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Heats of Formation, Structures and Relative Stabilities of Some Tetraazapentalene-Related Molecules

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13. ABSTRACT *(Maximum 200 words)*

A density functional procedure has been used to compute gas phase heats of formation for a group of high nitrogen molecules, primarily tetraazapentalene derivatives. Optimized structures and relative energies were computed for the key molecular framework and several isomeric forms. It is speculated that the unexpected tetraazapentalene stability that is observed experimentally is related to the relatively positive character of the triply-coordinated nitrogens.

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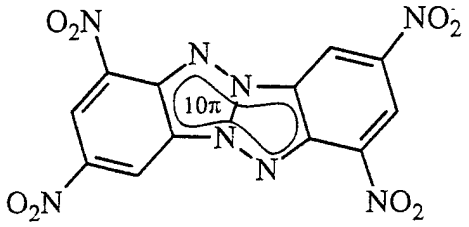
Introduction

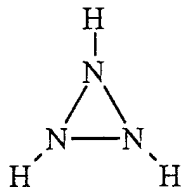
There is considerable and increasing interest in the stabilities and other properties of high-nitrogen compounds that contain several linked nitrogens (nitrogen catenation) [1-25]. While this feature is frequently associated with instability [3], this is not always the case. For example, the tetraazapentalene derivative **1**, known as TACOT, has exceptional thermal stability, with a melting/decomposition temperature of 378 °C [26].

1



While such high-nitrogen compounds are of fundamental interest due to the chain of nitrogens, many of them are also potentially important as energetic materials, due to the formation of the very stable N_2 as an ultimate decomposition product. This has indeed been one of the motivating factors of many of the studies cited [1-25], which focus upon *proposed* molecules with anticipated desirable properties, rather than existing ones.

Nitrogen catenation is typically associated with increased energy content, as reflected for example in the heat of formation. Thus, the experimental gas phase $\Delta H^{\circ}_{f,298}$ of hydrazoic acid, HN_3, is 70.29 kcal/mole [27]; the DZP-MBPT(2) calculated value for triaziridine, **2**, is 104.15 kcal/mole [6]. On a calories/gram basis, which is what is relevant for predicting detonation performance [28], these are 1635 and 2314 cal/g, respectively. These magnitudes are better appreciated when it is noted that the gas phase heat of formation of RDX (**3**), a leading military explosive, is only 206 cal/g [29, 30].



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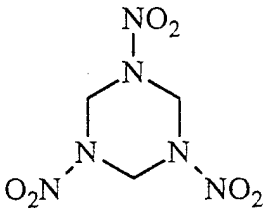

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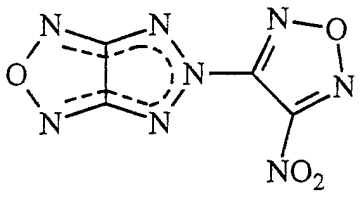
Our first objective in the present work has been to further explore the relationship between nitrogen catenation and energy content, by computing the heats of formation of **4** - **9**. **4**, known as NOTO and a liquid at room temperature, is the only one of these that has actually been synthesized [31]. The tetraazapentalenes **5** and **6** are not known, but various of their derivatives

have been prepared [32-36], including **1** [26]. **7** [37] and **8** and **9** [38] have been proposed and synthesis efforts are underway. While **4** is not a tetraazapentalene, its azide analogue could in principle form **7** by elimination of N_2 and ring closure [31].



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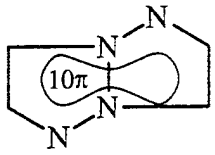

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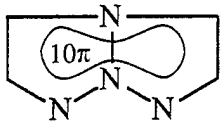

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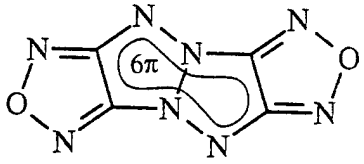

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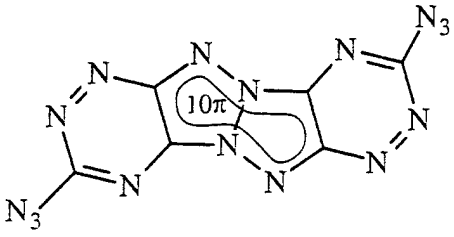

