

Aza[10]annulene: Next Higher Aromatic Analogue of Pyridine

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The aza[10]annulene isomers (CH)₉N derived from “twist”, “heart”, “naphthalene-like”, and “azulene-like” [10]annulenes by replacement of a CH group by nitrogen were investigated at the CCSD(T)/DZd//B3LYP/6-311+G** level of theory. Except for the twist structure, all aza[10]annulenes studied were found to be aromatic. As the transannular repulsion is reduced in the aza[10]annulenes, the aromatic isomers become competitive energetically with the twist form.

Aza[10]annulene, the next larger monocyclic homologue of pyridine complying with the Hückel $4n + 2$ rule, has received much less attention^{1–3} than [10]annulene, the benzene analogue.^{4–13} The (CH)₁₀ species prepared by van Tamelen and Burkoth⁴ and by Masamune and co-workers^{5–7} in the late 1960s did not exhibit aromatic properties because strain disfavors the planar or near-planar configurations.⁸ Extensive recent computations have identified the olefinic “twist” structure **1a** (Chart 1) as the most stable [10]annulene (CH)₁₀.^{9–13}

Structural modifications that stabilize the aromatic conformations of [10]annulene by counteracting the strain can be applied. Thus, Vogel's^{14–20} bridged annulenes include 2,7-methanoaza (**A**, Chart 2) and 3,8-methanoaza[10]annulene,^{2,3} as well as their alkoxy derivatives.^{21,22} These are the only aza[10]annulene derivatives known to us, although Paquette et al. have sug-

Chart 1. Schematic Representation of (CH)₉X Isomers

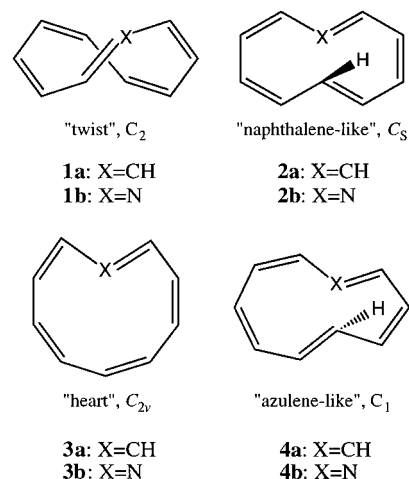
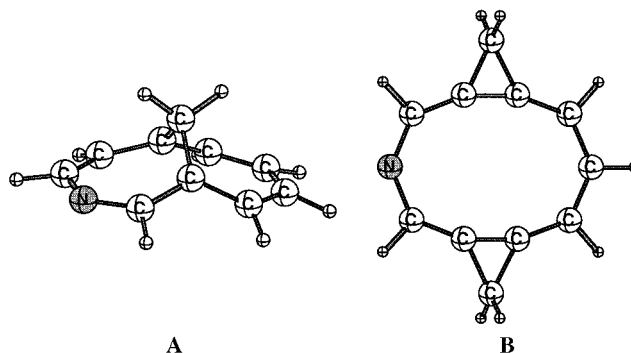


Chart 2. 1,6-Methano-2-aza[10]annulene (**A**) and 1,6-Biscyclopropa[10]annulene (**B**)^a



^a Geometries computed at B3LYP/6-31G* are shown.

gested that substituted aza[10]annulenes might be intermediates in ring-opening reactions.¹

Another strategy is to incorporate three- or four-membered rings externally. This design, which leads to aromatic [10]annulenes,²³ might be extended, for example, to the aza analogue, **B** (Chart 2). However, the parent aza[10]annulene should offer inherently more favorable aromatic prospects. Anastassiou pointed out in 1972 that transannular repulsion in [10]annulenes should

