Structures and Energies of 10-Azatriquinacene and Its Hydrogenation Products: A Computational Study

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Enthalpies of formation and hydrogenation, vertical ionization potentials, and proton affinities of 10-azatriquinacene and its hydrogenation products have been computed at the B3LYP/6-311+G** level of density functional theory. Like the parent triquinacene, 10-azatriquinacene is not homoaromatic on the basis of the energetic, geometric, and magnetic criteria. The hyperfine coupling constants of the nitrogen-centered cation radicals are also calculated.

Introduction

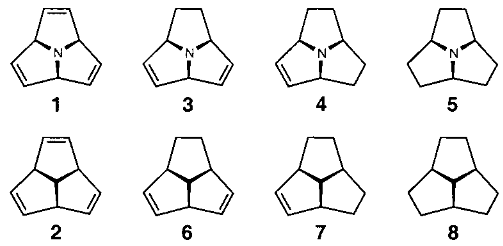
Recently, Mascal et al.[1] successfully synthesized and characterized 10-azatriquinacene (NC_9H_9, **1**) which is the first heteroanalogue of the isoelectronic parent triquinacene ($C_{10}H_{10}$, **2**). It is interesting to note that **2** was prepared by Woodward et al. more than 35 years ago.[2] In addition to their aesthetic structures, **1** differs from **2** in chemical and physical properties which should confer unique reactivity on the basis of a nitrogen lone pair. Apart from the still missing 10-azatriquinene (**4**, tetrahydro-10-azatriquinacene), Mascal et al. also reported two other hydrogenation products of **1**, i.e., 10-azatriquinadiene (**3**, dihydro-10-azatriquinacene) and 10-azatriquinane (**5**, perhydro-10-azatriquinacene),[1,3] the corresponding aza analogues of the parent hydrocarbons (**6**−**8**), as illustrated in Scheme 1.

This synthesis enabled the systematic study of the electronic properties of the nitrogen center on the changing environment from stepwise hydrogenation and also a unique comparison with their parent hydrocarbons and similar tertiary amine series, especially on the basis of geometric, energetic, and magnetic properties for **1**. Here, we carried out systematic density functional computations on the structures, enthalpies of formation and hydrogenation, ionization potentials, proton affinities of the neutral compounds, and the spin properties of the single electron in nitrogen-centered cation radicals to aid in further experimental investigations.

Computational Details

Geometry optimizations were carried out at the (U)B3LYP/6-311+G** density functional level of theory.[4] All optimized structures were characterized by frequency calculations at the (U)B3LYP/6-31G* level. The calculated number of imaginary frequencies (NImag) will determine whether the optimized structures are energy minima (NImag = 0), transition states (NImag = 1), or higher order saddle points (NImag > 1) on the potential energy surfaces. All the calculations were carried out by using the Gaussian98 program.[5] The computed energetic data and Cartesian coordinates of the optimized geometries are given in the Supporting Information.

Scheme 1. 10-Azatriquinacene (1) and Its Hydrogenation Products (3−5) and Their Parent Hydrocarbons (2, 6−8)



Results and Discussion

The expected neutral homoaromaticity of triquinacene (**2**) was definitively disproved by a newly determined enthalpy of formation from its energy of combustion in a microcalorimeter and by systematic computational analysis from geometric, energetic, and magnetic aspects.[6] It was found that **2** does not possess delocalized structural

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Table 1. Calculated Enthalpies ($\Delta H_f°$, kcal/mol) of Formation,[a] Compared to the Experimental Values (in brackets)

	1 (NC_9H_9)	**3** (NC_9H_{11})	**4** (NC_9H_{13})	**5** (NC_9H_{15})
$\Delta H_f°$	79.2	51.1	22.3	−6.4
	2 ($C_{10}H_{10}$)	**6** ($C_{10}H_{12}$)	**7** ($C_{10}H_{14}$)	**8** ($C_{10}H_{16}$)
$\Delta H_f°$ [b]	57.2 [57.51 ± 0.70]	29.6 [30.5 ± 1.0]	2.3 [3.0 ± 1.0]	−24.7 [−24.47 ± 0.86]

[a] At the B3LYP/6-311+G** level. [b] Taken from ref 6.

parameters, aromatic stabilization energies, and exalted diamagnetic susceptibility or significant NICS (nucleus independent chemical shifts[7]) values. The long and controversial discussion on the possible homoaromatic stabilization of **2** was mainly due to the abnormally low enthalpy of hydrogenation.[8]