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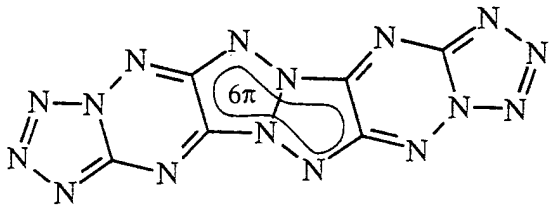

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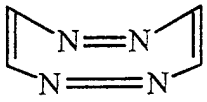
In the second phase of this work, we have focused specifically upon the tetraazapentalene **5**. As one step toward gaining insight into the unexpected stabilities of some of its derivatives [26, 32-34], e.g. **1**, we investigated the isomeric structures that could result from rupture of the central N–N bond. This yields an eight-membered ring, for which possible representations are **10** - **12**.



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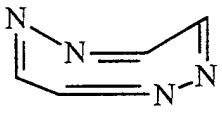

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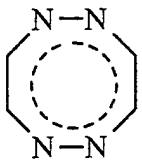

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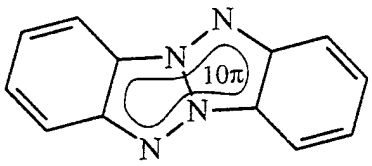
Methods

We compute standard gas phase heats of formation by a previously-described procedure [39]. It involves a density functional calculation of ΔE for the formation reaction at 0 K (Gaussian 92/DFT [40], Becke exchange [41] and Perdew correlation [42] functionals, 6-31G** basis set) followed by conversion to ΔH at 298 K and finally the introduction of empirical correction terms for the C, N and O atoms. For **7** - **9**, this procedure was modified by the use of an accurate stoichiometry-based relationship to obtain the vibrational energies at 298 K [43].

For **5** and **10-12**, optimized geometries and vibrational frequencies were initially obtained at the AM1 level [44]. It was verified that the singlet state of **12** is lower in energy than the triplet, contrary to the situation in 1,3,5,7-cyclooctatetraene [45, 46]. The AM1 structures were used as starting points for density functional geometry optimizations for each molecule (Gaussian 92/DFT [40], Becke exchange [41] and Lee, Yang and Parr correlation [47] functionals, 6-31G** basis set).

Results

Our computed heats of formation for **4** - **9** are listed in Table 1. The calculated density functional vibrational frequencies for **5** and **6** are all real, meaning that their structures correspond to energy minima, even though these molecules are not known in the unsubstituted form. The only relevant comparisons with experimental data that we can make involve the benzo derivatives **13** - **16**, for which gas phase heats of formation have been determined [48], as shown below. If one extrapolates from the dibenzo- and monobenzo- forms **13** and **14** to the unsubstituted parent molecule **5**, and from **15** and **16** to **6**, then the values for **5** and **6** are approximately 130 and 124 kcal/mole, respectively. These are in very satisfactory agreement with our results.



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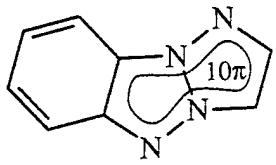
$\Delta H^{\circ}_{f,298}$ = 142.8 kcal/mole [48]



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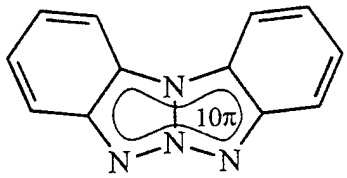
136.4 [48]



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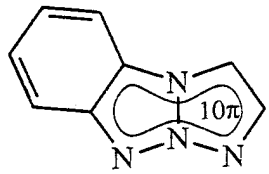
132.1 [48]



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128.2 [48]

The vibrational frequencies for the AM1 optimized geometries of **5**, **10** and **11** confirm that they are associated with energy minima. For **12**, however, there is one AM1 imaginary frequency; it indicates a tendency to rearrange to **11**.

