Proton affinities of amino group functionalizing 2D and 3D boron compounds

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Afinidades protónicas del grupo amino en compuestos 2D y 3D de boro

Afinitats protòniques del grup amino en compostos 2D i 3D de bor

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SUMMARY

We report quantum-chemical computations of Proton Affinities (PA) of icosahedral amino boranes, carboranes and Co-containing metallacarboranes with a relative error of ~ 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 ($B_3H_6N_3$) reduces the error to ~ 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 $B_{12}H_{12}^{(2-)}$, $CB_{11}H_{12}^{(-)}$, *(ortho, meta, para)*-$C_2B_{10}H_{12}$, and the metallacarborane $[3\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^{(-)}$= COSAN the most similar system to be compared with is the anion $NH_2\text{-}BH_3^{(-)}$ – computed PA(B3LYP/cc-pVTZ) = 1505 kJ·mol^{-1} – rather than methylamine CH_3NH_2 or borazine, the two latter with experimental PA of 900 and 803 kJ·mol^{-1} respectively. The largest PA for a given isomer correspond, following this order, to: 1-NH_2-$B_{12}H_{11}^{(2-)}$, $^{(-)}BH_3NH_2$, 12-NH_2-$CB_{11}H_{11}^{(-)}$, *cisoid* 8-NH_2-COSAN, *transoid* 9-NH_2-COSAN, 9-NH_2-1,2-$C_2B_{10}H_{11}$, 9-NH_2-1,7-$C_2B_{10}H_{11}$, and 2-NH_2-1,12-$C_2B_{10}H_{11}$. The rule for larger PA applies for isomers with the NH_2 groups farthest aways from (non-metal) carborane C(cage) atoms. Pyramidalization energy computation shows an enhanced facility for planarization of the amino group in *cisoid* 8-NH_2-COSAN as compared to *cisoid* 1-NH_2-COSAN.

Keywords: Proton affinity; metallaheteroborane; superacid; quantum chemistry; delocalization energy; DFT.

RESUMEN

En este trabajo presentamos cálculos químico-cuánticos de las Afinidades Protónicas (PA) de los aminoboranos icosaédricos, de los carboranos y de los metalacarboranos que contienen Co con un error relativo del ~ 2% - cuando se dispone de datos experimentales – por medio de los funcionales B3LYP y BP86. Uso de conjuntos de base mayor para sistemas simples como el NH_3, CH_3NH_2, y la borazina ($B_3H_6N_3$) reduce el error a un ~ 0.5 % indicando la validez de estos funcionales para estos cálculos y la predicción de PA para datos experimentales no disponibles con carboranos y metalocarboranos. Las PA calculadas demuestran que la sustitución de un átomo exo H por un grupo NH_2 en $B_{12}H_{12}^{(2-)}$, $CB_{11}H_{12}^{(-)}$, (*orto, meta, para*)-$C_2B_{10}H_{12}$, y el metalacarborano $[3\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^{(-)}$ = COSAN el sistema más similar con el que se puede comparar es el anión $NH_2\text{-}BH_3^{(-)}$ – PA(B3LYP/cc-pVTZ) = 1505 kJ·mol-1 – en comparación con la metilamina CH_3NH_2 o la borazina, los dos últimos con PA experimentales de 900 y 803 kJ·mol^{-1} respectivamente. La mayor PA para un isómero determinado corresponde, siguiendo este orden a: 1-NH_2-$B_{12}H_{11}^{(2-)}$, $^{(-)}BH_3NH_2$, 12-NH_2-$CB_{11}H_{11}^{(-)}$, *cisoide* 8-NH_2-COSAN, *transoide* 9-NH_2-COSAN, 9-NH_2-1,2-$C_2B_{10}H_{11}$, 9-NH_2-1,7-$C_2B_{10}H_{11}$, y 2-NH_2-1,12-$C_2B_{10}H_{11}$. La norma para PA mayores se aplica a isómeros con los grupos NH_2 bastante más alejados de los átomos C del carborano (no metálico). El cálculo de la energía de piramidalización demuestra una mayor facilidad para la planarización del grupo amino en *cisoide* 8-NH_2-COSAN si se compara con *cisoide* 1-NH_2-COSAN.

Palabras clave: Afinidad protónica; metaloheteroborano; superácido; química cuántica; energía de deslocalización; DFT.

