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Josep M Oliva-Enrich, Stéphane Humbel, Juan Z Dávalos, Josef Holub, Drahomír Hnyk. Proton affinities of amino group functionalizing 2D and 3D boron compounds. *Afinidad*, 2018, 75 (584), pp.260-266. hal-02138836

HAL Id: hal-02138836

<https://hal.science/hal-02138836>

Submitted on 24 May 2019

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PROTON AFFINITIES OF AMINO GROUP FUNCTIONALIZING 2D AND 3D BORON COMPOUNDS

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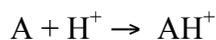
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Abstract: We report quantum-chemical computations of Proton Affinities (PA) of icosahedral amino boranes, carboranes and Co-containing metallocarboranes with a relative error of $\sim 2\%$ - when experimental data available - by means of the B3LYP and BP86 functionals. Use of larger basis sets for simple systems such as NH_3 , CH_3NH_2 , and borazine ($\text{B}_3\text{H}_6\text{N}_3$) reduces the error to $\sim 0.5\%$ indicating the validity of these functionals for these computations and prediction of PA for unavailable experimental data on amino-derived (car)boranes and metalla(car)boranes. The computed PA show that, from an electronic structure point of view, when substituting an *exo* H atom by an NH_2 group in $\text{B}_{12}\text{H}_{12}^{(2-)}$, $\text{CB}_{11}\text{H}_{12}^{\ominus}$, (*ortho*, *meta*, *para*)- $\text{C}_2\text{B}_{10}\text{H}_{12}$, and the metallocarborane $[\text{3-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^{\ominus}$ \equiv COSAN the most similar system to be compared with is the anion $\text{NH}_2\text{-BH}_3^{\ominus}$ - computed $\text{PA}(\text{B3LYP}/\text{cc-pVTZ}) = 1505 \text{ kJ}\cdot\text{mol}^{-1}$ - rather than methylamine CH_3NH_2 or borazine, the two latter with experimental PA of 900 and 803 $\text{kJ}\cdot\text{mol}^{-1}$ respectively. The largest PA for a given isomer correspond, following this order, to: 1- $\text{NH}_2\text{-B}_{12}\text{H}_{11}^{(2-)}$, $\text{BH}_3\text{NH}_2^{\ominus}$, 12- $\text{NH}_2\text{-CB}_{11}\text{H}_{11}^{(-)}$, *cisoid* 8- $\text{NH}_2\text{-COSAN}$, *transoid* 9- $\text{NH}_2\text{-COSAN}$, 9- $\text{NH}_2\text{-1,2-C}_2\text{B}_{10}\text{H}_{11}$, 9- $\text{NH}_2\text{-1,7-C}_2\text{B}_{10}\text{H}_{11}$, and 2- $\text{NH}_2\text{-1,12-C}_2\text{B}_{10}\text{H}_{11}$. The rule for larger PA applies for isomers with the NH_2 groups farthest away from (non-metal) carborane C(cage) atoms. Pyramidalization energy computation shows an enhanced facility for planarization of the amino group in *cisoid* 8- $\text{NH}_2\text{-COSAN}$ as compared to *cisoid* 1- $\text{NH}_2\text{-COSAN}$.

1. Introduction

The chemistry of polyhedral heteroboranes [1] and metallaheteroboranes [2] is, in many aspects, orthogonal to organic chemistry; namely, transferability of named reaction mechanisms, such as those shown in the list of organic reactions (S_N1 , S_N2 , ...), about a thousand [3], do not have the equivalence or parallel in polyhedral heteroborane chemistry. Therefore, tabulation of thermochemical properties for these systems is important in order to assess and predict reaction mechanisms when combining heteroboranes with organic molecules or even biomolecules [4, 5, 6]. Indeed, the electronegativity (χ) of B versus H is reversed when compared with C: $\chi(B) < \chi(H) < \chi(C)$, and therefore we should consider the exo H atoms in polyhedral boranes as hydrides. A recent example of significant changes in thermochemical character, is the predicted superacidity when substituting the benzene ring by an *ortho*-carborane cage in phthalic acid [7].

