

# Gas phase acidities of N-substituted amine-boranes

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**Abstract** Complexation energies and acidities of 19 primary, secondary and tertiary amine-boranes were investigated using MP2/6-311+G(d,p) and B3LYP/6-311+G(d,p) methods. Gas phase acidities for free amines were also calculated. Acidity values for studied complexes range from 327.3 to 349.1 kcal mol<sup>-1</sup> and the most acidic are the ones with direct connection between deprotonation center and a  $\pi$ -system. Results obtained by both computational methods are in good agreement with each other and with known experimental data. Addition of BH<sub>3</sub> increases the acidity of amines by 30 to 50 kcal mol<sup>-1</sup>. This enhancement effect was compared to the respective effect witnessed in phosphine-boranes and traced back to changes of charge delocalization on nitrogen. A question about the structural stability of several deprotonated amine-borane anions in the gas phase was also raised.

**Keywords** Ab initio calculations · Acidity · Amines · Boranes · Complex · Gas phase

## Introduction

Compounds formed by the association of amines and boranes have been known since the nineteenth century [1, 2]. During

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the last decade such species have gained more attention as possible hydrogen storage materials and reagents in organic chemistry [3, 4]. Recent research has revealed several interesting properties most notably that of the dihydrogen bond [5–7] and related “molecular tweezer” effect [8–11]. So far vast majority of amine-borane related publications have been focusing on the catalyzed removal of hydrogen. The effects of halogen and methyl substitutions on complexation energies and proton affinities have also been widely studied [12–17]. Bulkier substituents and especially their effect on deprotonation reactions have received much less attention. Studies of the gas-phase proton transfer reactions give information about intrinsic properties and are therefore closely related to possible applications.

There have been quite a few works concerning acidities of N-substituted amine-boranes. More than 10 years ago Ren et al. investigated some borane complexes which included trimethylamine-borane and triethylamine-borane [18]. The experiments revealed that the acidity of trimethylamine-borane is between that of water and naphthalene. Acidity value of 384.0±2.0 kcal mol<sup>-1</sup> was assigned to the complex. They also estimated that the coordination of Me<sub>3</sub>N by BH<sub>3</sub> leads to an  $\alpha$ -CH acidity increase of about 18 kcal mol<sup>-1</sup>. Experimental acidity for triethylamine-borane could not be determined due to an elimination reaction resulting in the removal of an ethyl group.

Very recently a paper reporting the experimental acidities of several amine-boranes was published [19]. Gas-phase acidities measured by ESI-MS and Cooks kinetic method were in a good agreement with the results of G4 calculations. Authors used PhCH<sub>2</sub>NH<sub>2</sub>BH<sub>3</sub> as a model to compare N-H deprotonation and a possible intramolecular reaction starting from B-H deprotonation. It was found that the B-H deprotonation pathway is energetically too demanding. We have also found that to be true for most of the amine-boranes, but there seem to be some exceptions.

Deprotonation of some closely related phosphine-boranes have also been studied [20]. Although quantum chemical

and photoelectron spectroscopic research has revealed differences in bond properties comparing amine-boranes to phosphine-boranes and different synthesis procedures are needed [21], it is reasonable to believe that the substituent effects are similar. The most interesting finding that relates to our study concerns 2-chloroethyl amine-borane. It was found computationally and confirmed experimentally that there are reaction pathways leading to  $\text{Cl}^-$  release.

Lately we have reported the gas-phase chemistry of protonated amine-boranes [22] and the aim of this paper is to present the gas phase acidities. We have systematically studied several  $\text{R}^1\text{R}^2\text{R}^3\text{N-BH}_3$  complexes by means of computational methods. It is shown in the literature that the addition of  $\text{BH}_3$  greatly enhances the gas phase acidity of phosphines [20] and the same is also true for amines [19].

### Computational details

The calculations were carried out using GAUSSIAN 09 [23] program package. In our work we used MP2 [24–28] and B3LYP [29] (DFT) methods with 6–311+G(d,p) [30–33] bases set. For each species full conformational search was done and vibrational analyzes for zero-point energies and thermal corrections were performed. All stationary points were found to be true minima ( $\text{NImag}=0$ ). In the case of complexation energies basis set superposition error (BSSE) was calculated using counterpoise (CP) method of Boys and Bernardi [34–36]. The BSSE estimations for complexation reactions were approximately  $5 \text{ kcal mol}^{-1}$  in the case of MP2/6-311+G(d,p).