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RESUM

En aquest treball presentem càlculs químic-quàntics de les Afinitats Protòniques (PA) dels aminoborans icosaèdrics, de carborans i metalacarborans que contenen Co amb un error relatiu del ~ 2% - quan es disposa de dades experimentals – amb els grups funcionals B3LYP i BP86. L'ús de bases més grans per sistemes simples com el NH_3, CH_3NH_2, i la borazina ($B_3H_6N_3$) redueix l'error a un ~ 0.5 % , indicant la validesa d'aquests funcionals per aquestes computacions i la predicció de PA per dades experimentals no disponibles de carborans i metalacarborans. Les PA calculades demostren que la substitució d'un àtom exo H per un grup NH_2 en $B_{12}H_{12}^{(2-)}$, $CB_{11}H_{12}^{(-)}$, (*orto, meta, para*)-$C_2B_{10}H_{12}$, i el metalacarborà [3-Co(1,2-$C_2B_9H_{11})_2]^{(-)}$ = COSAN el sistema mes similar amb el que es pot comparar es l'anió NH_2-$BH_3^{(-)}$ – PA(B3LYP/cc-pVTZ) = 1505 kJ·mol^{-1} – en comparació amb la metilamina CH_3NH_2 o la borazina, els dos últims amb PA experimentals de 900 i 803 kJ·mol^{-1} respectivament. La PA mes gran per un isòmer determinat correspon, seguint aquest ordre a: 1-NH_2-$B_{12}H_{11}^{(2-)}$, $^{(-)}BH_3NH_2$, 12-NH_2-$CB_{11}H_{11}^{(-)}$, *cisoid* 8-NH_2-COSAN, *transoid* 9-NH_2-COSAN, 9-NH_2-1,2-$C_2B_{10}H_{11}$, 9-NH_2-1,7-$C_2B_{10}H_{11}$, i 2-NH_2-1,12-$C_2B_{10}H_{11}$. La norma per PA mes grans s'aplica a isòmers amb els grups NH_2 mes lluny dels àtoms C del carborà (no metàl·lic). El càlcul de l'energia de piramidalització demostra una facilitat més gran per la planarització del grup amino en *cisoid* 8-NH_2-COSAN si es compara amb *cisoid* 1-NH_2-COSAN.

Paraules clau: Afinitat protònica; metaloheteroborrà; superàcid; química quàntica; energia de deslocalització; DFT.

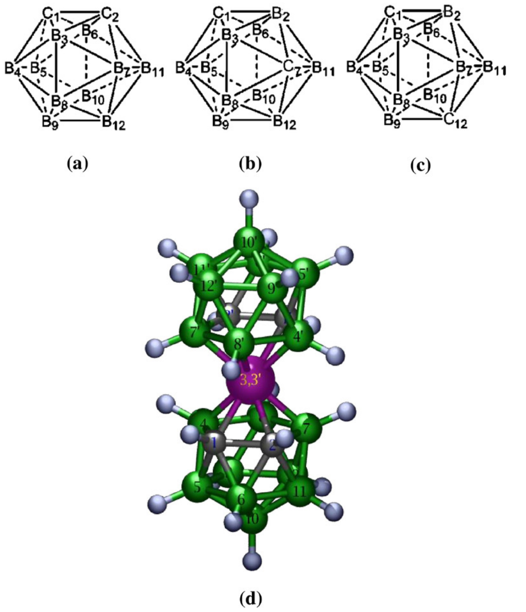
INTRODUCTION

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 combinining 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

$$A + H^+ \longrightarrow AH^+$$

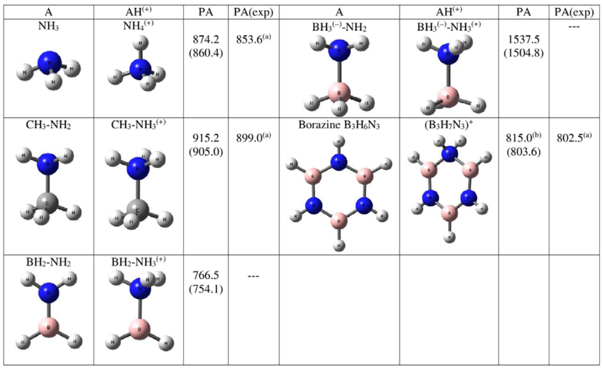
In our case here, the A system corresponds to the following amino-derived systems: ammonia NH_3, methylamine CH_3NH_2, boranamine BH_2NH_2, $^{(-)}BH_3NH_2$, borazine $B_3H_6N_3$ – the equivalent of benzene by substituting every two consecutive C atoms by B and N – and the following icosahedral (car)boranes, (*ortho*, *meta*, *para*)-carborane and Cobalt metallacarboranes: 1-(NH_2)-$B_{12}H_{11}^{(2-)}$, all symmetry-unique (SU) isomers in *n*-(NH_2)-$CB_{11}H_{11}^{(-)}$, *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-$C_2B_9H_{11}$)]$^{(-)}$. 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 NH_2 group substituting *exo* H atoms leads in many cases to more than one positional isomer for a given structure.