A very useful thermochemical property in gas-phase chemistry is the proton affinity (PA), namely, the *attraction force* of a system A towards a proton H^+ or *vice versa*; we should note that even He can be protonated [8]. Tabulation of PA for many systems have been published in the literature [9]. According to the IUPAC, the proton affinity (PA) is defined as the negative of the enthalpy change in the gas phase reaction ($PA = -\Delta_r H^0$) between a proton and the chemical species concerned, to give the conjugate acid of that species, as shown below



In our case here, the A system corresponds to the following amino-derived systems: ammonia NH_3 , methylamine CH_3NH_2 , boranamine BH_2NH_2 , ${}^{\circ}BH_3NH_2$, borazine $B_3H_6N_3$ – the equivalent of benzene by substituting every two consecutive C atoms by B and N – and the following icosahedral (car)boranes, (*ortho*, *meta*, *para*)-carborane and Cobalt metallacarboranes: $1-(NH_2)-B_{12}H_{11}^{(2)}$, all symmetry-unique (SU) isomers in $n-(NH_2)-CB_{11}H_{11}^{(1)}$, $n-(NH_2)-(o, m, p)$ -carboranes and *cisoid* and *transoid* [$(n-NH_2-1,2-C_2B_9H_{10})-3,3'$ -Co(1,2- $C_2B_9H_{11}$)] $^{(1)}$. The notation for the latter will be simplified as $n-NH_2-COSAN$

[10]. The enumeration of cage atoms in the icosahedral carborane cages and the cobaltacarboranes is shown in Figure 1, and the optimized structures of the molecules included in this work are displayed in Table 1 through Table 7. Thus, for *ortho*, *meta* and *para*-carboranes – Figure 1a, Figure 1b and Figure 1c – the C positions are (1,2), (1,7) and (1,12) respectively. As shown in Table 1 through Table 7 the position of the NH₂ group substituting *exo* H atoms lead in many cases to more than one positional isomer for a given structure.

2. Computational Methods

The electronic structure computations for the determination of PA were carried out with the program Gaussian09 [11] and the B3LYP [12, 13] and BP86 [12, 14, 15] hybrid Hartree-Fock/DFT functionals for the non-metal systems and with the BP86 functional only for all isomers derived from substituting one *exo* H atom by an amino group NH₂. For selected 1-NH₂-COSAN and 8-NH₂-COSAN isomers of *cisoid* and *transoid* Co complexes we also used the B3LYP functional for comparative purposes. In the computations we used a double- ζ basis set plus a set of polarization functions for non-H atoms, known as 6-31G* [16]. For the Co complexes we used the same basis set (6-31G*) for (H, B, C, N) atoms and an all-electron basis set for Co, known as augmented Wachter basis set [17], without the *f* functions: this basis set is defined as AE1. For the computation of delocalization energies, we used the block-localized wavefunction (BLW) formalism [18] with a modified version of the GAMESS program [19] at either the Hartree-Fock (HF) or the BP86 density-functional level of theory and the same AE1 basis set.

3. Results and discussion

3.1 Proton Affinities (PA)

Table 1 shows the electronic structure computations for simple amino compounds and the corresponding protonated species. We have included borazine, the benzene equivalent with alternative B-N bonds in the hexagonal skeleton, given the interesting feature that protonation of borazine on the B atom gives H₂ and the radical B₃N₃H₅^(\cdot) [20]. This is supported by our computations. As shown in Table 1, the computed PA compare well when

experimental data are available: a difference of $15 \text{ kJ}\cdot\text{mol}^{-1}$ reduces to $5 \text{ kJ}\cdot\text{mol}^{-1}$, from a double-zeta (6-31G*) to triple-zeta basis (cc-pVTZ) and the B3LYP functional. Since our goal is to predict PA for amino compounds derived from boranes, carboranes and metallacarboranes, for which experimental data are not available, we need to mimic the closest possible system when comparing amino-boron compounds. Therefore we computed the PA for boranamine BH_2NH_2 and the ${}^{\ominus}\text{BH}_3\text{NH}_2$ anion, whose protonated species in the latter is the charge-transfer complex ${}^{\ominus}\text{BH}_3\text{NH}_2^{(\oplus)}$. Table 1 shows that the PA for BH_2NH_2 and ${}^{\ominus}\text{BH}_3\text{NH}_2$ are $767 \text{ kJ}\cdot\text{mol}^{-1}$ and $1538 \text{ kJ}\cdot\text{mol}^{-1}$ respectively (B3LYP/6-31G*). The PA of BH_2NH_2 is lower than in NH_3 , but increases considerably – doubles! – in ${}^{\ominus}\text{BH}_3\text{NH}_2$. As for borazine, protonation on N atom gives a PA of $815 \text{ kJ}\cdot\text{mol}^{-1}$ (double-zeta) which lowers to $804 \text{ kJ}\cdot\text{mol}^{-1}$ (triple-zeta) very close to the experimental value of $803 \text{ kJ}\cdot\text{mol}^{-1}$ [21].