It is interesting to speculate if **1** might be homoaromatic due to the introduced nitrogen center instead of the >CH− unit. Since there are no thermodynamic data available for **1** and its related compounds (**3**−**5**) experimentally, it is hard to gain any insight into the possible aromatic character of **1**. However, computations can provide these quantities very easily and in reasonable accuracy, as in the case of **2** and **6**−**8** (Table 1).[6]

To derive the enthalpies of formation of **1** and its hydrogenation products **3**−**5**, we employed the reaction eqs 1−4 and the enthalpies of formation of their parent hydrocarbons and isobutane ($HC(CH_3)_3$) as well as trimethylamine ($N(CH_3)_3$) as references.

$$\mathbf{1} + HC(CH_3)_3 = \mathbf{2} + N(CH_3)_3 \qquad \Delta H_r(\mathbf{1}) = 4.7\ \text{kcal/mol} \quad (1)$$

$$\mathbf{3} + HC(CH_3)_3 = \mathbf{6} + N(CH_3)_3 \qquad \Delta H_r(\mathbf{3}) = 5.8\ \text{kcal/mol} \quad (2)$$

$$\mathbf{4} + HC(CH_3)_3 = \mathbf{7} + N(CH_3)_3 \qquad \Delta H_r(\mathbf{4}) = 7.1\ \text{kcal/mol} \quad (3)$$

$$\mathbf{5} + HC(CH_3)_3 = \mathbf{8} + N(CH_3)_3 \qquad \Delta H_r(\mathbf{5}) = 8.4\ \text{kcal/mol} \quad (4)$$

Using the enthalpy of reaction ($\Delta H_r(\mathbf{1})$, eq 1), corrected to 298.15 K, and the enthalpies of formation[9] of $HC(CH_3)_3$, (−32.11 kcal/mol), $N(CH_3)_3$ (−5.67 kcal/mol), and **2** (the new experimental value 57.51 ± 0.70 kcal/mol),[6] the enthalpy of formation of **1** is estimated to be 79.2 kcal/mol. A similar procedure (eqs 2−4) with the enthalpy of formation of **6** (30.5 ± 0.1 kcal/mol), **7** (3.0 ± 1.0 kcal/mol), and **8** (−24.47 ± 0.86 kcal/mol)[6] gives the enthalpies of formation for **3**, **4**, and **5** to be 51.1, 22.3, and −6.4 kcal/mol, respectively.

On this basis, the stepwise enthalpy of hydrogenation can be estimated from the difference between the enthalpies of formation, −28.1 kcal/mol (**3** → **1**) for the first; −28.8 kcal/mol (**4** → **3**) for the second, and −28.7 kcal/mol (**5** → **4**) for the third C═C bond, and these are approximately equal. This indicates that the three C═C double bond are essentially independent and do not interact, and therefore **1** is not homoaromatic energetically.

Apart from this, the enthalpies of stepwise hydrogenation of **1** can also be evaluated using the homodesmotic reaction eqs 5−7 in which cyclopentane (C_5H_{10}) and cyclopentene (C_5H_8) are taken as reference molecules, and this is the method used by Miller, Schulman, and Disch[10] for estimating the stabilization energy for **2**.

$$\mathbf{1} + C_5H_{10} = \mathbf{3} + C_5H_8 \qquad \Delta H_r(\mathbf{1}) = -1.6\ \text{kcal/mol} \quad (5)$$

$$\mathbf{3} + C_5H_{10} = \mathbf{4} + C_5H_8 \qquad \Delta H_r(\mathbf{3}) = -1.6\ \text{kcal/mol} \quad (6)$$

$$\mathbf{4} + C_5H_{10} = \mathbf{5} + C_5H_8 \qquad \Delta H_r(\mathbf{4}) = -1.1\ \text{kcal/mol} \quad (7)$$

Using the difference in enthalpy of formation between cyclopentene (C_5H_8) and cyclopentane (C_5H_{10})[8] of −26.94 ± 0.13 kcal/mol and the enthalpies of reaction (ΔH_r), corrected to 298.15 K, the calculated stepwise enthalpies of hydrogenation are −28.5 for **1**, −28.6 for **3**, and −28.0 kcal/mol for **4**. These approximately identical data rule out any possible homoaromatic character from the energetic criteria of aromaticity.

In addition, the C═C double bond length and the nonbonded C···C distance of **1** (1.329 vs 2.563 Å), nearly the same as that of **2** (1.333 vs 2.533 Å), do not show any trend of bond length equalization due to possible homoconjugation or cyclic delocalization. This localized nature is also found in the protonated form (**1H**$^+$) indicated by the C═C bond lengths of 1.314 and 1.315 Å from X-ray analysis.[1] In addition to the energetic and geometric aspects, the magnetic criterion, defined on the basis of the calculated NICS value at the center of the three C═C double bonds of only −3.7 ppm, does not show any homoaromatic property of **1**. It turns out that **1**, like its parent hydrocarbon **2**, does not exhibit homoaromaticity. Moreover, the hydrogenation products (**3**−**5**) have the same structural pattern as their parent hydrocarbons (**6**−**8**),[6] i.e., **3** and **4** are C_1-symmetrical whereas **5** has C_3 symmetry.