(a) (b) (c)

(d)

Figure 1. *Atom labels for: (a) ortho-carborane 1,2-$C_2B_{10}H_{12}$, (b) meta-carborane 1,7-$C_2B_{10}H_{12}$, (c) para-carborane 1,12-$C_2B_{10}H_{12}$, (d) transoid Cobalt bis(dicarbollide) [3-Co($C_2B_9H_{11}$)$_2$]$^{(-)}$. Hydrogen atoms are not shown for clarity in (ortho, meta, para)-carborane.*

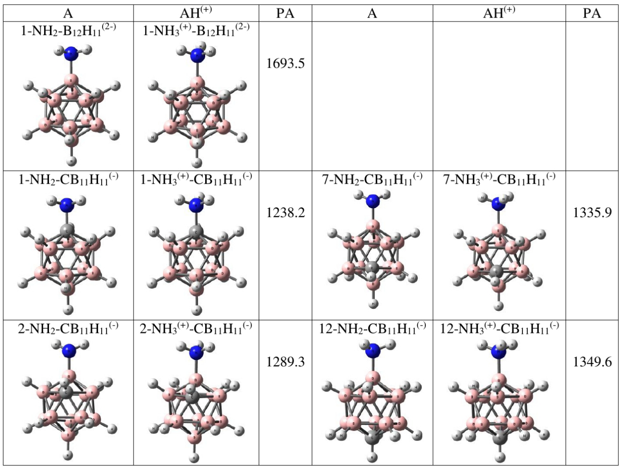
Table 1. *Optimized structures and Proton Affinities (PA, in kJ·mol^{-1}) in CH_3-NH_2/$NH_3^{(+)}$, BH_2-NH_2/$NH_3^{(+)}$, and $BH_3^{(-)}$-NH_2/$NH_3^{(+)}$, with PA = $-\Delta_r H^0$ of the process A + $H^{(+)} \longrightarrow AH^{(+)}$. B3LYP/6-31G* computations, in parentheses B3LYP/cc-pVTZ computations.*



A	AH$^{(+)}$	PA	PA(exp)	A	AH$^{(+)}$	PA	PA(exp)
NH_3	$NH_4^{(+)}$	874.2 (860.4)	853.6$^{(a)}$	$BH_3^{(-)}$-NH_2	$BH_3^{(-)}$-$NH_3^{(+)}$	1537.5 (1504.8)	---
CH_3-NH_2	CH_3-$NH_3^{(+)}$	915.2 (905.0)	899.0$^{(a)}$	Borazine $B_3H_6N_3$	$(B_3H_7N_3)^+$	815.0$^{(b)}$ (803.6)	802.5$^{(a)}$
BH_2-NH_2	BH_2-$NH_3^{(+)}$	766.5 (754.1)	---				

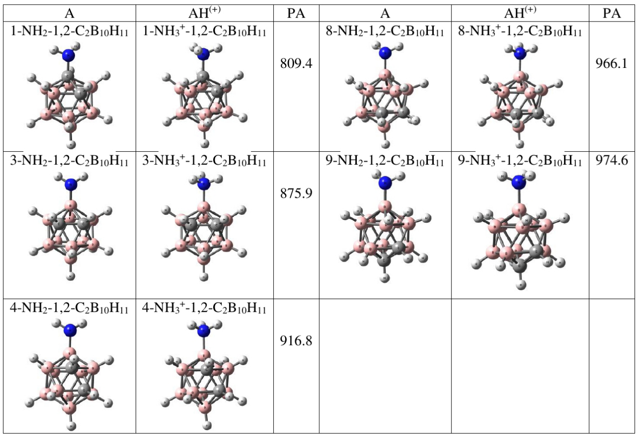
(a) See Reference [9]. (b) PA for protonation on the N atom. Protonation on B atom gives H_2, see Reference [20].

