiazapentacenes have *positive* ECREs (see Table 1) and thus are stabilized by aromaticity. Since all energetic effects other than aromaticity are canceled out in the ECRE procedure, the ECRE difference between the 4n+2 π dihydrodiazapentacenes and their corresponding 4n+2 π azapentacenes depends only on the different number of Clar rings present and the antiaromaticity of the dihydropyrazine rings of the dihydroazapentacens. Thus, the ECRE difference between **5a**-H_2 (+65.3 kcal/mol) and **5a** (+70.5 kcal/mol) accounts for the antiaromaticity of the dihydropyrazine ring, as both species can have only one Clar ring. Note that this 5.2 kcal/mol destabilization is only half the ECRE (−11.7 kcal/mol) of the parent dihydropyrazine, planar-**1**-H_2 (see Table 1).

By contrast, both **5b**-H_2 and **5c**-H_2 have *more positive* ECRE values (ca. 10 kcal/mol) than their 4n+2 π **5b** and **5c** counterparts (see Table 1) and thus are more aromatic! Both **5b**-H_2 and **5c**-H_2 benefit from having two (instead of one) Clar rings, although they also suffer from the antiaromaticity of their dihydropyrazine rings (ca. 5 kcal/mol). Thus, the Clar stabilization for **5b**-H_2 and **5c**-H_2 is about 15 kcal/mol (ca. 3 kcal/mol per ring). This may be compared to the ECRE per ring difference (2.9 kcal/mol) between phenanthrene (165.2 kcal/mol, two Clar rings) and anthracene (157.5 kcal/mol, one Clar ring).

The ECRE per ring of the diazaacenes (Figure 2, red triangles) decreases linearly across the series ($N = 1-5$), as expected for the acenes,[10] since larger 4n+2 π systems have less aromatic

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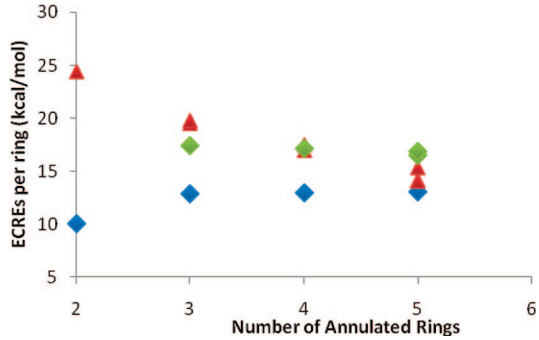

FIGURE 2. Extra cyclic resonance energies (ECREs) per ring vs the number of annulated rings ($N = 2-5$) for dihydroazaacenes (**2**-H_2 to **5(a−c)**-H_2; blue and green rhomboids) and diazaacenes (**2** to **5(a−c)**; red triangles). The 1,4-dihydroazaacenes (**2**-H_2, **3a**-H_2, **4a**-H_2 and **5a**-H_2; blue rhomboids) can have only one Clar ring, and thus have less ECRE per ring compared to their isomers (**3b**-H_2, **4b**-H_2 and **5(b−c)**-H_2; green rhomboids) with two Clar rings. All BLW data were computed at the B3LYP/6-31G* level.

stabilization per ring. The positions of the pyrazine rings do not influence the aromaticity of these species significantly. However, the ECRE per ring of the 4n π dihydrodiazaacenes are similar for $N = 3$, 4 and 5, but depend on the positions of the dihydropyrazine rings. The **b** and **c** isomers have greater ECREs (Figure 2, green rhomboids) than their 1,4-dihydro relatives (**a** isomers, Figure 2, blue rhomboids), since they can have two (instead of one) Clar rings, and thus are more aromatic.

Remarkably, the interspersed 8π electron dihydropyrazine ring of the dihydrodiazapentacenes **5(a−c)**-H_2 is not destabilized by antiaromaticity appreciably, but is stabilized by its ethenamine conjugations and its placement results in a greater number of Clar rings for **5b**-H_2 and **5c**-H_2.

