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# *Ab initio* prediction of ring strain enthalpies of cyclic amine-boranes

Thomas M. Gilbert

*Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115 USA*

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**Abstract**

Ring strain enthalpies for a series of cyclic amine-boranes (1-azonia-2-boratacycloalkanes) were calculated from MP4(SDTQ)/6-31G*//MP2/6-31G* energies by the group equivalent method. Small rings exhibit smaller RSEs than do the corresponding cycloalkanes; larger rings exhibit RSEs essentially identical to those of the corresponding cycloalkanes. 

*Keywords*: Boron heterocycles; nitrogen heterocycles; steric and strain effects; computer-assisted methods

The concept of ring strain enthalpy (RSE) has aided our understanding of the energetics and reactivities of carbocycles and heterocycles [1]. To date, no RSE data for the boron-nitrogen-carbon heterocycles $H_2\overline{B(CH_2)_nCH_2NH_2}$ (1-azonia-2-boratacarbocycles) have appeared. Such data would help interpret some curious experimental results. For example, the ring systems $H_2\overline{B(CH_2)_nNMe_2}$ are known for n = 3 - 12, but the three- and four-membered rings (n = 1, 2) are not [2]. This suggests, intriguingly, that the BN bond strengths and the RSEs of the smaller rings are similar.

We computed the *ab initio* geometries (MP2/6-31G* level; no geometric restrictions) and energies [MP4(SDTQ)/6-31G* level] [3] of the series of 1-azonia-2-boratacycloalkanes $H_2\overline{B(CH_2)_nCH_2NH_2}$ (n = 0-5; Table 1), and of the molecules required to calculate the RSEs by group equivalent methods [4]. Only the lowest energy conformers of **1a** – **6a** and **1c** – **6c** located were used in the RSE calculations; all of these were confirmed as potential energy minima with only real vibrational frequencies through frequency calculations at the HF/6-31G* or MP2/6-31G* levels. The energies at 298.15 K, 1 atm were calculated using data from the same frequency calculations. In order to test the self-consistency of the group equivalents

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for these heterocycles, we determined the RSEs with two independent calculations. The equations used were:

*RSE Equations, Method 1:*

$$H_2\overline{BCH_2NH_2} + H_3BNH_3 = H_3BNH_2CH_2BH_2NH_3$$

$$H_2\overline{BCH_2(CH_2)_nCH_2NH_2} + (n+1)H_3CCH_3 = CH_3CH_2BH_2NH_2CH_2CH_3 + nCH_3CH_2CH_3$$

*RSE Equation, Method 2:*

$$H_2\overline{BCH_2(CH_2)_nCH_2NH_2} + H_2BCH_2CH_2NH_2 + CH_3CH_3 = H_2BCH_2(CH_2)_nCH_2NH_2 + CH_3CH_2BH_2NH_2CH_2CH_3$$

Method 2 is independent only for rings with five or more members, so only one RSE was determined for **1c** and **2c**. The RSEs from the two methods are similar, although the RSE2 values are systematically smaller than the RSE1 values, and the difference between them appears to increase with ring size. If real, it is unclear from what basis this deviation arises.

It can be seen that the RSE for the amine-borane analogue of cyclohexane, **4a**, is slightly negative, a result we attribute to computational errors (basis set and model) and to the assumptions made in the group equivalent method. The error is insignificant compared to the bond and reaction energies of the compound.

The data form two sets, one where the cyclic amine-boranes exhibit RSEs considerably smaller than those of the corresponding cycloalkanes (**1c**, **2c**, **3c**), and one where the RSEs of both types of compounds are essentially identical (**4c**, **5c**, **6c**). Explaining this is straightforward. The RSEs of **1c** - **3c** are smaller because the BC and BN bonds present (Table 2) are longer than the corresponding CC bonds in the cycloalkanes, providing some strain relief. The effect is such that both 1-azonia-2-boratacyclopentane **3c**, and 1-azonia-2-boratacyclohexane **4c**, are essentially strain-free. Once the ring is sufficiently large, as for **4c** - **6c**, the effect diminishes and the RSE becomes comparable to that of the cycloalkane.

A useful "rule-of-thumb" can be extracted from the data. In the ΔE Column of Table 1 are the energy differences between each cyclic amine-borane and the corresponding acyclic amine-borane. Unlike carbon systems, the two are stoichiometrically identical because the BN bond is dative, not covalent. ΔE represents the energy required to form the ring; i.e., it includes the BN bond strength, the RSE, and the energy required to rehybridize the boron atom from $sp^2$ to $sp^3$. That is, to simple order,

$$E_{(acyclic)} - E_{(cyclic)} = \Delta E = E_{(BN\ bond\ strength)} - E_{(rehybridization)} - RSE \qquad (1)$$

Table 1

MP4(SDTQ)/6-31G* energies [5], cyclic/acyclic differences, and RSEs of acyclic and cyclic amine-boranes and their group equivalents