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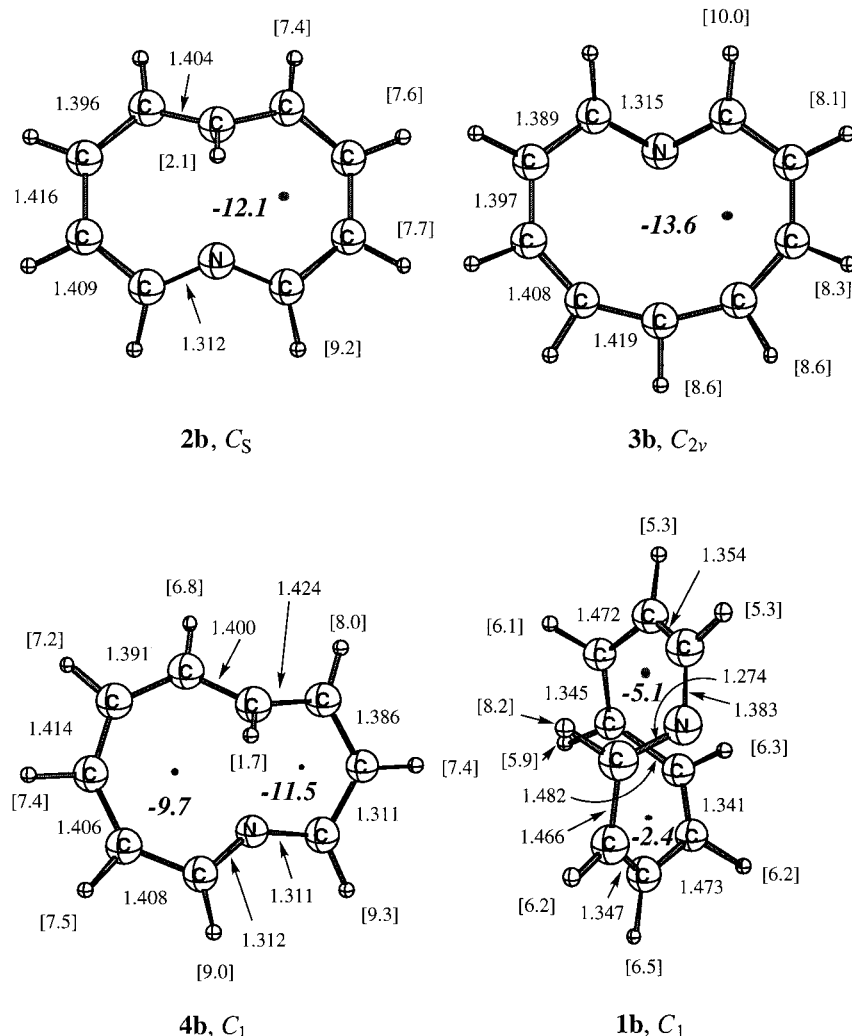


Figure 1. Geometries (bond lengths are in Å), NICS values (in italics), and $\delta(^1\text{H})$ relative to TMS [in brackets] of aza[10]annulene isomers at the B3LYP/6-311+G** level of theory. The NICS points are located in the geometric centers of the “rings” of adjacent atoms.

be reduced, for example, when the nitrogen in **2** replaces a CH group (Chart 1).²⁴ The “aza-naphthalene-like”, “aza-azulene-like”, or “aza-heart” isomers might be 10π aromatic homologues of pyridine. We now report our theoretical investigation of the stability of the aromatic aza[10]annulene structures relative to their olefinic counterparts.

Experience with [10]annulene computations^{10,11,25} serves as a guide. The evaluation of **1a–4a** was complicated by the tendency of second-order Møller–Plesset perturbation and density functional theory to overestimate the relative stability of the aromatic minimum **3a**, which was found to be lower in energy than **1a** at MP2/DZd and B3LYP/DZd.¹⁰ However, higher level CCSD(T)/DZd single-point computations on the B3LYP/DZd geometries,¹¹ as well as on CCSD(T)/DZd optimized geometries, predict the “twisted” olefinic structure **1a** to be more stable than the aromatic isomer **3a** by 6.0 and 6.3 kcal mol⁻¹, respectively.²⁵ This insignificant difference between the geometries indicates that B3LYP annulene structures (which require much less computer time to optimize) should be adequate for higher level single-point computations.