### Results and discussion

We have studied 19 amine-borane complexes ( $\text{R}^1\text{R}^2\text{R}^3\text{N-BH}_3$ ) with large variety of substituents. They include primary, secondary, and tertiary amines. We will report firstly the stability and then the gas phase acidity of all the studied complexes and corresponding amines. The thermodynamic data in Table 1 correspond to the complexation reaction. Our calculations confirm that the formation of amine-borane in the gas phase is a thermodynamically favored process (Gibbs free energy changes calculated with MP2 are between  $-12$  and  $-22 \text{ kcal mol}^{-1}$ ) and therefore the complexation equilibria is shifted strongly toward the product formation.

Gas phase acidity (GA) is defined as the Gibbs free energy changes of the deprotonation reaction, and GA-s for all studied species are presented in Table 2. We can see that the difference between MP2 and B3LYP acidities is in the vast majority of cases less than  $2 \text{ kcal mol}^{-1}$ , which can be considered a usual uncertainty for both methods. Mean absolute deviation

**Table 1** Reaction enthalpies ( $\Delta\text{H}$ ) and Gibbs free energies ( $\Delta\text{G}$ ) for all studied complexation reactions calculated with B3LYP/6-311+G\*\* and MP2/6-311+G\*\* methods. All values are presented in  $\text{kcal mol}^{-1}$  and corrected for BSSE using CP

| Complex                     | B3LYP            |                  | MP2              |                  |
|-----------------------------|------------------|------------------|------------------|------------------|
|                             | $\Delta\text{H}$ | $\Delta\text{G}$ | $\Delta\text{H}$ | $\Delta\text{G}$ |
| Ammonia-borane              | -23.8            | -14.4            | -23.5            | -14.1            |
| Methylamine-borane          | -26.1            | -17.4            | -29.0            | -18.4            |
| Trifluoroethylamine-borane  | -24.9            | -14.3            | -26.0            | -15.4            |
| 2-Chloroethylamine-borane   | -24.8            | -14.2            | -26.2            | -15.2            |
| Allylamine-borane           | -27.4            | -16.9            | -30.0            | -19.3            |
| Propargylamine-borane       | -26.5            | -16.0            | -29.2            | -18.6            |
| Adamantylamine-borane       | -25.9            | -15.5            | -27.4            | -16.5            |
| Benzylamine-borane          | -27.9            | -17.3            | -29.1            | -18.2            |
| Aniline-borane              | -19.1            | -9.3             | -22.1            | -12.1            |
| Propylamine-borane          | -28.4            | -17.2            | -27.1            | -16.8            |
| c-Propylamine-borane        | -26.1            | -15.7            | -27.3            | -17.3            |
| Dimethylamine-borane        | -29.3            | -18.3            | -32.0            | -21.0            |
| Aziridine-borane            | -28.5            | -17.8            | -29.2            | -18.5            |
| Azetidine-borane            | -31.2            | -20.6            | -32.7            | -21.8            |
| Pyrrolidine-borane          | -30.4            | -19.6            | -32.6            | -21.8            |
| Ethenylmethylamine-borane   | -19.7            | -8.9             | -23.5            | -12.9            |
| Trimethylamine-borane       | -28.2            | -17.4            | -32.7            | -22.1            |
| Pyridine-borane             | -27.4            | -18.3            | -27.8            | -17.9            |
| Ethenyldimethylamine-borane | -18.8            | -7.2             | -25.0            | -13.5            |

between the results is  $1.0 \text{ kcal mol}^{-1}$  and root mean square deviation is  $1.4 \text{ kcal mol}^{-1}$ . That can be considered a good agreement and for the sake of simplicity we use MP2 results in further discussion.

The stability of the complex is dependent on the electron density donated to the borane by the free amine and that in turn is related to parameters (like the nature and the number of substituents) influencing the gas phase acidity. For example the electron withdrawing groups and  $\pi$ -systems reduce the charge on nitrogen thus reducing the strength of the complex, at the same time they also increase the acidity by having a stabilizing effect on the deprotonated species. Therefore it can be predicted that amine-boranes with very high N-H acidity would be unstable. To design a stable highly acidic species an alternative deprotonation center must be introduced. Protonation and complexation are not so directly related, both are Lewis acid–base reactions, but there is a significant difference, as the proton is a hard non-polarizable Lewis acid, while the borane is a soft acid and therefore much more polarizable.