The density functional energies and optimized geometries for **5** and **10** - **12** are given in Table 2. For **12**, optimizations were performed for both the spin-restricted singlet and the spin-unrestricted triplet states; the latter is 2.8 kcal/mole higher in energy. However a stability test of the spin-restricted singlet indicated an instability with respect to becoming spin-unrestricted [49]. A subsequent search found a spin-unrestricted singlet that is 2.1 kcal/mole lower in energy than the spin-restricted. The total spin operator (S^2) gave a value of 0.5806 (0.0161 after annihilation of the first spin contaminant). This seems to suggest that **12** can be regarded as an open-shell singlet.

Discussion

Heats of Formation

The expectation of high energy content being associated with nitrogen catenation is borne out by the heats of formation in Table 1. All are greater by at least a factor of four, on a calories/gram basis, than the 206 cal/g of RDX, **3** [29, 30]. Particularly striking are the high heats of formation of the unsubstituted tetraazapentalenes **5** and **6**; indeed more than 75% of the magnitudes of $\Delta H^{\circ}_{f,298}$ (cal/g) of **7** - **9** can be viewed as coming from **5**. The high energy content of this molecular framework is especially notable in view of the stabilities shown by some of its derivatives [26, 32-34].

Structures and relative stabilities of 5 and 10 - 12

We find the tetraazapentalene **5** to be clearly the most stable of the isomers described in Table 2. This is in full accord with experimental observations [33, 34].

In **5**, each carbon and each doubly-coordinated nitrogen is considered to provide one electron to the π system, and each triply-coordinated nitrogen to contribute two [48]. The difference between the nitrogens is that the doubly-coordinated have highly-localized lone pairs, centered in the molecular plane [46], which do not become part of the π system, whereas the lone pairs of the triply-coordinated but planar nitrogens are presumably above and below the plane [50], and hence are available as π electrons. The total of ten π electrons satisfies the $4n + 2$ rule, and **5** is accordingly classified as aromatic [45, 51]. This is fully supported by the geometry given in Table 2; the molecule is planar, and the bonds in the rings are all within 0.05 Å of each other in length, despite being of three different types: N–N, C–N and C–C.

The central N–N bond in **5** is 0.048 Å longer than the other two, consistent with a crystallographic study of **14**, in which the difference was found to be 0.032 Å [52]. This suggests that the central N–N bond may be the weakest of the three, and emphasizes the importance of investigating the structures resulting from its rupture.

In contrast to **5**, the systems **10** - **12** each have eight π electrons, which corresponds to $4n$. The fully-conjugated planar structure **12** is therefore antiaromatic, and its instability relative to **10** and **11** is not surprising [45, 53-58]. Structures **10** and **11** have boat conformations and clearly localized double bonds, as can be seen from the bond lengths in Table 2. **11** is significantly more stable than **10**; this may be due in part to the destabilizing effect in **10** of having π electrons localized between the lone pairs of the nitrogens. It is interesting to note that some of the early tetraazapentalenes synthesized were initially thought to be derivatives of **10** or **11** [33, 59, 60]; this misconception was subsequently corrected through crystallographic studies [33, 61, 62].

In seeking insight into the stability of the tetraazapentalene framework **5**, it is important to recognize the relatively positive characters of the triply-coordinated nitrogens. Attention was already drawn to this in an earlier computational study of the molecular electrostatic potential of **5** [46]. This showed the anticipated strong negative regions associated with the lone pairs of the doubly-coordinated nitrogens, centered in the molecular plane; however the triply-coordinated ones have no negative regions, neither in nor above the molecular plane. Their absence is not simply a necessary consequence of having a triply-coordinated nitrogen in a planar configuration, since examples are known where such systems do have very significant negative potentials [50, 63, 64]. It may be that the relatively positive natures of these nitrogens (which were also predicted much earlier at a semiempirical level [48]) reflect a combination of (a) the inclusion of their lone pairs in the π system of the molecule, and subsequent greater polarizability, and (b) the electron-attracting powers of the doubly-coordinated nitrogens, which can have a marked effect upon available π electronic charge [65]. The delocalization of electronic charge away from the triply-coordinated positions may sufficiently diminish the electron-rich nature of the chain of nitrogens to significantly stabilize the system.