The aza[10]annulene isomers (Chart 1 and Figure 1), derived from **1a–4a** by systematic replacements of CH groups by nitrogen (giving **1b–4b**), are investigated at the CCSD(T)/DZd/B3LYP/6-311+G**^{26–30} level.³¹ In addition, four positional isomers of **1b** were found to be higher lying minima on the C₉H₉N PES; they are not

(26) All geometries were optimized fully at B3LYP/6-31G* and B3LYP/6-311+G** using Becke’s²⁷ three-parameter hybrid functional in conjunction with the correlation functional of Lee, Yang, and Parr²⁸ as implemented in Gaussian 94.³¹ Harmonic vibrational frequencies were computed analytically at B3LYP/6-31G*.

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considered further here. Vibrational frequencies were computed at B3LYP/6-31G*.

In contrast to [10]annulene, there is only one "naphthalene-like" aza[10]annulene isomer (**2b**). Note that the CC bond lengths in **2b**, like those in **3b** and **4b**, do *not* alternate significantly, in contrast to the olefinic patterns found in the hydrocarbon analogues **2a** and **4a**.⁹ The aromaticity of aza[10]annulenes was evaluated by computing the nucleus-independent chemical shifts (NICS)³² using the GIAO³³ approach. The high negative NICS values of **2b**, **3b**, and **4b** (see Figure 1) indicate diamagnetic ring currents that are associated with aromaticity. In addition, the hydrogen atoms located above the aromatic π systems are strongly shielded, as indicated by their upfield chemical shifts: $\delta(^1\text{H}) = 2.1$ for **2b** and 1.7 for **4b** (with respect to TMS). The aza-heart form **3b** is the most stable aromatic aza[10]annulene form. Isomers **2b** and **4b** are 0.5 and 1.6 kcal mol⁻¹ higher in energy, respectively, at CCSD(T)/DZd//B3LYP/6-311+G** (Table 1).

However, the best olefinic twist isomer **1b** is 2.1 kcal mol⁻¹ more stable than aromatic **3b**. Although replacing a CH group by N is ca. 4 kcal mol⁻¹ more favorable for the aromatic heart (**3a** vs **3b**) than for the olefinic twist structure (**1a** vs **1b**), this is not quite enough to switch the energy order of these isomers: the olefinic form (**1b**) is still slightly more stable than any aromatic isomer, **2b**, **3b**, and **4b**. Note that the heart isomer (**3b**) is 1 kcal

Table 1. Relative Energies (in kcal mol⁻¹) of Various Aza[10]annulene Minima

species	B3LYP/6-311+G**	CCSD(T)/DZd
1b , C ₁	9.4	0
2b , C _s	1.9	2.6 ^a (2.6) ^b
3b , C _{2v}	0	2.1 ^a (3.6) ^b
4b , C ₁	3.6	3.7 ^a (4.0) ^b

^a Single point computations using the B3LYP/6-311+G** geometries. ^b ZPVE (B3LYP/6-31G*) corrected relative energies are given in parentheses.

mol⁻¹ higher in energy than **2b** when zero-point vibrational energies are taken into account. The CH/N replacement is unfavorable for the naphthalene-like isomers: whereas **2a** is only 0.5 kcal mol⁻¹ less stable than twist **1a**,⁹ the aza derivative **2b** is 2.6 kcal mol⁻¹ less stable than **1b**.

In summary, Anastassiou's²⁴ 1972 suggestion is verified: replacement of an "inner" CH group by nitrogen in (CH)₁₀ structures makes the aromatic heart isomer (**3b**) more competitive energetically. However, the olefinic twist structure (**1b**) is still significantly more stable.

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Supporting Information Available: Absolute energies, zero-point vibrational energies, and Cartesian coordinates for **1b-4b** are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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