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REGULAR ARTICLE

Theoretical study of neutral and protonated triple bonded molecules formed between C, N, Si, P, B and Al

Ibon Alkorta · Isabel Rozas · José Elguero

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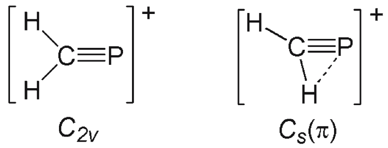
Abstract A theoretical study of the possible protonation sites of simple molecules formed by C, N, Si, P, B and Al that present a triple bond between those atoms has been carried out. The calculations performed include MP2 and CCSD(T) methods with the aug-cc-pVTZ basis set. The nature of the protonated species has been analyzed with the Atoms In Molecules methodology.

Keywords Protonation · Ab initio methods · Triple bonded molecules · Atoms in molecules

1 Introduction

In a recent paper, our group has studied the protonation of HCP for the interest of the neutral molecule, on the one hand, and for the discussions about the structure of the protonated compound, on the other. The results obtained indicated that even though protonation can occur on the C atom providing a C_{2v} protonated system, the non–classical $C_s(\pi)$ structure is usually preferred [1] (Scheme 1). Thus, it can be thought that, in general, protonation at the π system is preferred; however, in the mentioned study it was found that the potential surface in that region is relatively flat, and that the $C_s(\pi)$ and C_{2v} structures can be easily interconverted. In addition, protonation of triple bonds is usually the first step in the reaction of the studied triple bonded systems with acids (water, formic acid, urea) [2,3] or with enzymes [4,5].



Scheme 1

These findings puzzled our curiosity and considering that the π clouds, even though weak, are known HB acceptors, we decided to approach the study of the protonation of all possible triple bonded molecules containing two heavy atoms from the second and third periods of the Periodic Table (P.T.). Thus, the protonation of all molecules containing every possible combination of B, C, N, Al, Si and P triple bonded has been considered both over the π system and over each of the heavy atoms.

2 Computational methods

The geometries of all the compounds (neutral and protonated) have been fully optimized with the program Gaussian-03 [6] using, in a first approach, the hybrid method Becke3LYP [7,8] and then, optimising at the second-order Møller–Plesset MP2 [9–12] method with the Dunning aug-cc-pVTZ basis set [13,14]. To improve the treatment of the electron correlation effects further optimisations with the CCSD(T) [15,16] method and the same basis set were performed. The nature

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Contribution to the Serafin Fraga Memorial Issue.

To Serafin, a free spirit and a good friend.

I. Alkorta (✉) · J. Elguero
Instituto de Química Médica, CSIC,
Juan de la Cierva 3, 28006 Madrid, Spain
e-mail: ibon@iqm.csic.es

I. Rozas (✉)
Centre of Synthesis and Chemical Biology, School of Chemistry,
Trinity College Dublin, Dublin 2, Ireland
e-mail: rozasi@tcd.ie

Table 1 ZPE corrected energy (a.u.) and triple bond distances (Å) of all neutral molecules calculated at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels

System	Symm.	MP2/aug-cc-pVTZ		CCSD(T)/aug-cc-pVTZ	
		E_{ZPE}	$d(X \equiv Y)$	E_{ZPE}	$d(X \equiv Y)$
HBNH	$C_{\infty v}$	−80.611575	1.246	−80.636765	1.245
HBPH	C_s	−366.743367	1.688	−366.821249	1.707
HCCH	$D_{\infty h}$	−77.137531	1.212	−77.165827	1.210
HCN	$C_{\infty v}$	−93.243974	1.167	−93.265279	1.160
HCSiH	C_s	−328.087814	1.631	−328.129820	1.667
HCP	$C_{\infty v}$	−379.443658	1.560	−379.475418	1.555
NN	$D_{\infty h}$	−109.359818	1.114	−109.375469	1.104
HNAlH	C_s	−297.782928	1.658	−297.806276	1.658
NSiH	$C_{\infty v}$	−344.182878	1.625	−344.199503	1.592
NP	$C_{\infty v}$	−395.531036	1.529	−395.550696	1.508
HALPH	C_s	−583.99473	2.134	−584.057182	2.157
HSiSiH	C_{2h}	−579.134664	2.103	−579.184766	2.122
HSiP	$C_{\infty v}$	−630.449424	1.985	−630.489555	1.980
PP	$D_{\infty h}$	−681.773366	1.927	−681.810750	1.916

of the compounds as a potential energy minimum has been established, at all levels of computation, by verifying that no imaginary frequencies were obtained. The lowest level of computation was used to explore all possible protonation sites by adding a proton to each of the heavy atoms connected by the triple bond and in a perpendicular approach to the triple bond itself.