Nucleus Independent Chemical Shifts (NICS). We evaluated NICS for **6**, **6**-H_2, **8** and planar-**8**-H_2 employing the localized molecular orbital (LMO) NICS with the most sophisticated $NICS_{\pi zz}$ index (see Methods).[26c,d] NICS points were computed at each of the individual heavy atom ring centers of the polycyclic compounds. The LMO approach separates the total shielding of the molecule into the localized molecular orbital contributions of bonds, lone pairs and core electrons,[29] and thus is especially useful for evaluating the aromaticities of the individual rings of polycyclic aromatic compounds, since it can distinguish the *local* and *remote* contributions of the π system to a specific ring. *Local* $NICS(0)_{\pi zz}$ values include only the contributions of the double bonds and lone pairs that are directly associated with the designated ring, while the *remote* $NICS(0)_{\pi zz}$ values include only those that are not directly involved. The *total* $NICS(0)_{\pi zz}$ incorporates all of the individual LMO contributions (both *local* and *remote* $NICS(0)_{\pi zz}$) and characterizes the aromaticity of the designated ring. The overall aromaticity of the molecule is evaluated by the *total* $NICS(0)_{\pi zz}$ sums ($\Sigma NICS(0)_{\pi zz}$) of all of the rings.

As expected by their 4n+2 π electrons count, both **6** and **8** are aromatic and have large diatropic *total* $\Sigma NICS(0)_{\pi zz}$ values (−182.3 ppm for **6** and −183.2 ppm for **8**) (see Figure 3). Note that the replacement of the four Ns in **6** has very little effect on its aromaticity, as compared to **8**. As shown in Figure 3, the *local* $NICS(0)_{\pi zz}$ of the individual benzenoid rings are largely diatropic and do not differ much from the *total* $NICS(0)_{\pi zz}$ values

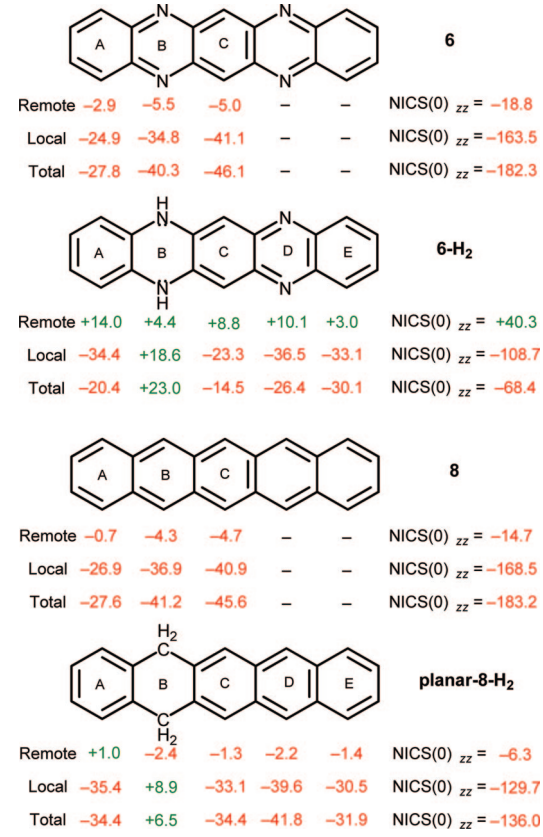

FIGURE 3. LMO $NICS(0)_{\pi zz}$ data (computed at the PW91/IGLOIII level) for the individual rings of **6**, **6**-H_2,**8** and planar-**8**-H_2. *Local* refers to $NICS(0)_{\pi zz}$ values including only π MOs that belong to the designated ring. The *remote* $NICS(0)_{\pi zz}$ are defined by the π MO contributions that are not directly involved with the designated ring. The *total* $NICS(0)_{\pi zz}$ incorporates all of the individual LMO contributions. The sums of the *local*, *remote* and *total* $NICS(0)_{\pi zz}$ values of the individual rings, $\Sigma NICS(0)_{\pi zz}$, are presented at the end of each corresponding row. The Clar rings (rings A and D for both **6**-H_2 and planar-**8**-H_2, ring C for **6** and **8**) are distinguished by their more negative *local* and *total* $NICS(0)_{\pi zz}$ values compared to their adjacent benzenoid rings.

(see Figure 3). The central Clar rings (ring C) of both **6** and **8** have the most negative *total* $NICS(0)_{\pi zz}$ values, and are the most aromatic (see Figure 3).[30] This is in line with Fowler's ring current plots of the linear acenes, which show diatropic current density concentration toward the central ring.[31] Thus, the *remote* $NICS(0)_{\pi zz}$ values are small for the outer ring (ring A), but slightly diatropic for the inner rings (rings B and C).