The second aspect of this paper concerns the physical properties (vertical ionization potential, VIP; proton affinity, PA; and hyperfine coupling constants) of these tertiary amines and their radical cations. We have shown recently the changes of the VIP for a set of amines, $N(iPr)_n(cPr)_{3-n}$ ($n = 0-3$), as a function of the degree of the nitrogen center pyramidalization, and found that tricyclopropylamine ($N(cPr)_3$) has the highest (8.44 eV) and triisopropylamine ($N(iPr)_3$) the lowest (7.18 eV) VIP due to their large structure difference.[11] We found also

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Table 2. Calculated[a] and Experimental (in brackets) Vertical Ionization Energies (VIP, eV) and the Sum of the Three CNC Angles (in degrees)

	1 (NC_9H_9)	**3** (NC_9H_{11})	**4** (NC_9H_{13})	**5** (NC_9H_{15})
ΣCNC	326.2	326.1	327.3	328.3
VIP	8.03	7.90	7.76	7.62 [7.80][c]

	N(*i*Pr)$_3$	N(*i*Pr)$_2$(*c*Pr)	N(*i*Pr)(*c*Pr)$_2$	N(*c*Pr)$_3$
ΣCNC[b]	355.1	345.9	338.9	333.3
VIP[b]	7.13 [7.18]	7.56 [7.79]	7.93 [8.14]	8.26 [8.44]

[a] At the B3LYP/6-311+G**//B3LYP/6-311+G** level. [b] Taken from ref 11. [c] Taken from ref 13.

Table 3. Calculated[a] Total Atomic Spin Density (ρ) at the Nitrogen Center and Hyperfine Coupling Constants (in Gauss) of the Radical Cations

	$1^{+\bullet}$ ($NC_9H_9^{+\bullet}$)	$3^{+\bullet}$ ($NC_9H_{11}^{+\bullet}$)	$4^{+\bullet}$ ($NC_9H_{13}^{+\bullet}$)	$5^{+\bullet}$ ($NC_9H_{15}^{+\bullet}$)
ΣCNC	338.6	340.7	343.3	345.7
ρ(N)	0.753	0.774	0.807	0.839
N	20.6	19.3	18.6	17.5
C_α	−6.0	−3.1 to −8.4	−5.4 to −8.4	−6.9
H_α	57.0	58.1 to 35.3	54.8 to 32.2	40.2
C_β	5.4	5 to 10	8.9 to 4.6	2.1 to 7.5
H_β	−0.3	0.9 to −0.8	1.3 to −1.0	1.1 to −0.6

[a] At the UB3LYP/6-311+G** level.

the conformational change of the cyclopropyl rings in N(*c*Pr)$_3$ upon single oxidation.[11]

In contrast to N(*i*Pr)$_3$ which exhibits a nearly planar nitrogen center,[12] **1** and **3**−**5** have highly pyramidalized nitrogen centers. Consequently, smaller changes of the VIP are expected. Nevertheless, some changes between **1** and **5** should be detectable (Table 2). The VIP of **5** was determined both experimentally (7.80 eV) and computationally (7.68 eV) by Mascal et al.,[13] and they are close to the value (7.62 eV) of our computation. As shown in Table 2, the largest VIP is computed for **1**, while the smallest is for **5**. Their difference of 0.41 eV is much smaller than that (1.26 eV) between N(*c*Pr)$_3$ and N(*i*Pr)$_3$.[11] Note that the nitrogen center in **1** is only 2.1° more pyramidal than in **5**, whereas this difference is much larger (21.8°) between N(*c*Pr)$_3$ and N(*i*Pr)$_3$.

Despite the narrow range of VIP, significant changes are computed for the hyperfine coupling constants for the nitrogen-centered cation radical. Because of their rigid structure skeletons, no large conformation change of the radical cations is expected. Indeed, we found that all of them have the same structural patterns as their neutral counterparts, in contrast to the N(*c*Pr)$_3$ radical cation.[11] The radical cations have a less pyramidal (or more planar) nitrogen center than the corresponding neutral compounds, as indicated by the sum of the CNC angles (Table 3 vs Table 2), and the biggest difference of 17.4° is found between **5** and $\mathbf{5}^{+\bullet}$. This is in line with the general phenomenon at the nitrogen center upon ionization.[14] As shown in Table 3, large hyperfine coupling constants are found at the nitrogen and the neighbor methine (C−H) hydrogen (C−H$_\alpha$) centers and both the carbon and the remnant hydrogen centers have small or negligible couplings, but the difference between C$_\alpha$ and C$_\beta$ is around 10 G. In addition, the spin density at the nitrogen center of the radical cation increases from **1** to **3**−**5**, while hyperfine coupling constants decrease.