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



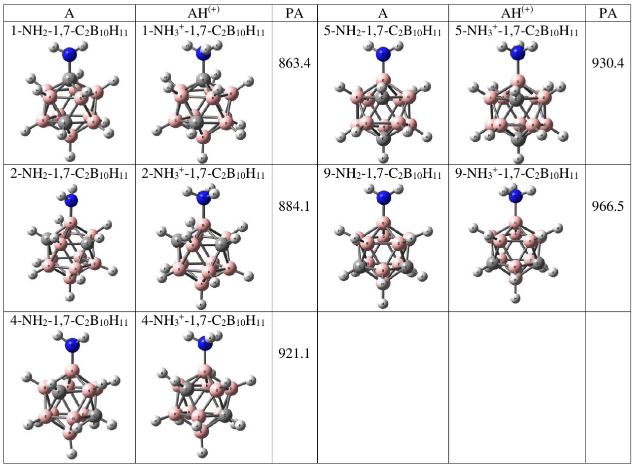
A	AH$^{(+)}$	PA	A	AH$^{(+)}$	PA
1-NH_2-$B_{12}H_{11}^{(2-)}$	1-$NH_3^{(+)}$-$B_{12}H_{11}^{(2-)}$	1693.5			
1-NH_2-$CB_{11}H_{11}^{(-)}$	1-$NH_3^{(+)}$-$CB_{11}H_{11}^{(-)}$	1238.2	7-NH_2-$CB_{11}H_{11}^{(-)}$	7-$NH_3^{(+)}$-$CB_{11}H_{11}^{(-)}$	1335.9
2-NH_2-$CB_{11}H_{11}^{(-)}$	2-$NH_3^{(+)}$-$CB_{11}H_{11}^{(-)}$	1289.3	12-NH_2-$CB_{11}H_{11}^{(-)}$	12-$NH_3^{(+)}$-$CB_{11}H_{11}^{(-)}$	1349.6

Table 3. Optimized structures and Proton Affinities (PA, in kJ·mol^{-1}) for systems where a hydrogen atom is substituted by an amino group in ortho-carborane 1,2-$C_2B_{10}H_{12}$, with PA = $-\Delta_r H^0$ of the process A + $H^{(+)} \longrightarrow AH^{(+)}$. B3LYP/6-31G computations.*



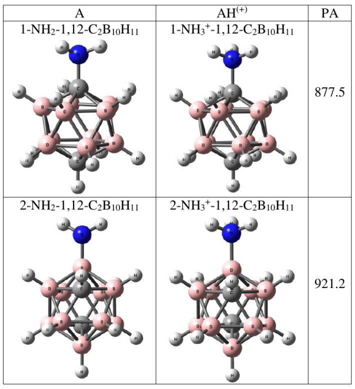
A	AH$^{(+)}$	PA	A	AH$^{(+)}$	PA
1-NH_2-1,2-$C_2B_{10}H_{11}$	1-NH_3^+-1,2-$C_2B_{10}H_{11}$	809.4	8-NH_2-1,2-$C_2B_{10}H_{11}$	8-NH_3^+-1,2-$C_2B_{10}H_{11}$	966.1
3-NH_2-1,2-$C_2B_{10}H_{11}$	3-NH_3^+-1,2-$C_2B_{10}H_{11}$	875.9	9-NH_2-1,2-$C_2B_{10}H_{11}$	9-NH_3^+-1,2-$C_2B_{10}H_{11}$	974.6
4-NH_2-1,2-$C_2B_{10}H_{11}$	4-NH_3^+-1,2-$C_2B_{10}H_{11}$	916.8			

Table 4. *Optimized structures and Proton Affinities (PA, in kJ·mol^{-1}) for systems where a hydrogen atom is substituted by an amino group in meta-carborane 1,7-$C_2B_{10}H_{12}$, with PA = $-\Delta_r H^0$ of the process A + $H^{(+)} \longrightarrow AH^{(+)}$. B3LYP/6-31G* computations.*



A	AH$^{(+)}$	PA	A	AH$^{(+)}$	PA
1-NH_2-1,7-$C_2B_{10}H_{11}$	1-NH_3^+-1,7-$C_2B_{10}H_{11}$	863.4	5-NH_2-1,7-$C_2B_{10}H_{11}$	5-NH_3^+-1,7-$C_2B_{10}H_{11}$	930.4
2-NH_2-1,7-$C_2B_{10}H_{11}$	2-NH_3^+-1,7-$C_2B_{10}H_{11}$	884.1	9-NH_2-1,7-$C_2B_{10}H_{11}$	9-NH_3^+-1,7-$C_2B_{10}H_{11}$	966.5
4-NH_2-1,7-$C_2B_{10}H_{11}$	4-NH_3^+-1,7-$C_2B_{10}H_{11}$	921.1			