Planar-**8**-H_2 also is overall aromatic (*total* $\Sigma NICS(0)_{\pi zz} = -136.0$ ppm), but less so than **6** and **8**, as it involves a nonaromatic cyclohexadiene ring (ring B; *total* $NICS(0)_{\pi zz} = +6.5$ ppm) (see Figure 3, bottom). Ring B reduces the global aromaticity of planar-**8**-H_2, but has very little effect on the aromaticities of its adjacent benzenoid rings. Thus, all of the rings have small *remote* $NICS(0)_{\pi zz}$ values. By contrast, the aromaticity of **6**-H_2 (*total* $\Sigma NICS(0)_{\pi zz} = -68.4$ ppm) is greatly reduced by the delocalized paratropic contribution of ring B. Note the significant *remote* $NICS(0)_{\pi zz}$ of rings A (+14.0 ppm) and C (+8.8 ppm) (see Figure 3). However, the remote

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contributions of the benzenoid rings to ring B is rather small (*remote* NICS(0)$_{\pi zz}$ = +4.4 ppm, Figure 3). Remarkably, the diatropic contributions of the benzenoid rings are localized, but the paratropicity of the 8π electron dihydropyrazine ring is delocalized and experienced throughout the system.[32,33] Note also that the *total* NICS(0)$_{\pi zz}$ value (+23.0 ppm) for ring B of **6-**H_2 is remarkably less than the *total* NICS(0)$_{\pi zz}$ of planar-**1-**H_2 (+70.6 ppm). Thus, the dihydropyrazine ring of **6-**H_2 is much less antiaromatic than planar-**1-**H_2.

Despite having 4n π electrons, the individual benzenoid rings of dihydrodiazapentacenes exhibit magnetic characteristics of aromaticity. The antiaromaticity of the dihydropyrazine ring is attenuated.[32] The behavior of the [n]phenylenes,[33−35] in which the aromaticity of the benzenoid rings are weakened by the adjacent antiaromatic cyclobutadiene subunits, is similar.[36] The dihydrodiazapentacenes differ, since their enamine contributions are strongly stabilizing, independent of their effects on the aromaticity.

Conclusions

Our RE and ECRE evaluations of the 4n π electron dihydrodiazapentacenes reveal that they are stabilized by aromaticity as well as by the ethenamine conjugations of their dihydropyrazine rings. However, the internal 8π electron dihydropyrazine rings in these 4n π electron species are slightly antiaromatic according to our NICS data (Figure 3). The dihydrodiazapentacenes with "inner" dihydropyrazine moieties (**5b-**H_2, **5c-**H_2) can have two Clar rings and thus are more aromatic than those with an outer dihydropyrazine ring (**5a-**H_2) as well as the 4n+2 π electron diazapentacenes (**5a**−**c**). Compared to their parent acenes and azaacene derivatives,[10,13] dihydrodiazaacenes are more viable due to the stabilizing ethenamine conjugations. Dihydrodiazapentacenes are magnetically aromatic overall, although less than their 4n+2 π counterparts (see Figure 3 for numerical values).

The dihydrodiazaacenes differ from other formal 4n-π-systems like the benzannulated cyclobutadienes, which show antiaromatic properties (magnetic effects, higher energies, etc.). The dihydrodiazapentacenes are different since the stabilizing ethenamine moieties compensate for the 4n π-electron ring character.

Our study rationalizes the long known (!) but puzzling existence of the dihydrodiazapentacenes and provides a conceptual basis for designing larger viable heteroacenes and cyclacenes, with potential applications as organic-thin film transistors.[24]

Methods

All geometries were optimized at the B3LYP/6-311+G** level as implemented in Gaussian98.[37]Harmonic vibrational frequencies, computed at the same DFT level, established the character of the stationary points. Both NICS[26] and BLW[25] were computed employing the planar geometries of all compounds. Although **1-**H_2, **2-**H_2, **3(a**−**b)-**H_2, **4(a**−**b)-**H_2, and **8-**H_2 are not planar, their nonplanar minima are not much lower in energy; the planarization energies of **1-**H_2 (C_{2v}; 3.3 kcal/mol lower in energy than D_{2h} form) and **8-**H_2 (C_s; 2.7 kcal/mol lower in energy than the C_{2v} form) are small, while those of **2-**H_2, **3(a**−**b)-**H_2 and **4(a**−**b)-**H_2 are negligible (less than 0.5 kcal/mol). **5(a**−**c)-**H_2, **6-**H_2, **7-**H_2 and **1**-**8** all have planar minima.

NICS[26] were computed with the individual gauge for localized orbitals (IGLO) method[29] (implemented in the deMon NMR program)[38] at the PW91/IGLOIII level, employing the Pipek-Mezey localization algorithm.[39] We employ the most recommended NICS$_{\pi zz}$ index which extracts the out-of-plane (*zz*) tensor component of the isotropic NICS and includes only the π MO contributions.[26c,d] Negative NICS(0)$_{\pi zz}$ values due to diamagnetic shieldings indicate aromaticity. Positive NICS(0)$_{\pi zz}$ values due to paramagnetic shieldings indicate antiaromaticity.