Turning now to polyhedral (car)boranes, substitution of an H atom by an amino group in the icosahedral dianion $\text{B}_{12}\text{H}_{12}^{(2-)}$, gives the single isomer $1\text{-NH}_2\text{-B}_{12}\text{H}_{12}^{(2-)}$, with a computed PA of $1694 \text{ kJ}\cdot\text{mol}^{-1}$, as shown in Table 2. This value is closer to the PA of ${}^{\ominus}\text{BH}_3\text{NH}_2$ with $\text{PA} = 1538 \text{ kJ}\cdot\text{mol}^{-1}$ as compared to the PA values in NH_3 , CH_3NH_2 , BH_2NH_2 and Borazine, as shown in Table 1. In Table 2 we show the PA for the four isomers derived from substituting one H atom by an NH_2 group in the icosahedral anion $\text{CB}_{11}\text{H}_{12}^{\ominus}$: $1\text{-NH}_2\text{-CB}_{11}\text{H}_{11}^{\ominus}$, $2\text{-NH}_2\text{-CB}_{11}\text{H}_{11}^{\ominus}$, $7\text{-NH}_2\text{-CB}_{11}\text{H}_{11}^{\ominus}$ and $12\text{-NH}_2\text{-CB}_{11}\text{H}_{11}^{\ominus}$. Interestingly, the larger the PA when the farther the NH_2 group from C atom in position 1:

$$\text{PA}(1) < \text{PA}(2) < \text{PA}(7) < \text{PA}(12)$$

with a difference of $\text{PA}(12) - \text{PA}(1) = 110 \text{ kJ}\cdot\text{mol}^{-1}$, and $\text{PA}(12) = \text{PA}(12\text{-NH}_2\text{-CB}_{11}\text{H}_{11}^{\ominus}) = 1350 \text{ kJ}\cdot\text{mol}^{-1}$, which is lower than $\text{PA}(1\text{-NH}_2\text{-B}_{12}\text{H}_{12}^{(2-)})$ by $344 \text{ kJ}\cdot\text{mol}^{-1}$. Therefore the substitution of a B atom by a C atom in the cage, leading to a decrease of charge from -2 to -1, are indications of lower PA.

As for icosahedral *ortho*, *meta* and *para*-carboranes, in Table 3 we display the different computed PA (PA° , PA^{m} , PA^{p}) for the isomers derived from substituting one H atom by an NH_2 group. Given the point-group symmetries of *ortho* (C_{2v}), *meta* (C_{2v}) and *para* (D_{5d})

carboranes, we have five, five and two different isomers, respectively; see also Figure 1 for figuring out the symmetry-unique (SU) isomers according to the cage atom labels. As for *ortho* carborane, the PA increases the farther the NH₂ group from the two C atoms in the cage, as in the previous case for the amino isomers of CB₁₁H₁₂⁽¹⁾:

$$PA^o(1) < PA^o(3) < PA^o(4) < PA^o(8) < PA^o(9)$$

with a difference $PA^o(9) - PA^o(1) = 165 \text{ kJ}\cdot\text{mol}^{-1}$, with the largest PA for the 9-NH₂-1,2-C₂B₁₀H₁₁ isomer: $PA^o(9) = 975 \text{ kJ}\cdot\text{mol}^{-1}$, larger than in NH₃, but much lower than in the 1-NH₂-B₁₂H₁₁⁽²⁾ and 12-NH₂-CB₁₁H₁₁⁽¹⁾ molecules.

As regards to *meta*-carboranes, Table 4, we observe a similar behaviour for the amino isomers, with increasing PA as the NH₂ group is located farther from the C atoms, thus:

$$PA^m(1) < PA^m(2) < PA^m(4) < PA^m(5) < PA^m(9)$$

with a difference $PA^m(9) - PA^m(1) = 104 \text{ kJ}\cdot\text{mol}^{-1}$. Finally, for *para*-carborane, the two amino isomers follow the same rule, with $PA^p(1) < PA^p(2)$, with a difference of $PA^p(2) - PA^p(1) = 63 \text{ kJ}\cdot\text{mol}^{-1}$, as shown in Table 5. As for the largest PA for a given amino positional isomer, we have:

$$PA^o(9) = 975 > PA^m(9) = 967 > PA^p(2) = 921, \text{ all values in kJ}\cdot\text{mol}^{-1}.$$