Table 5. *Optimized structures and Proton Affinities (PA, in kJ·mol^{-1}) for systems where a hydrogen atom is substituted by an amino group in para-carborane 1,12-$C_2B_{10}H_{12}$, with PA = $-\Delta_r H^0$ of the process A + $H^{(+)} \longrightarrow AH^{(+)}$. B3LYP/6-31G* computations.*



A	AH$^{(+)}$	PA
1-NH_2-1,12-$C_2B_{10}H_{11}$	1-NH_3^+-1,12-$C_2B_{10}H_{11}$	877.5
2-NH_2-1,12-$C_2B_{10}H_{11}$	2-NH_3^+-1,12-$C_2B_{10}H_{11}$	921.2

COMPUTATIONAL METHODS

The electronic structure computations for the determination of PA where carried out with the program Gaussian09[11] and the B3LYP[12,13] and BP86[11, 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 NH_2. For selected 1-NH_2-COSAN and 8-NH_2-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

Table 6. *Optimized structures and Proton Affinities (PA, in kJ·mol^{-1}) for systems where a hydrogen atom is substituted by an amino group in transoid [3-Co(1,2-$C_2B_9H_{11}$)$_2$]$^{(-)}$, with PA = $-\Delta_r H^0$ of the process A + $H^{(+)}$ $\longrightarrow$ $AH^{(+)}$. BP86/AE1 computations. COSAN ≡ [3-Co($C_2B_9H_{11}$)$_2$]$^-$.*

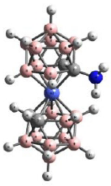
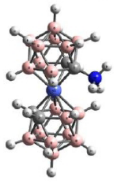
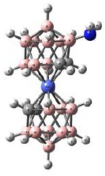
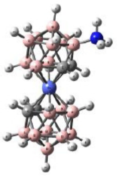
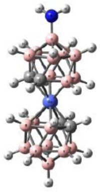
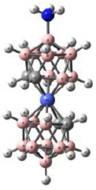
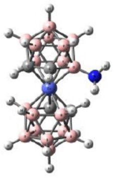
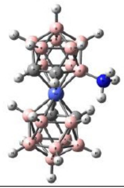
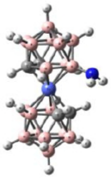
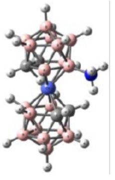
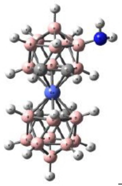
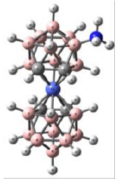
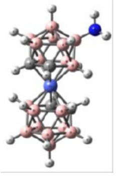
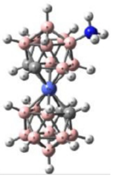
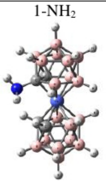
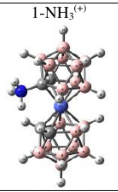
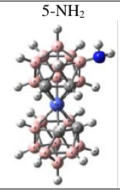
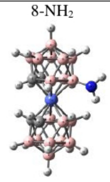
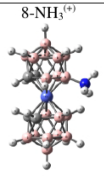
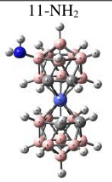
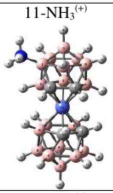
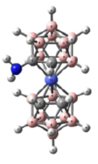
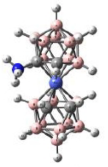
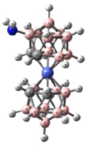
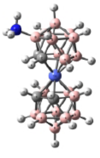
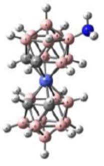
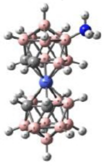
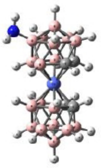
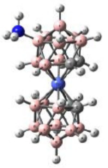
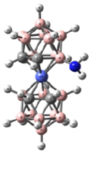
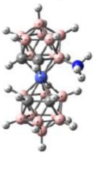
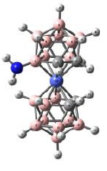
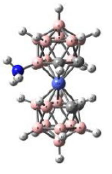
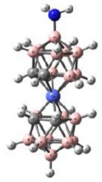
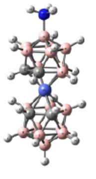
A	AH$^{(+)}$	PA	A	AH$^{(+)}$	PA	A	AH$^{(+)}$	PA
1-NH_2-COSAN 	1-$NH_3^{(+)}$-COSAN 	1209.5	6-NH_2-COSAN 	6-$NH_3^{(+)}$-COSAN 	1197.5	10-NH_2-COSAN 	10-$NH_3^{(+)}$-COSAN 	1251.1
4-NH_2-COSAN 	4-$NH_3^{(+)}$-COSAN 	1260.4	8-NH_2-COSAN 	8-$NH_3^{(+)}$-COSAN 	1262.1			
5-NH_2-COSAN 	5-$NH_3^{(+)}$-COSAN 	1231.8	9-NH_2-COSAN 	9-$NH_3^{(+)}$-COSAN 	1276.2			