All studied amine-boranes except the three tertiary amines behave as N-H acids. The acidities of N-H group vary from  $327.3$  to  $349.1 \text{ kcal mol}^{-1}$ . For the strong majority of investigated complexes (12 out of 16 N-H acids) the effect of substituent is

**Table 2** Gas phase acidities (GA, Gibbs free energies for deprotonation reaction) calculated with B3LYP/6-311+G\*\* and MP2/6-311+G\*\* methods. All values in kcal mol<sup>-1</sup>. Asterisk (\*) marks the possibility of intramolecular rearrangements in deprotonated complexes

| Complex                      | GA(B3LYP) | GA(MP2) |
|------------------------------|-----------|---------|
| Ammonia-borane               | 348.2     | 349.2   |
| Methylamine-borane           | 348.1     | 349.5   |
| Trifluoroethylamine-borane * | 332.4     | 333.9   |
| 2-Chloroethylamine-borane *  | 337.7     | 338.0   |
| Allylamine-borane *          | 343.8     | 345.1   |
| Propargylamine-borane *      | 341.0     | 342.3   |
| Adamantylamine-borane        | 346.4     | 345.6   |
| Benzylamine-borane *         | 342.1     | 343.1   |
| Aniline-borane *             | 324.0     | 327.3   |
| Propylamine-borane           | 346.2     | 346.6   |
| c-Propylamine-borane         | 342.6     | 343.5   |
| Dimethylamine-borane         | 345.7     | 347.3   |
| Aziridine-borane             | 342.5     | 342.5   |
| Azetidine-borane             | 346.0     | 346.1   |
| Pyrrolidine-borane           | 345.1     | 345.4   |
| Ethenylmethylamine-borane    | 324.4     | 328.0   |
| Trimethylamine-borane        | 385.9     | 386.0   |
| Pyridine-borane              | 364.8     | 365.0   |
| Ethyldimethylamine-borane *  | 374.1     | 373.7   |

minimal and the acidity falls between 341.9 and 349.1 kcal mol<sup>-1</sup>. There are four primary or secondary amine-boranes standing out: aniline-borane (327.3 kcal mol<sup>-1</sup>), ethenylmethylamine-borane (328.0 kcal mol<sup>-1</sup>), trifluoroethylamine-borane (333.5 kcal mol<sup>-1</sup>) and 2-chloroethylamine-borane (337.6 kcal mol<sup>-1</sup>). The common feature between the first two is a direct connection of deprotonation center to a  $\pi$ -system, which helps to stabilize the negative charge of the anion. The other two, trifluoroethylamine-borane and 2-chloroethylamine-borane, have both electron withdrawing halogen atoms in the substituent. The three complexes composed of tertiary amines (trimethylamine-borane, pyridine-borane, and ethenyldimethylamine-borane) are the least acidic because they must act like C-H acids.

In Tables 2 and 3 seven complexes are marked with asterisk. Our search for deprotonation centers revealed that for those amine-boranes the removal of proton from boron may lead to structural rearrangements. Although the end products of intramolecular reactions initiated by B-H deprotonation are more stable than the optimized outcome of N-H deprotonation, the kinetics for all of them are not known. Common feature between the seven is the repositioning of the BH<sub>2</sub>NH<sub>2</sub> group. In the case of allylamine-borane, 2-chloroethylamine-borane and ethenyldimethylamine-borane the energy gap between the rearranged and the most stable normal structure was quite high, respectively 16, 30 and 42 kcal mol<sup>-1</sup>. The energy difference for the remaining four was below 5 kcal mol<sup>-1</sup>.

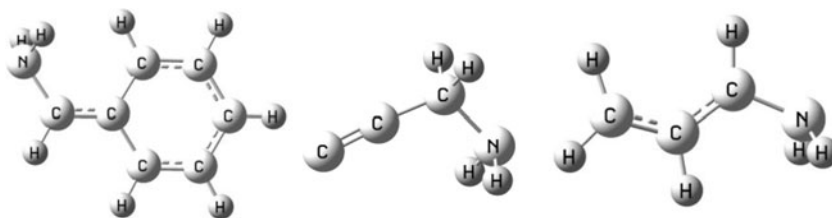
To estimate the probabilities of different deprotonations we have calculated so-called vertical ionization energies (proton