Block-localized wave function (BLW). Both the REs and the ECREs were computed employing Mo's *ab initio* valence bond (VB) based block localized wave function (BLW) method.[25] All BLW computations were performed at the B3LYP/6-31G* DFT level[25h] as implemented in the GAMESS R5 version.[40] The BLW method preserves the concepts of VB theory, but is more efficient, especially for studying the conjugations and aromaticities of large systems, due to its molecular orbital (MO)-based computations.[25]

BLW can compute REs directly without recourse to reference compounds, by comparing the total energy of the fully delocalized structure (completely optimized employing regular canonical molecular orbitals) to its most stable hypothetical resonance structure, optimized following the imposed constraints. The latter is optimized employing BLW orbitals,[25] constructed by partitioning all the electrons and basis functions into several subspaces to form sets of localized MOs, in which orbitals of the same subspaces are mutually orthogonal but those of different subspaces overlap freely. This procedure "disables" the intramolecular interactions among the selected subgroups and gives the total energy of the hypothetical localized structure.[25] The ECREs are derived from the REs of monocyclic or polycyclic aromatic compounds by comparison with acyclic conjugated references with the same number and type of conjugation (see below).[41]

Note that REs and ECREs are conceptually different. The ECRE measures the extra stabilization (or destabilization) associated with aromaticity (or antiaromaticity),[28] but the RE measures the overall π conjugation stabilization, which *includes* the energetic consequences related to aromaticity and antiaromaticity.[25,27] We adopt the Pauling−Wheland resonance energy definition, based on the total energy difference between the fully delocalized conjugated compound and that of its most stable resonance contributor.[27] By definition, the REs are always positive, but the ECREs can be either positive or negative. Positive ECREs indicate aromaticity and negative ECREs indicate antiaromaticity. ECREs of nonaromatic systems are close to zero.

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As polycyclic compounds can have several different resonance contributors, different localization schemes can be applied. However, we select a BLW localization scheme for each of the compounds based on the natural bond length alternations of their perimeter; C−C bonds longer than 1.40 Å are assigned a single bond, those that are less than 1.40 Å are assigned double bonds, the remaining double bonds are added to appropriate positions to complete the conjugation. While other BLW localization schemes are possible, their RE values are nearly identical to those based on the scheme defined here (an example for **5b-**H_2 is provided in the Supporting Information, Figure 1S). Based on the selected BLW localization scheme, the Clar rings are assigned to the sextet rings (with three double bonds within a ring). When two adjacent sextet rings share a common double bond, the Clar ring is assigned to the one with smaller bond length alternation around the ring.

The ECREs of the dihydrodiazaacenes and diazaacenes are evaluated by their REs minus the RE sums of appropriate number and types of acyclic conjugation references, which are selected based on the specific BLW localization scheme applied for each of the polycyclic compounds (see Scheme 1).[28,41] For benzenoid rings, each Clar ring is assigned three syn butadienes (**syn-11**); the Kekule rings are assigned one syn and two anti butadienes, but one syn and two "averages" (**avg-11**, the averaged RE of syn and anti butadiene) for those adjacent to a Clar ring. The butadiene units that interact with the Clar rings are neither syn nor anti, but are averaged. This removes ambiguities in selecting appropriate acyclic references.[41]

For the dihydropyrazine moieties, the choice of acyclic references depend on the positions of the dihydro rings: those with two adjacent kekule rings are assigned four ethenamines, but those with only one adjacent kekule ring are assigned two ethenamines and one diaminoethylene. When two ethenamines interact with an adjacent Clar ring, they are taken as an average between two ethenamines and one diaminoethylene (**avg-14**). On this basis, all energetic effects other than aromaticity and antiaromticity are canceled out in the ECRE procedure. Thus, **5b-**H_2 (RE = 291.3 kcal/mol, Table 1) has eight **syn-11**, four **avg-11**, two **9** and two **avg-14** conjugation units (see Table S1, Supporting Information). The resulting ECRE value derived for **5b-**H_2, based on the REs of these acyclic references, is 82.5 kcal/mol (Table 1).

Acknowledgment. We dedicate this paper to Prof. K. P. C. Vollhardt on the occasion of his 63rd birthday. We thank the Georgia Institute of Technology, the University of Georgia, and the National Science Foundation (Grants CHE 0548423 and CHE 0716718) for financial support.

Supporting Information Available: Gaussian archives and detailed LMO NICS(0)$_{\pi zz}$ data. This material is available free of charge via the Internet at http://pubs.acs.org.

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