Summary

We have explored computationally certain aspects of the relationships between energy content, structure and relative stability for a group of molecules related to the tetraazapentalene **5**. Large, positive heats of formation were obtained. Structure **5** is significantly more stable than any of the isomers that are formed by the rupture of its central N–N bond. It is speculated that the unexpected stability observed for this molecular framework, despite its four linked nitrogens, is related to the relatively positive character of the two triply-coordinated nitrogens.

Acknowledgement

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Table 1. Calculated gas phase heats of formation, $\Delta H^{\circ}_{f,298}$.

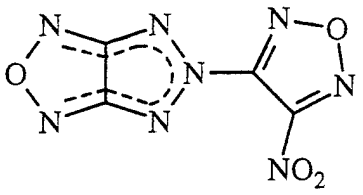
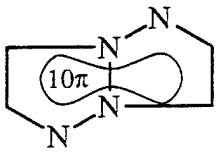
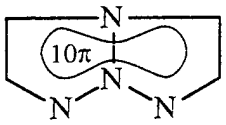
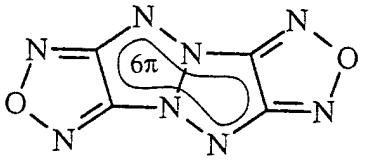
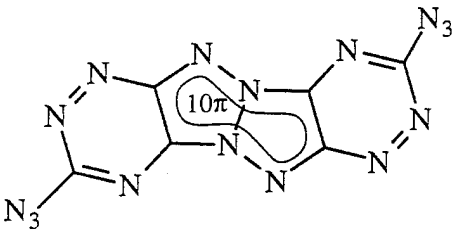
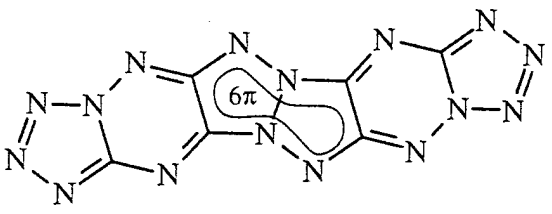
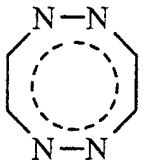
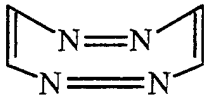
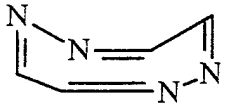
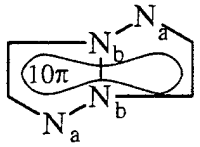
	Molecule	$\Delta H^{\circ}_{f,298}$, kcal/mole	$\Delta H^{\circ}_{f,298}$, cal/g
4		202	903
5		124	1151
6		125	1158
7		253	1318
8		426	1439
9		442	1493

Table 2. Calculated (DFT/B-LYP/6-31G**) energies and structures.

Molecule		Total energy (hartrees)	Relative energy (kcal/mole)	Distances (Å)	Angles (deg)
12		-373.5624	47.0	N–N: 1.238 C–N: 1.325 C–C: 1.444	N–N–C: 141.3 N–C–C: 128.7 planar molecule
10		-373.5667	44.3	N–N: 1.263 C–N: 1.439 C–C: 1.353	N–N–C: 122.7 N–C–C: 125.1 boat structure[a]
11		-373.6061	19.6	N–N: 1.387 C–N: 1.297 C–C: 1.497	N–N–C: 119.8 N–C–C: 124.2 boat structure[b]
5		-373.6373	0.0	N_a–N_b: 1.349 N_b–N_b: 1.397 C–N_a: 1.372 C–N_b: 1.382 C–C: 1.397	N–N–N: 112.9 N_b–N_a–C: 102.8 N_b–N_b–C: 106.5 N_a–C–C: 113.4 N_b–C–C: 104.5 planar molecule

[a]The nitrogens form the bottom of the boat. The angle between the bottom and the sides is 131.4°.

[b]The bottom of the boat is formed by opposite carbons and nitrogens, and is at an angle of 128.1° with the sides.