**Table 3** Comparison between the calculated gas phase acidities (GA) of the complexes and the respective free amines. All values in kcal mol<sup>-1</sup>. Asterisk (\*) marks the possibility of intramolecular rearrangements in deprotonated complexes

| Complex                      | Complex | Free amine |           | Change<br>$\Delta$ GA |
|------------------------------|---------|------------|-----------|-----------------------|
|                              |         | GA(MP2)    | exp. [37] |                       |
| Ammonia-borane               | 349.2   | 398.1      | 396.4     | 48.9                  |
| Methylamine-borane           | 349.5   | 396.7      | 395.0     | 47.2                  |
| Trifluoroethylamine-borane * | 333.9   | 375.4      |           | 41.6                  |
| 2-Chloroethylamine-borane *  | 338.0   | 324.6      |           | -13.4 <sup>a</sup>    |
| Allylamine-borane *          | 345.1   | 383.4      |           | 38.3 <sup>b</sup>     |
| Propargylamine-borane *      | 342.3   | 369.1      |           | 26.7 <sup>b</sup>     |
| Adamantylamine-borane        | 345.6   | 383.7      |           | 38.2                  |
| Benzylamine-borane *         | 343.1   | 375.8      |           | 32.7 <sup>b</sup>     |
| Aniline-borane *             | 327.3   | 360.6      | 359.3     | 33.4                  |
| Propylamine-borane           | 346.6   | 391.3      | 391.4     | 44.6                  |
| c-Propylamine-borane         | 343.5   | 384.8      |           | 41.3                  |
| Dimethylamine-borane         | 347.3   | 388.3      | 388.3     | 41.0                  |
| Aziridine-borane             | 342.5   | 383.1      |           | 40.6                  |
| Azetidine-borane             | 346.1   | 388.0      |           | 41.9                  |
| Pyrrolidine-borane           | 345.4   | 382.8      |           | 37.3                  |
| Ethenylmethylamine-borane    | 328.0   | 362.7      |           | 34.7                  |
| Trimethylamine-borane        | 386.0   | 403.9      | >398.4    | 17.8                  |
| Pyridine-borane              | 365.0   | 382.7      | 384.4     | 17.8                  |
| Ethyldimethylamine-borane *  | 373.7   | 393.8      |           | 20.1                  |

a – deprotonation of 2-chloroethylamine is followed by the removal of Cl<sup>-</sup> and thus this is not the true acidity value. b – deprotonation center changes from N-H in complex into C-H in free amine