We now turn to the amino-metallacarboranes, when an H atom is substituted by an NH₂ group in one of the ligands in the [Co(C₂B₉H₁₁)₂]⁽¹⁾ ≡ COSAN complex [22] for all possible regioisomers, whose protonation on N gives the zwitterion [(*n*-NH₃⁺-1,2-C₂B₉H₁₀)-3,3'-Co(1,2-C₂B₉H₁₁)]⁽¹⁾ ≡ *n*-NH₃⁺-COSAN. The atom labels of this well-known complex are depicted in Figure 1d, with the *transoid* structure, with the two C atoms in one ligand farthest away from the two C atoms of the other ligand by a rotation of 180°, with respect to the *cisoid* structure. The structure *transoid* [3-Co-(1,2-C₂B₉H₁₁)₂] has C_{2h} symmetry and therefore the following positions are equivalent for every ligand: C(1) ≡ C(2), B(4) ≡ B(7),

B(5) \equiv B(11), B(9) \equiv B(12), as shown in Figure 1d. Thus only seven NH₂ isomers must be considered: C(1), B(4), B(5), B(6), B(8), B(9) and B(10). The results reported for these complexes - *transoid* and *cisoid* - correspond to BP86/6-31G* quantum-chemical computations [14]. In Table 6 we report the PA for the seven NH₂ isomers from *transoid* [(*n*-NH₂-1,2-C₂B₉H₁₀)-3,3'-Co(1,2-C₂B₉H₁₁)]^(L) \equiv *n*-NH₂-COSAN. We should emphasize that 8-NH₃⁽⁺⁾-COSAN has been synthesized [23]. Note that in all these complexes the Co atom bears a formal charge of Co⁽³⁺⁾, since every capped cage ligand bears a formal charge of (C₂B₉H₁₁)⁽²⁻⁾, and the total charge of the system is therefore $q = -1$. As shown in Table 6, the PA follow the order:

$$PA^{\text{trans}}(6) < PA^{\text{trans}}(1) < PA^{\text{trans}}(5) < PA^{\text{trans}}(10) < PA^{\text{trans}}(4) < PA^{\text{trans}}(8) < PA^{\text{trans}}(9)$$

the lowest PA corresponds to the NH₂ group attached to B(6), and the largest PA to NH₂ in positions B(8) and B(9). The difference between maximum and minimum is $PA^{\text{trans}}(9) - PA^{\text{trans}}(6) = 78 \text{ kJ}\cdot\text{mol}^{-1}$.

As regards to the *cisoid* structures of the complex [(*n*-NH₂-1,2-C₂B₉H₁₀)-3,3'-Co(1,2-C₂B₉H₁₁)]^(L), in Table 7 we show the computed PA for the different isomers. The structure *cisoid* [3-Co-(1,2-C₂B₉H₁₁)₂] has only C₂ symmetry, which relates one ligand with the other, without atom equivalences in the same ligand and therefore we have to take into account all, resulting in eleven NH₂ isomers: C(1), C(2), B(4), B(5), B(6), B(7), B(8), B(9), B(10), B(11) and B(12), with the following order relation for PA

$$PA^{\text{cis}}(1) < PA^{\text{cis}}(2) < PA^{\text{cis}}(6) < PA^{\text{cis}}(5) < PA^{\text{cis}}(11) < PA^{\text{cis}}(4) = PA^{\text{cis}}(10) < PA^{\text{cis}}(9) < PA^{\text{cis}}(7) = PA^{\text{cis}}(12) < PA^{\text{cis}}(8)$$

The largest PA corresponds to NH₂ in position B(8) and the lowest for position C(1), with a difference of $PA^{\text{cis}}(8) - PA^{\text{cis}}(1) = 178 \text{ kJ}\cdot\text{mol}^{-1}$.

Comparison of PA from *transoid* and *cisoid* structures, shows that the largest PA corresponds to the *cisoid* [(8-NH₂-1,2-C₂B₉H₁₀)-3,3'-Co(1,2-C₂B₉H₁₁)]^(L) \equiv 8-NH₂-COSAN

with PA = 1315 kJ·mol⁻¹. Analysis of Table 1 through Table 7 shows that for the icosahedral carboranes, the farther the NH₂ group from the C(cage) atom, the larger the PA. As for the *cisoid* and *transoid* *n*-NH₂-COSAN complexes, we can clearly see the largest PA for *cisoid* 8-NH₂-COSAN, with PA(B3LYP/6-31G*) = 1315 kJ·mol⁻¹.