Table 7. *Optimized structures and Proton Affinities (PA, in kJ·mol^{-1}) for systems where a hydrogen atom is substituted by an amino group in cisoid [3-Co(1,2-$C_2B_9H_{11}$)$_2$]$^{(-)}$, with PA = $-\Delta_r H^0$ of the process A + $H^{(+)}$ $\longrightarrow$ $AH^{(+)}$. BP86/AE1 computations. COSAN ≡ [3-Co($C_2B_9H_{11}$)$_2$]$^-$. The notation n-NH_2 indicates the position of the amino group in n-NH_2-COSAN.*

A	AH$^{(+)}$	PA	A	AH$^{(+)}$	PA	A	AH$^{(+)}$	PA	A	AH$^{(+)}$	PA
1-NH_2 	1-$NH_3^{(+)}$ 	1137.0	5-NH_2 	5-$NH_3^{(+)}$ 	1222.4	8-NH_2 	8-$NH_3^{(+)}$ 	1314.7	11-NH_2 	11-$NH_3^{(+)}$ 	1233.0
2-NH_2 	2-$NH_3^{(+)}$ 	1170.4	6-NH_2 	6-$NH_3^{(+)}$ 	1183.6	9-NH_2 	9-$NH_3^{(+)}$ 	1284.4	12-NH_2 	12-$NH_3^{(+)}$ 	1287.3
4-NH_2 	4-$NH_3^{(+)}$ 	1252.2	7-NH_2 	7-$NH_3^{(+)}$ 	1286.9	10-NH_2 	10-$NH_3^{(+)}$ 	1251.3			

program[19] at either the Hartree-Fock (HF) or the BP86 density-functional level of theory and the same AE1 basis set.

RESULTS AND DISCUSSION

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 H_2 and the radical $B_3N_3H_5^{(\cdot)}$[,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 kJ·mol^{-1} reduces to 5 kJ·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 avaliable, 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 $^{(-)}BH_3NH_2$ anion, whose protonated species in the latter is the charge-transfer complex $^{(-)}BH_3NH_2^{(+)}$. Table 1 shows that the PA for BH_2NH_2 and $^{(-)}BH_3NH_2$ are 767 kJ·mol^{-1} and 1538 kJ·mol^{-1} respectively (B3LYP/6-31G*). The PA of BH_2NH_2 is lower than in NH_3, but increases considerably – doubles! – in $^{(-)}BH_3NH_2$. As for borazine, protonation on N atom gives a PA of 815 kJ·mol^{-1} (double-zeta) which lowers to 804 kJ·mol^{-1} (triple-zeta basis cc-pVTZ) very close to the experimental value of 803 kJ·mol^{-1} [21].

Turning now to polyhedral (car)boranes, substitution of an H atom by an amino group in the icosahedral dianion $B_{12}H_{12}^{(2-)}$, gives the single isomer 1-NH_2-$B_{12}H_{12}^{(2-)}$, with a computed PA of 1694 kJ·mol^{-1}, a shown in Table 2. This value is closer to the PA of $^{(-)}BH_3NH_2$ with PA = 1538 kJ·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 $CB_{11}H_{12}^{(-)}$: 1-NH_2-$CB_{11}H_{11}^{(-)}$, 2-NH_2-$CB_{11}H_{11}^{(-)}$, 7-NH_2-$CB_{11}H_{11}^{(-)}$ and 12-NH_2-$CB_{11}H_{11}^{(-)}$. Interestingly, the larger the PA when the farther the NH_2 group from C atom in position 1:

$$PA(1) < PA(2) < PA(7) < PA(12)$$

with a difference of PA(12) – PA(1) = 110 kJ·mol^{-1}, and PA(12) = PA(12-NH_2-$CB_{11}H_{11}^{(-)}$) = 1350 kJ·mol^{-1}, which is lower than PA(1-NH_2-$B_{12}H_{12}^{(2-)}$) by 344 kJ·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^o, 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 NH_2 group from the two C atoms in the cage, as in the previous case for the amino isomers of $CB_{11}H_{12}^{(-)}$:

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

with a difference $PA^o(9)$ – $PA^o(1)$ = 165 kJ·mol^{-1}, with the largest PA for the 9-NH_2-1,2-$C_2B_{10}H_{11}$ isomer: $PA^o(9)$ = 975 kJ·mol^{-1}, larger than in NH_3, but much lower than in the 1-NH_2-$B_{12}H_{11}^{(2-)}$ and 12-NH_2-$CB_{11}H_{11}^{(-)}$ molecules.

As regards to *meta*-carboranes, Table 4, we observe a similar behaviour for the amino isomers, with increasing PA as the NH_2 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 kJ·mol^{-1}. Finally, for *para*-carborane, the two amino isomers follow tha same rule, with $PA^p(1) < PA^p(2)$, with a difference of $PA^p(2)$ – $PA^p(1)$ = 63 kJ·mol^{-1}, as shown in Table 5. As for the largest PA for a given amino positional isomer, we have:

$$PA^o(9) = 975 > PA^m(9) = 967 > PA^p(2) = 921.$$

We now turn to the amino-metallacarboranes, when an H atom is substituted by an NH_2 group in one of the ligands in the $[Co(C_2B_9H_{11})_2]^{(-)}$≡ COSAN complex[21] for all possible regioisomers, whose protonation on N gives the zwitterion [(*n*-NH_3^+-1,2-$C_2B_9H_{10}$)-3,3'-Co(1,2-$C_2B_9H_{11}$)]$^{(-)}$ ≡ *n*-NH_3^+-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 aways 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-$C_2B_9H_{11}$)$_2$]$^-$ has C_{2h} symmetry and therefore the following positions are equivalent for every ligand: C(1) ≡ C(2), B(4) ≡ B(7), B(5) ≡ B(11), B(9) ≡ B(12), as shown in Figure 1d. Thus only seven NH_2 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 NH_2 isomers from *transoid* [(*n*-NH_2-1,2-$C_2B_9H_{10}$)-3,3'-Co(1,2-$C_2B_9H_{11}$)]$^{(-)}$ ≡ *n*-NH_2-COSAN. We should emphasize that 8-$NH_3^{(+)}$-COSAN has been synthesized[22]. 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 $(C_2B_9H_{11})^{(2-)}$, and the total charge of the system is therefore $q = -1$. As shown in Table 6, the PA follow the order:

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

the lowest PA corresponds to the NH_2 group attached to B(6), and the largest PA to NH_2 in positions B(8) and B(9). The difference between maximum and minimum is $PA^{trans}(9)$ - $PA^{trans}(6)$ = 78 kJ·mol^{-1}.

As regards to the *cisoid* structures of the complex [(*n*-NH_2-1,2-$C_2B_9H_{10}$)-3,3'-Co(1,2-$C_2B_9H_{11}$)]$^{(-)}$, in Table 7 we show the computed PA for the different isomers. The structure *cisoid* [3-Co-(1,2-$C_2B_9H_{11}$)$_2$]$^-$ has only C_2 symmetry, which relates one ligand with the other, without atom equivalences in the same ligand and therefore we have to take into account all vertices in the ligand, resulting in eleven NH_2 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

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

The largest PA corresponds to NH_2 in position B(8) and the lowest for position C(1), with a difference of $PA^{cis}(8) - PA^{cis}(1) = 178$ kJ·mol^{-1}.

Comparison of PA from *transoid* and *cisoid* structures, shows that the largest PA corresponds to the *cisoid* $[(8\text{-}NH_2\text{-}1,2\text{-}C_2B_9H_{10})\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})]^{(-)} \equiv$ 8-NH_2-COSAN with PA = 1315 kJ·mol^{-1}. Analysis of Table 1 through Table 7 shows that for the icosahedral carboranes, the farthest the NH_2 group from the C(cage) atom, the larger the PA. As for the *cisoid* and *transoid n*-NH_2-COSAN complexes, we can clearly see the largest PA for *cisoid* 8-NH_2-COSAN, with PA(B3LYP/6-31G*) = 1315 kJ·mol^{-1}.