**Fig. 1** Structures of C-H deprotonated benzylamine, propargylamine and allylamine

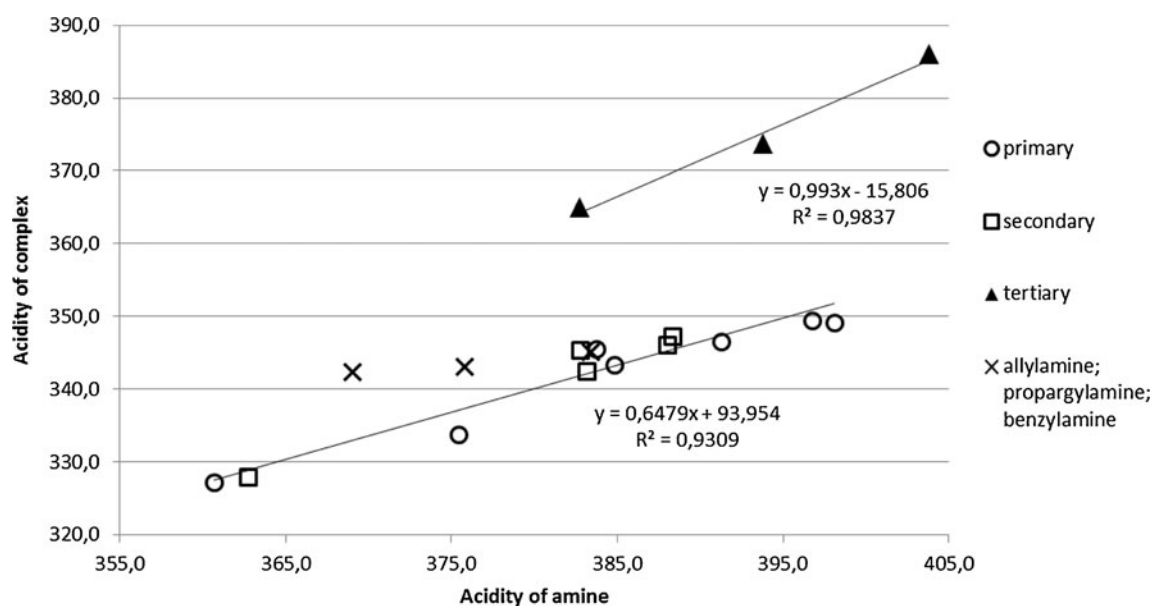


removal energies without geometry relaxation) for both N-H and B-H hydrogens. Deprotonation from amine group is always favored by 76 to 83 kcal mol<sup>-1</sup>. Martin-Comer et al. [19] have calculated transition states for reaction pathways leading to the rearranged structure in the case of benzylamine-borane and also concluded that it is energetically too demanding. This conclusion is supported by experimental data as the measurements included benzylamine-borane and four other complexes we have raised questions about (trifluoroethylamine-borane, allylamine-borane, propargylamine-borane, aniline-borane) and the results were in excellent agreement with N-H deprotonation [19]. The questions about the complexes with largest energy difference between the rivaling end products (2-chloroethylamine-borane and ethyldimethylamine-borane) still remain. For analogous chloromethylphosphine-borane it is reported [20] that deprotonation leads to intramolecular rearrangement. Ethyldimethylamine-borane differs from the other potentially B-H deprotonated complexes as it does not have N-H hydrogen. Since intramolecular reactions can make it impossible to determine the equilibrium acidity we have used N-H deprotonated structures further. Exact data for all structures can be found in [Supplementary information](#).

In Table 3 we compare the acidities of amines to the respective amine-borane complexes. The known experimental values are given and agree quite well with our calculations. The average acidity enhancement effect of BH<sub>3</sub> for N-H acids is 41 kcal mol<sup>-1</sup> and 19 kcal mol<sup>-1</sup> for C-H acids. This means that the stabilizing effect of BH<sub>3</sub> in anion is very strong. Unlike the complexes, not all primary and secondary amines act like N-H acids. Benzylamine, propargylamine and allylamine are C-H acids in gas phase. The structures of their deprotonated forms are given in Fig. 1.

Special behavior is shown by 2-chloroethylamine. Calculations reveal that its deprotonation leads to the removal of Cl<sup>-</sup>. Similar result was also witnessed during protonation center search for 2-chloroethylamine-borane and was reported in literature and confirmed experimentally in the case of chloromethylphosphine [20]. Thus it is reasonable to presume that the removal of Cl<sup>-</sup> may be characteristic to such species and determining the true equilibrium acidity may not be possible.

The correlations between the acidities of amines and respective BH<sub>3</sub> complexes are presented on Fig. 2. There are two series, first corresponds to N-H acids ( $G_{A_{\text{complex}}} = 0.65G_{A_{\text{amine}}} + 94$ ,  $R^2 = 0.93$ ) and second to C-H acidic tertiary



**Fig. 2** Correlations between the acidities of complex and free amine. Primary, secondary and tertiary amines are marked separately. Since primary and secondary amines are N-H acids in both forms (with three

exceptions, allylamine, propargylamine and benzylamine), they follow the same correlation. Tertiary amines are C-H acids in complex and in free form

amines ( $GA_{\text{complex}} = 0.99GA_{\text{amine}} - 16$ ,  $R^2 = 0.98$ ). Benzylamine, propargylamine and allylamine form potentially a third series because their deprotonation center changes from C-H to N-H upon complexation with  $BH_3$ . 2-Chloroethylamine was also discarded from correlation due to  $Cl^-$  ejection. Although all primary and secondary amines with N-H deprotonation center have been correlated together, there are 2+2 amines which strongly influence the correlation equation. Those are ammonia, methylamine, aniline and ethenylmethylamine, the weakest and the strongest among studied N-H acidic amines.

The acidifying effect of  $BH_3$  complexation on the ammonia and methylamine is almost  $50 \text{ kcal mol}^{-1}$ . Those two are the two weakest acids among the studied N-H acids and the smallest amines studied. Such a big acidity enhancement caused by  $BH_3$  addition is easily explained by comparing the size (or polarizability) of the anions. Complex formation greatly increases the molecular volume where the negative charge of anion can delocalize as witnessed by the biggest decrease of negative NBO charge on the nitrogen atom in the anion (see Table 4) upon complexation. The addition of  $BH_3$  directly to the protonation center greatly improves charge delocalization and the effect is most pronounced in small molecules like ammonia and methylamine.