3.2 Delocalization energies

In this section we analyze the -NH₂ pyramidalization energy and delocalization energy for the systems: NH₂-BH₃^(^o), *cisoid* 1-NH₂-COSAN and *cisoid* 8-NH₂-COSAN. For the localized computations we first de-pyramidalize the Nitrogen, thus defining a plane of symmetry nearby this atom - say the (xy) plane. We shall then use the label σ for orbitals that are symmetric, in this (xy) plane, and π for orbitals that are antisymmetric by the mirror image of this plane (p_z , d_{xz} , d_{yz} orbitals of the Nitrogen).

The localization of the two electrons of the nitrogen lone pair was obtained in the BLW framework by an orbital optimization restricted to the 4π gaussian functions on the N atom ($2p_z$, $3p_z$, d_{xz} , d_{yz}). The remaining electrons of the system were then described by orbitals that were optimized using all other gaussian functions of the AE1 basis set. For the delocalized energy computation, we simply relaxed this constraint.

De-pyramidalization was obtained through a geometry optimization with the unique constraint of a fixed dihedral angle involving the NH₂ group and the connecting atom, either C(1) (for 1-NH₂-COSAN) or B(8) (for 8-NH₂-COSAN).

Table 8. BP86/AE1 pyramidalization energy PE(kJ·mol⁻¹) for representative systems. Pyram = pyramidalized.

System	Energy(au)	PE
Planar ^(^o) BH ₃ -NH ₂	-82.59099	0.0
Pyram ^(^o) BH ₃ -NH ₂	-82.60321	-32.1
Planar 1-NH ₂ -COSAN	-2051.63027	0.0
Pyram 1-NH ₂ -COSAN	-2051.63831	-21.1
Planar 8-NH ₂ -COSAN	-2051.66748	0.0
Pyram 8-NH ₂ -COSAN	-2051.66912	-4.3

Table 9. Delocalization energies ΔE ($\text{kJ}\cdot\text{mol}^{-1}$) for representative systems, with n -COSAN $\equiv n$ -NH₂-COSAN.

Method	System	Energy (au)	ΔE
BP86	^o BH ₃ NH ₂ Deloc	-82.59087	-22.7
BP86	Localized	-82.58223	---
HF	^o BH ₃ NH ₂ Deloc	-81.99215	-17.6
HF	Localized	-81.99884	---
HF	1-COSAN Deloc	-2044.85090	-55.7
HF	Localized	-2044.87213	---
HF	8-COSAN Deloc	-2044.89384	-44.8
HF	Localized	-2044.91091	----

As shown in Table 8, the pyramidalization energies show that N is particularly easy to planarize in *cisoid* 8-NH₂-COSAN: only 4.3 $\text{kJ}\cdot\text{mol}^{-1}$, much lower as compared to ^oBH₃-NH₂ and 1-NH₂-COSAN. As shown in Table 9, the delocalization energy was calculated in the NH₂-BH₃⁽⁻⁾ anion at two levels of theory: BP86 and HF. The value is $\sim 20 \text{ kJ}\cdot\text{mol}^{-1}$, slightly larger at the BP86 level as compared to HF level. As the results are very close with both levels of theory, but the wave function convergence is faster at the HF level, we considered only HF for the Cobalt complexes. The delocalization obtained in 1-NH₂-COSAN and 8-NH₂-COSAN is significantly larger in the complexes, about 50 $\text{kJ}\cdot\text{mol}^{-1}$. It is slightly larger in 1-NH₂-COSAN than in 8-NH₂-COSAN but the difference is small (5 $\text{kJ}\cdot\text{mol}^{-1}$). The delocalization isosurfaces, as shown in Figure 2, display a delocalization that corresponds to small π bonding between the N atom and the first neighbor, C(1) in 1-NH₂-COSAN and B(8) in 8-NH₂-COSAN. A similar feature was observed in other cases [24].

4. Conclusions

The following conclusions come out from strickly quantum-chemical computations of Hartree-Fock (HF) and hybrid-HF – Density Functional Theory (DFT) methods:

While carboranes do not really increases the PA of amines: $PA(NH_3) \approx 850 \text{ kJ}\cdot\text{mol}^{-1}$, $PA(1-NH_2-1,12-C_2B_{10}H_{11}) \approx 877 \text{ kJ}\cdot\text{mol}^{-1}$, COSAN systems increase very significantly the PA, with $PA(8-NH_2-COSAN) \approx 1260 \text{ kJ}\cdot\text{mol}^{-1}$, which is almost as large as $PA(^{\ominus}BH_3NH_2) \approx 1530 \text{ kJ}\cdot\text{mol}^{-1}$, with 8-NH2-COSAN possibly more stable from an experimental viewpoint. A simple computation of the PA in HSO_4^{\ominus} to give H_2SO_4 gives the value of $PA(B3LYP/6-31G^*) = 1330 \text{ kJ}\cdot\text{mol}^{-1}$ (understood as the acidity enthalpy for the process $H_2SO_4 \rightarrow HSO_4^{\ominus} + H^+$ [25]) thus showing the increased PA for NH_2 -substituted (car)boranes and metallacarboranes, larger than in HSO_4^{\ominus} for 1- $NH_2-B_{12}H_{11}^{(2-)}$, $^{\ominus}BH_3NH_2$ and 12- $NH_2-CB_{11}H_{11}^{(\ominus)}$. As for the cobaltacarborane *cisoid* 8- $NH_2-COSAN$, the PA is only $15 \text{ kJ}\cdot\text{mol}^{-1}$ lower than in HSO_4^{\ominus} , hence proving the enhanced stability of the corresponding zwitterion from protonation of the NH_2 group.

5. Acknowledgements

We are grateful to Professor Lluís Victori (IQS, Ramon Llull University, Barcelona) and Professor Joan O. Grimalt (Institute of Environmental Assessment and Water Research, CSIC, Barcelona), for reading the manuscript. Y. Mo is gratefully acknowledged for the BLW code, which was used for the computation of electronic delocalization effects.

FIGURES

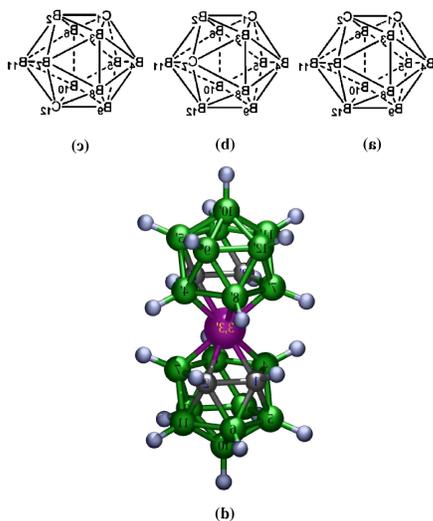


FIGURE 1
CAPTIONS

Figure 1. Atom labels for: (a) *ortho*-carborane 1,2-C₂B₁₀H₁₂, (b) *meta*-carborane 1,7-C₂B₁₀H₁₂, (c) *para*-carborane 1,12-C₂B₁₀H₁₂, (d) *transoid* Cobalt bis(dicarbollide) [3-Co(C₂B₉H₁₁)₂]⁽¹⁾. Hydrogen atoms are not shown for clarity in (*ortho*, *meta*, *para*)-carborane.

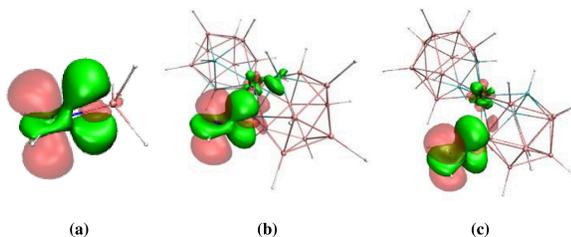


FIGURE 2

Figure 2. Isosurface of density variation when the localization constraint is released in (a) NH₂-BH₃⁽¹⁾, (b) 1-NH₂-COSAN, (c) 8-NH₂-COSAN. Red and green density lobes correspond, respectively, to negative and positive electron density differences. Hence the delocalization is from the NH₂ lone pair to the rest of the molecule. The isovalue surface for electron density differences is set to 10⁻³ atomic units.

TABLES

Table 1. Optimized structures and Proton Affinities (PA, in $\text{kJ}\cdot\text{mol}^{-1}$) in $\text{CH}_3\text{-NH}_2/\text{NH}_3^{(+)}$, $\text{BH}_2\text{-NH}_2/\text{NH}_3^{(+)}$, and $\text{BH}_3^{(-)}/\text{NH}_3^{(+)}$, with $\text{PA} = -\Delta_r H^0$ of the process $\text{A} + \text{H}^{(+)} \rightarrow \text{AH}^{(+)}$. B3LYP/6-31G* computations, in parentheses B3LYP/cc-pVTZ computations.