Delocalization energies

In this section we analyze the -NH_2 pyramidalization energy and delocalization energy for the systems: NH_2-$BH_3^{(-)}$, *cisoid* 1-NH_2-COSAN and *cisoid* 8-NH_2-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 NH_2 group and the connecting atom, either C(1) (for 1-NH_2-COSAN) or B(8) (for 8-NH_2-COSAN).

As shown in Table 8, the pyramidalization energies show that N is particularly easy to planarize in *cisoid* 8-NH_2-COSAN: only 4.3 kJ.mol^{-1}, much lower as compared to $^{(-)}BH_3$-NH_2 and 1-NH_2-COSAN. As shown in Table 9, the delocalization energy was calculated in the NH_2-$BH_3^{(-)}$ anion at two levels of theory: BP86 and HF. The value is ~ 20 kJ.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-NH_2-COSAN and 8-NH_2-COSAN is significantly larger in the complexes, about 50 kJ.mol^{-1}. It is slightly larger in 1-NH_2-COSAN than in 8-NH_2-COSAN but the difference is small (5 kJ.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-NH_2-COSAN and B(8) in 8-NH_2-COSAN. A similar feature was observed in other cases[23].

Table 8. *BP86/AE1 pyramidalization energy PE(kJ·mol^{-1}) for representative systems. Pyram = pyramidalized.*

System	Energy(au)	PE
Planar $^{(-)}BH_3$-NH_2	-82.59099	0.0
Pyram $^{(-)}BH_3$-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 (kJ·mol^{-1}) for representative systems, with n-COSAN ≡ n-NH_2-COSAN. HF = Hartree-Fock.*

Method	System	Energy (au)	ΔE
BP86	$^{(-)}BH_3NH_2$ Deloc	-82.59087	−22.7
BP86	Localized	-82.58223	---
HF	$^{(-)}BH_3NH_2$ 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	----

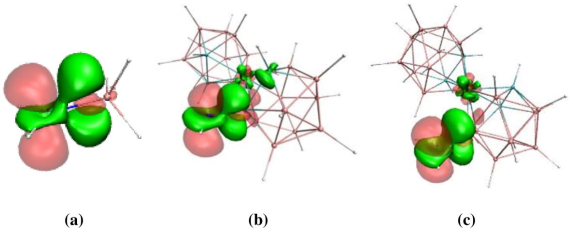


Figure 2. *Isosurface of density variation when the localization constraint is released in (a) NH_2-$BH_3^{(-)}$, (b) 1-NH_2-COSAN, (c) 8-NH_2-COSAN. Red and green density lobes correspond, respectively, to negative and positive electron density differences. Hence the delocalization is from the NH_2 lone pair to the rest of the molecule. The isovalue surface for electron density differences is set to 10^{-3} atomic units.*

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) ≈ 850 kJ·mol^{-1}, PA(1-NH_2-1,12-$C_2B_{10}H_{11}$) ≈ 877 kJ·mol^{-1}, COSAN systems increase very significantly the PA, with PA(8-NH_2-COSAN) ≈ 1260 kJ·mol^{-1}, which is almost as large as PA ($^{(-)}BH_3NH_2$) ≈ 1530 kJ·mol^{-1}, with 8-NH_2-COSAN possibly more stable from an experimental viewpoint. A simple computation of the PA in $HSO_4^{(-)}$ to give H_2SO_4 gives the value of PA(B3LYP/6-31G*) = 1330 kJ·mol^{-1} (understood as the acidity enthalpy for the process $H_2SO_4 \longrightarrow HSO_4^{(-)} + H^{+}$,[24]) thus showing the increased PA for NH_2-substituted (car)boranes and metallacarboranes, larger than in $HSO_4^{(-)}$

for $1\text{-}NH_2\text{-}B_{12}H_{11}^{(2-)}$, $^{(-)}BH_3NH_2$ and $12\text{-}NH_2\text{-}CB_{11}H_{11}^{(-)}$. As for the cobaltacarborane *cisoid* $8\text{-}NH_2$-COSAN, the PA is only 15 kJ·mol^{-1} lower than in $HSO_4^{(-)}$, hence proving the enhanced stability of the corresponding zwitterion from protonation of the NH_2 group.

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