| Compound | MP4 Energy[a] | ΔE[b] | RSE1[c] | RSE2[d] |
|---|---|---|---|---|
| $CH_3CH_3$ | -79.452204 | | | |
| $BH_3NH_3$ | -82.830560 | | | |
| $CH_3CH_2CH_3$ | -118.602908 | | | |
| $CH_3BH_2NH_2CH_3$ | -161.132051 | | | |
| $H_3BNH_2CH_2BH_2NH_3$ | -203.670007 | | | |
| $CH_3CH_2BH_2NH_2CH_2CH_3$ | -239.431449 | | | |
| $H_2BCH_2NH_2$, **1a** | -120.782043 | | | |
| $H_2\overline{BCH_2NH_2}$, **1c** | -120.804401 | 14.0 | 22.6 | |
| Cyclopropane | | | 27.6 | |
| $H_2BCH_2CH_2NH_2$, **2a** | -159.935904 | | | |
| $H_2\overline{BCH_2CH_2NH_2}$, **2c** | -159.956631 | 13.0 | 14.8 | |
| Cyclobutane | | | 26.2 | |
| $H_2BCH_2CH_2CH_2NH_2$, **3a** | -199.085524 | | | |
| $H_2\overline{BCH_2CH_2CH_2NH_2}$, **3c** | -199.127060 | 26.1 | 2.4 | 1.7 |
| Cyclopentane | | | 6.3 | |
| $H_2BCH_2CH_2CH_2CH_2NH_2$, **4a** | -238.234903 | | | |
| $H_2\overline{BCH_2CH_2CH_2CH_2NH_2}$, **4c** | -238.283075 | 30.2 | -0.9 | -2.4 |
| Cyclohexane | | | 0.0 | |
| $H_2BCH_2CH_2CH_2CH_2CH_2NH_2$, **5a** | -277.384648 | | | |
| $H_2\overline{BCH_2CH_2CH_2CH_2CH_2NH_2}$, **5c** | -277.421846 | 23.3 | 6.6 | 4.5 |
| Cycloheptane | | | 6.4 | |
| $H_2BCH_2CH_2CH_2CH_2CH_2CH_2NH_2$, **6a** | -316.534274 | | | |
| $H_2\overline{BCH_2CH_2CH_2CH_2CH_2CH_2NH_2}$, **6c** | -316.564840 | 19.2 | 11.4 | 8.6 |
| Cyclooctane | | | 9.9 | |

[a]Energy corrected to 298.15 K, 1 atm, in hartree molecule$^{-1}$.

[b]ΔE = E(acyclic) – E (cyclic) (see Eqn. 1), in kcal mol$^{-1}$.

[c]Ring Strain Enthalpy for cyclic amine boranes calculated using group equivalents, Method 1, in kcal mol$^{-1}$. RSEs for cycloalkanes taken from S. W. Benson, *Thermochemical Kinetics*, Wiley Interscience: New York, 1976.

[d]Ring Strain Enthalpy for cyclic amine boranes calculated using group equivalents, Method 2, in kcal mol$^{-1}$.

If we assume that the BN bond strength and the $E_{(rehybridization)}$ are the same for any cyclic amine-borane, we can say:

$$\Delta E_A - \Delta E_B = (RSE)_B - (RSE)_A \qquad (2)$$

So if we computationally determine the energies on the left side of the equation, and we estimate an RSE for one of the compounds, we can calculate the other RSE. One approach is to assume that, as in cyclohexane, the RSE of the 1-azonia-2-boratacyclohexane **4c** is zero. Then Equation 2 gives: RSE (**2c**) = 17.2 kcal mol$^{-1}$, RSE (**3c**) = 4.1 kcal mol$^{-1}$, RSE (**5c**) = 6.9 kcal mol$^{-1}$, RSE (**6c**) = 11.0 kcal mol$^{-1}$. These are all within 2.5 kcal mol$^{-1}$ of the values

calculated by the group equivalent method 1, but required only optimization of the cyclic and acyclic compounds. The procedure thus provides a quick, reasonably accurate estimate of the RSEs for these systems. Even for the highly strained **1c**, where the rehybridization and BN bond strength energies are probably very different from those of the larger rings, the cyclic/acyclic comparison gives RSE (**1c**) = 16.2 kcal $mol^{-1}$, only 6 kcal $mol^{-1}$ different from the group equivalent value. We plan to examine whether this rule-of-thumb holds for other systems such as cyclic amine-alanes and phosphine-boranes.

Table 2
MP2/6-31G* Optimized Structural Data (distances in Å, angles in degrees) for Cyclic Amine-Boranes

| Compound | BN | BC | NC | CBN | CNB |
|---|---|---|---|---|---|
| **1c** | 1.626 | 1.575 | 1.509 | 56.2 | 60.2 |
| **2c** | 1.701 | 1.640 | 1.505 | 83.7 | 85.9 |
| **3c** | 1.689 | 1.632 | 1.493 | 99.4 | 107.1 |
| **4c** | 1.653 | 1.615 | 1.489 | 105.2 | 113.0 |
| **5c** | 1.663 | 1.621 | 1.490 | 110.1 | 115.9 |
| **6c** | 1.686 | 1.614 | 1.491 | 109.7 | 119.0 |

As an aside, Equation 1 allows estimation of the rehybridization energy. The energy of the BN bond in $H_3B{\leftarrow}NH_3$ is in the range 28.7 (calculated) - 31.1 (experimental) kcal $mol^{-1}$ [5]. If we choose 29.9 kcal $mol^{-1}$ as an average, and use the energies and RSEs of **2c** - **6c**, the average $E_{(rehybridization)}$ = 0.7 kcal $mol^{-1}$. This is negligible, so to acceptable accuracy, the RSE of a 1-azonia-2-boratacycloalkane is simply the difference between the energies of the cyclic and acyclic analogues, corrected for the strength of the extra BN bond in the former.

Given these results, it is surprising that no three- or four-membered 1-azonia-2-boratacycloalkanes have been isolated. The BN bond energy is larger than the calculated RSEs for **1c** and **2c** (though admittedly not much), so the cyclic compounds should be more stable than the acyclic ones. The BN bond energy can be increased if needed by substituting donor groups onto the nitrogen and/or acceptor groups onto the boron. We hope experimenters will reattempt to prepare these interesting small-ring systems.

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