**Table 5** The comparison between the acidities of amines and phosphines and their borane complexes. Acidities of phosphines and phosphineboranes presented in this table are experimental values obtained by Hurtado et al. [20]. All values in  $\text{kcal mol}^{-1}$

| R        | $RNH_2$ | $RPH_2$ | $\Delta$ | $RNH_2BH_3$ | $RPH_2BH_3$ | $\Delta$ |
|----------|---------|---------|----------|-------------|-------------|----------|
| Methyl   | 396.7   | 365.8   | 30.9     | 349.5       | 337.5       | 12.1     |
| Benzyl   | 375.8   | 357.0   | 18.8     | 343.1       | 329.9       | 13.2     |
| Phenyl   | 360.6   | 348.3   | 12.3     | 327.3       | 328.6       | -1.4     |
| c-Propyl | 384.8   | 360.9   | 23.9     | 343.5       | 336.7       | 6.7      |

The other two acids, which strongly influence correlation, are the two strongest acids among studied amines, aniline and ethenylmethylamine. However, the acidity enhancement effect of  $BH_3$  is only about  $34 \text{ kcal mol}^{-1}$  for those species. The  $\pi$ -system close to deprotonation center, like in those molecules, has a noticeable role in delocalizing the charge in anion. Since  $\pi$ -system already stabilizes the anion by charge delocalization (the increase of charge on nitrogen upon deprotonation in those free amines is smallest among studied N-H acids, see Table 4), the additional delocalization effect of  $BH_3$  on acidity of amine-borane complex is smaller.

The acidity trends reflect on the changes in calculated natural bond orbital (NBO) charges. One can argue that

**Table 4** NBO charges on nitrogen in complex and in free amine, in neutral and deprotonated forms. All values are presented as elementary charges.  $\Delta$  – increase of negative charge on nitrogen after deprotonation.  $\Delta\Delta$  – charge increase difference on nitrogen comparing complex and free amine

|                             | Complex |         |          | Free amine          |         |          | $\Delta\Delta$ |
|-----------------------------|---------|---------|----------|---------------------|---------|----------|----------------|
|                             | Deprot. | Neutral | $\Delta$ | Deprot.             | Neutral | $\Delta$ |                |
| Ammonia-borane              | -1.101  | -0.840  | 0.261    | -1.501              | -0.837  | 0.664    | 0.403          |
| Methylamine-borane          | -0.927  | -0.709  | 0.219    | -1.193              | -0.845  | 0.348    | 0.129          |
| Trifluoroethylamine-borane  | -0.909  | -0.714  | 0.196    | -1.158              | -0.844  | 0.314    | 0.118          |
| 2-Chloroethylamine-borane   | -0.935  | -0.713  | 0.223    | -0.891 <sup>a</sup> | -0.855  | –        | –              |
| Allylamine-borane           | -0.917  | -0.705  | 0.212    | -0.870 <sup>b</sup> | -0.837  | –        | –              |
| Propargylamine-borane       | -0.896  | -0.694  | 0.202    | -0.855 <sup>b</sup> | -0.820  | –        | –              |
| Adamantylamine-borane       | -0.926  | -0.716  | 0.211    | -1.185              | -0.848  | 0.336    | 0.126          |
| Benzylamine-borane          | -0.916  | -0.700  | 0.216    | -0.861 <sup>b</sup> | -0.832  | –        | –              |
| Aniline-borane              | -0.839  | -0.712  | 0.127    | -0.967              | -0.826  | 0.141    | 0.014          |
| Propylamine-borane          | -0.930  | -0.715  | 0.215    | -1.179              | -0.843  | 0.337    | 0.121          |
| c-Propylamine-borane        | -0.921  | -0.703  | 0.217    | -1.172              | -0.837  | 0.335    | 0.118          |
| Ethenylmethylamine-borane   | -0.739  | -0.635  | 0.104    | -0.824              | -0.699  | 0.125    | 0.021          |
| Dimethylamine-borane        | -0.815  | -0.614  | 0.201    | -0.990              | -0.702  | 0.288    | 0.087          |
| Aziridine-borane            | -0.744  | -0.595  | 0.150    | -0.920              | -0.664  | 0.257    | 0.107          |
| Azetidine-borane            | -0.802  | -0.634  | 0.167    | -0.966              | -0.716  | 0.250    | 0.083          |
| Pyrrolidine-borane          | -0.813  | -0.619  | 0.194    | -0.950              | -0.697  | 0.253    | 0.058          |
| Pyridine-borane             | -0.537  | -0.484  | 0.053    | -0.620              | -0.509  | 0.110    | 0.057          |
| Ethenyldimethylamine-borane | -0.605  | -0.573  | 0.033    | -0.598              | -0.598  | 0.000    | -0.033         |
| Trimethylamine-borane       | -0.602  | -0.551  | 0.051    | -0.644              | -0.605  | 0.039    | -0.012         |