A	$\text{AH}^{(+)}$	PA	PA(ex p)	A	$\text{AH}^{(+)}$	PA	PA(ex p)
NH_3 	$\text{NH}_4^{(+)}$ 	874.2 (860.4)	853.6 ^(a))	$\text{BH}_3^{(-)}/\text{NH}_2$ 	$\text{BH}_3^{(-)}/\text{NH}_3^{(+)}$ 	1537.5 (1504.8)	---
$\text{CH}_3\text{-NH}_2$ 	$\text{CH}_3\text{-NH}_3^{(+)}$ 	915.2 (905.0)	899.0 ^(a))	Borazine $\text{B}_3\text{H}_6\text{N}_3$ 	$(\text{B}_3\text{H}_7\text{N}_3)^+$ 	815.0 ^(b) (803.6)	802.5 ^(a))
$\text{BH}_2\text{-NH}_2$ 	$\text{BH}_2\text{-NH}_3^{(+)}$ 	766.5 (754.1)	---				

(a) See Reference [9]. (b) PA for protonation on the N atom. Protonation on B atom gives H_2 , see Reference [20].

Table 2. Optimized structures and Proton Affinities (PA, in $\text{kJ}\cdot\text{mol}^{-1}$) for systems where a hydrogen atom is substituted by an amino group in $\text{B}_{12}\text{H}_{12}^{(2-)}$ and $\text{CB}_{11}\text{H}_{12}^{(-)}$ with $\text{PA} = -\Delta_r H^0$ of the process $\text{A} + \text{H}^{(+)} \rightarrow \text{AH}^{(+)}$. B3LYP/6-31G* computations.

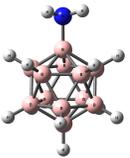
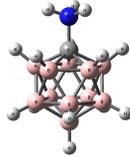
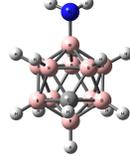
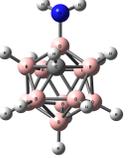
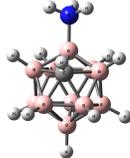
A	$\text{AH}^{(+)}$	PA	A	$\text{AH}^{(+)}$	PA
1-NH ₂ - $\text{B}_{12}\text{H}_{11}^{(2-)}$ 	1-NH ₃ ⁽⁺⁾ - $\text{B}_{12}\text{H}_{11}^{(2-)}$ 	1693.5			
1-NH ₂ - $\text{CB}_{11}\text{H}_{11}^{(-)}$ 	1-NH ₃ ⁽⁺⁾ - $\text{CB}_{11}\text{H}_{11}^{(-)}$ 	1238.2	7-NH ₂ - $\text{CB}_{11}\text{H}_{11}^{(-)}$ 	7-NH ₃ ⁽⁺⁾ - $\text{CB}_{11}\text{H}_{11}^{(-)}$ 	1335.9
2-NH ₂ - $\text{CB}_{11}\text{H}_{11}^{(-)}$ 	2-NH ₃ ⁽⁺⁾ - $\text{CB}_{11}\text{H}_{11}^{(-)}$ 	1289.3	12-NH ₂ - $\text{CB}_{11}\text{H}_{11}^{(-)}$ 	12-NH ₃ ⁽⁺⁾ - $\text{CB}_{11}\text{H}_{11}^{(-)}$ 	1349.6

Table 3. Optimized structures and Proton Affinities (PA, in $\text{kJ}\cdot\text{mol}^{-1}$) for systems where a hydrogen atom is substituted by an amino group in *ortho*-carborane 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$, with $\text{PA} = -\Delta_r H^0$ of the process $\text{A} + \text{H}^{(+)} \rightarrow \text{AH}^{(+)}$. B3LYP/6-31G* computations.

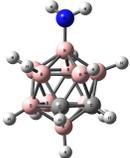
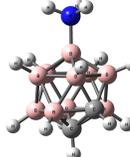
A	$\text{AH}^{(+)}$	PA	A	$\text{AH}^{(+)}$	PA
1- NH_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	1- NH_3^+ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	809.4	8- NH_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	8- NH_3^+ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	966.1
3- NH_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	3- NH_3^+ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	875.9	9- NH_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	9- NH_3^+ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	974.6
4- NH_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	4- NH_3^+ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	916.8			

Table 4. Optimized structures and Proton Affinities (PA, in $\text{kJ}\cdot\text{mol}^{-1}$) for systems where a hydrogen atom is substituted by an amino group in *meta*-carborane 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$, with $\text{PA} = -\Delta_r H^0$ of the process $\text{A} + \text{H}^{(+)} \rightarrow \text{AH}^{(+)}$. B3LYP/6-31G* computations.