Table 4. Calculated and Experimental (in brackets) Proton Affinity (kcal/mol)

	1 (NC_9H_9)	**3** (NC_9H_{11})	**4** (NC_9H_{13})	**5** (NC_9H_{15})
PA[a]	233.1	234.1	236.6	243.9
	NH_3	NH_2Me	$NHMe_2$	NMe_3
PA[a]	202.4	213.3	220.5	224.9
PA[b]	[204.0]	[214.1]	[220.6]	[225.1]

[a] At the B3LYP/6-311+G** + ΔZPE (B3LYP/6-31G*) level. [b] Taken from ref 15.

Because of the bowl-shaped structure of **1**, it is also interesting to study the proton affinity and Lewis acid coordination such as that of the lithium cation (Li$^+$) at the nitrogen center on both convex (exo) and concave (endo) sides of the bowl. Indeed, Mascal et al. already obtained the X-ray structures of the protonated 10-azatriquinacene (**1H**$^+$)[1] and 10-azatriquinane (**5H**$^+$)[3a] and both reveal only exo protonation.

At the B3LYP/6-31G* level, we found both the exo (exo-**1H**$^+$) and endo (endo-**1H**$^+$) forms as energy minima on the potential energy surface. However, the former is more stable than the latter by 59.0 kcal/mol (B3LYP/6-311+G** + ZPE (B3LYP/6-31G*)), indicating that exo protonation is more favored energetically and there is no possibility for any kind of competition between these two forms. On the basis of this and experimental observations, we have computed all the proton affinities (PA) of **1** and **3**−**5**. As given in Table 4, the excellent agreement between theory and experiment for the reference molecules ($NH_{3-n}Me_n$, $n = 0-3$[15]) gives us confidence about the reliability of the chosen computational method and therefore the accuracy of the resulting data. It is interesting to note that the PA increases, also only slightly, as the nitrogen center becomes more planar. Thus, the less pyramidal (more planar) the nitrogen center of the amine is, the smaller the vertical ionization potential (VIP) is, and the larger the proton affinity (PA) is.

In addition, we computed also the coordination enthalpy of Li$^+$ on the nitrogen center on both sides of the bowl. As expected, coordination at the exo side (exo-**1Li**$^+$) is more favored energetically than the endo side (endo-**1Li**$^+$), but the energy difference of 4.5 kcal/mol is much smaller than the protonation which is 59.0 kcal/mol (see above). In contrast to H$^+$ and Li$^+$, it is interesting to note that only endo coordination of transition metal fragment (Mo(CO)$_3$) with **2** was found in X-ray analysis.[16,17] In the endo complex, the computed Li$^+$−C distance of 2.449 Å is shorter than the Mo−C separation of 2.540 Å (average value)[16], but the former will be elongated by solvation.[18]

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Conclusion

The enthalpies of stepwise hydrogenation and formation of the newly synthesized 10-azatriquinacene (**1**) and its hydrogenation products (**3**−**5**) were computed by means of high-level density functional theory. Note that these physical properties are not available yet. As expected from its parent hydrocarbon (triquinacene, **2**) **1** is not homoaromatic on the basis of the calculated C═C bond length and has approximately identical enthalpies of hydrogenation of the three C═C bonds and a small NICS value (−3.7 ppm) at the center of the three C═C bonds. In addition to the thermodynamic data, the vertical ionization potentials and proton affinities of the neutral compounds and hyperfine couplings of the relaxed nitrogen-centered radical cations were also calculated. Upon stepwise hydrogenation, the VIP decreases and the PA increases. This reflects the trend of the planarity of the nitrogen centers. All these computed quantities should challenge and aid further experimental investigations.

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Supporting Information Available: Total electronic energies (E_{tot}, au) from B3LYP/6-311+G** full geometry optimization and zero-point energies (ZPE, kcal/mol) at the B3LYP/6-31G* level for all molecules used in the paper. Cartesian coordinates at (U)B3LYP/6-311+G** of the neutral and protonated forms of 10-azatriquinacene and its hydrogenation products and their radical cations and complexes with Li^+. This material is available free of charge via Internet at http://pubs.acs.org.

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