a – deprotonation of 2-chloroethylamine is followed by the removal of  $Cl^-$  and thus this is not the true acidity reaction. b – deprotonation center changes from C-H in free amine into N-H in complex



charges are not physical observables, and moreover are very dependent on the type. However, atomic charges have proven to be useful for discussing and rationalizing structural and reactivity differences [38]. Also, Schwarz has shown [39] that despite the differences in absolute values the trends in different calculated charges are almost the same. NBO charges on nitrogen are presented in Table 4. In the case of N-H acids, charges on nitrogen can be related to acidity. Stability of anion depends on the delocalization of negative charge left after the removal of proton and the negative charge increase on nitrogen is inversely related to the effectiveness of delocalization. Relationship between charge change difference  $\Delta\Delta$  (charge change difference on nitrogen, between deprotonations of complex and free amine) and  $\text{BH}_3$ -s acidity enhancement effect is not quantitative, but  $\Delta\Delta$  values are clearly the smallest for aniline and ethenylmethylamine, where  $\text{BH}_3$  provides small acidity increase and the highest for ammonia and methylamine, where the increase is higher.

Although we have only studied three tertiary amines, it seems that the effect of  $\text{BH}_3$  addition to the C-H acids is more or less constant (18–20 kcal mol<sup>-1</sup>) and considerably smaller compared to the N-H acids. Such behavior is expected because N-H center is directly linked to borane while C-H deprotonation centers are farther away.

Experimental acidities for some phosphine-boranes are known [20] and we can compare them with amine-boranes. Phosphines themselves are more acidic than respective amines and in the case of the substituents presented in Table 5 the difference ranges from 10 to 30 kcal mol<sup>-1</sup>. Since most of the acidity variance in studied amines and phosphines can be explained by charge delocalization, it is expected that the acidity enhancement of  $\text{BH}_3$  is larger in amine-boranes. Borane increases the acidity of phosphines by 20 to 30 kcal mol<sup>-1</sup> and the acidity of amines by 30 to 50 kcal mol<sup>-1</sup>. Despite the larger acidity increase borane-amines are still about 10 kcal mol<sup>-1</sup> less acidic than corresponding phosphine-boranes as the gap between acidities of free amines and phosphines is very large. Exceptional behavior is again shown by the phenyl substituted complexes. Acidity values of aniline-borane and phenylphosphine-borane are very close (within experimental and computational uncertainties). This can be explained by the strong charge delocalizing capability of the  $\pi$ -system which together with the  $\text{BH}_3$ -s acidity enhancement effect compensates the difference between nitrogen and phosphorus atom.

## Conclusions

Altogether 19 different amine-boranes were studied by the means of MP2/6-311+G(d,p) and B3LYP/6-311+G(d,p) calculations. Results obtained by both computational methods were in good agreement with each other and with known experimental data. All studied primary and secondary amine-boranes acted as N-H

acids. Acidity values for studied complexes range from 327.3 to 349.1 kcal mol<sup>-1</sup>. The most acidic complexes are the ones with direct connection between deprotonation center and a  $\pi$ -system, which helps to stabilize the charge left by the removal of a proton. The stabilities of deprotonated 2-chloroethylamine-borane and ethenyl dimethyl amine-borane are questionable and experiments would be needed for a reliable answer. Addition of  $\text{BH}_3$  was found to increase the acidity of amines by 30 to 50 kcal mol<sup>-1</sup>, which is about 20 kcal mol<sup>-1</sup> more than the similar enhancement witnessed in phosphine-boranes. The acidity enhancement can be traced back to the improved charge delocalization in anions formed upon deprotonation. Tertiary amines were much less acidic due to being C-H acids and the acidity enhancement due to complexation with  $\text{BH}_3$  was considerably smaller compared to studied N-H acidic complexes.

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