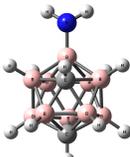
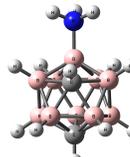
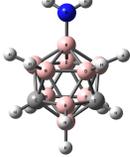
A	$\text{AH}^{(+)}$	PA	A	$\text{AH}^{(+)}$	PA
1- NH_2 -1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	1- NH_3^+ -1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	863.4	5- NH_2 -1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	5- NH_3^+ -1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	930.4
2- NH_2 -1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	2- NH_3^+ -1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	884.1	9- NH_2 -1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	9- NH_3^+ -1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	966.5
4- NH_2 -1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	4- NH_3^+ -1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	921.1			

Table 5. Optimized structures and Proton Affinities (PA, in $\text{kJ}\cdot\text{mol}^{-1}$) for systems where a hydrogen atom is substituted by an amino group in *para*-carborane 1,12- $\text{C}_2\text{B}_{10}\text{H}_{12}$, with $\text{PA} = -\Delta_r H^0$ of the process $\text{A} + \text{H}^{(+)} \rightarrow \text{AH}^{(+)}$. B3LYP/6-31G* computations.

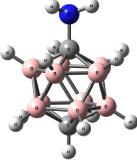
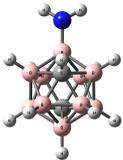
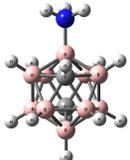
A	$\text{AH}^{(+)}$	PA
1- NH_2 -1,12- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	1- NH_3^+ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	877.5
2- NH_2 -1,12- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	2- NH_3^+ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{11}$ 	921.2

Table 6. Optimized structures and Proton Affinities (PA, in $\text{kJ}\cdot\text{mol}^{-1}$) for systems where a hydrogen atom is substituted by an amino group in *transoid* $[3\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^{(0)}$, with $\text{PA} = -\Delta_r H^0$ of the process $\text{A} + \text{H}^{(+)} \rightarrow \text{AH}^{(+)}$. BP86/AE1 computations. $\text{COSAN} \equiv [3\text{-Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$.

A	$\text{AH}^{(+)}$	PA	A	$\text{AH}^{(+)}$	PA	A	$\text{AH}^{(+)}$	PA
1-NH ₂ - COSAN	1-NH ₃ ⁽⁺⁾ - COSAN	1209 .5	6-NH ₂ - COSAN	6-NH ₃ ⁽⁺⁾ - COSAN	1197 .5	10-NH ₂ - COSAN	10-NH ₃ ⁽⁺⁾ - COSAN	1251 .1
4-NH ₂ - COSAN	4-NH ₃ ⁽⁺⁾ - COSAN	1260 .4	8-NH ₂ - COSAN	8-NH ₃ ⁽⁺⁾ - COSAN	1262 .1			
5-NH ₂ - COSAN	5-NH ₃ ⁽⁺⁾ - COSAN	1231 .8	9-NH ₂ - COSAN	9-NH ₃ ⁽⁺⁾ - COSAN	1276 .2			

Table 7. Optimized structures and Proton Affinities (PA, in $\text{kJ}\cdot\text{mol}^{-1}$) for systems where a hydrogen atom is substituted by an amino group in *cisoid* $[3\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^{(+)}$, with $\text{PA} = -\Delta_r H^0$ of the process $\text{A} + \text{H}^{(+)} \rightarrow \text{AH}^{(+)}$. BP86/AE1 computations. $\text{COSAN} \equiv [3\text{-Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$. The notation $n\text{-NH}_2$ indicates the position of the amino group in $n\text{-NH}_2\text{-COSAN}$.

A	$\text{AH}^{(+)}$	PA	A	$\text{AH}^{(+)}$	PA	A	$\text{AH}^{(+)}$	PA	A	$\text{AH}^{(+)}$	PA
1-NH ₂	1-NH ₃ ⁽⁺⁾	113 7.0	5-NH ₂	5-NH ₃ ⁽⁺⁾	122 2.4	8-NH ₂	8-NH ₃ ⁽⁺⁾	131 4.7	11-NH ₂	11-NH ₃ ⁽⁺⁾	123 3.0
2-NH ₂	2-NH ₃ ⁽⁺⁾	117 0.4	6-NH ₂	6-NH ₃ ⁽⁺⁾	118 3.6	9-NH ₂	9-NH ₃ ⁽⁺⁾	128 4.4	12-NH ₂	12-NH ₃ ⁽⁺⁾	128 7.3
4-NH ₂	4-NH ₃ ⁽⁺⁾	125 2.2	7-NH ₂	7-NH ₃ ⁽⁺⁾	128 6.9	10-NH ₂	10-NH ₃ ⁽⁺⁾	125 1.3			

6. References

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- ² A metallaheteroborane is the equivalent of an inorganic metal complex in which one or more ligands are polyhedral heteroboranes.
- ³ See https://en.wikipedia.org/wiki/List_of_organic_reactions
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