The topological properties of the electron charge density (molecular graphs and bond critical points, bcp) have been studied using the Atoms In Molecules methodology (AIM) with the AIMPAC [17,18] and MORPHY [19] programs using the wave function obtained at the MP2/aug-cc-pVTZ level.

3 Results

3.1 Study of the triple bonded neutral molecules

All possible combinations of triple bonded molecules containing B, C, N, Al, Si, and P atoms were optimised at both MP2 and CCSD(T) levels of theory and their nature as a minima, in all the cases, was confirmed by calculating the frequencies and verifying that all of them were positive. The ZPE corrected energy and group of symmetry of all these neutral molecules, as well as the triple bond distance obtained for the optimised structures in each case, are presented in Table 1.

Most of the triple bonded molecules are linear showing $D_{\infty h}$ or $C_{\infty v}$ symmetry. However, some of the systems where atoms of the third row are involved (HBPH, HCSiH, HNAlH, HAlPH or HSiSiH) present non linear structures with a *trans* disposition of the H atoms. It should be noted that as the atoms become larger, more orbitals are involved in the bonding thus allowing to different atomic configurations with multiple bonds. Good examples are the quintuple bond recently described for chromium and uranium dimers [20,21].

Triple bond distances of the optimised structures at both levels of theory are very similar. As expected by taking into account the atomic radii, they are shorter when the atoms involved belong to the second row of the P.T. (B, C, N) than when one or both of them belong to the third period (Al, Si, P).

3.2 Study of the protonated species of the triple bonded molecules

Neutral molecules were, then, tested for protonation on each of the heavy atoms and over the π system at DFT level. In most of the cases, protonation took place over one of the heavy atoms. Only those cations that were minima in the potential energy surface at B3LYP level were further optimised at MP2 and CCSD(T) levels. Additionally, the electron density topology of the systems that present the protonation on the π region of the molecules has been characterized within the AIM frame.

The different protonated structures obtained at both levels of computation their corresponding symmetry and their Proton Affinity are presented in Table 2. In addition, the gas-phase Basicities have been computed in each case and are also shown in Table 2. The available experimental proton affinity and basicity values are also included.

The Proton Affinity (PA, Table 2) has been calculated, at both levels of theory, as the difference in energy between neutral and protonated species, considering the ZPE corrections and including the 5/2(RT) factor that accounts for the translational energy and the Δ (PV) term of the proton [22]. The computed PA nicely reproduce the experimental data

Table 2 Proton affinities (PA) and gas phase Basicity (kJ/mol) of the triple bonded molecules calculated at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels

System	Sym.	PA		PA	Basicity	Basicity
		MP2	CCSD(T)	exp. [22]	CCSD(T)	exp. [22]
$[HHBNH]^+$	$C2v$	468.46	470.74		441.76	
$[HBNHH]^+$	$C2v$	759.76	770.28		741.27	
$[HBP–HH]^+$	$Cs(\pi)$	826.44	735.93		704.93	
$[HCCH–H]^+$	$C2v(\pi)$	634.92	647.30	641.4	619.92	616.7
$[HCNH]^+$	$C\infty v$	703.35	711.37	712.9	679.66	681.6
$[HHCSiH]^+$	Cs	844.54	853.58		822.90	
$[HCSiHH]^+$	$C2v$	676.29	696.71		665.24	
$[HCP–H]^+$	$Cs(\pi)$	660.15	–		–	
$[HHCP]^+$	$C2v$	650.60	683.90	699.0	656.32	666.5
$[NN–H]^+$	$C2v(\pi)$	292.04(*)	307.54(*)		280.21(*)	
$[NNH]^+$	$C\infty v$	486.31	494.19	493.8	464.24	464.5
$[HHNAlH]^+$	$C2v$	977.52	987.79		955.67	
$[HNSiH]^+$	Cs	858.58	885.88		855.28	
$[NSiHH]^+$	$C2v$	445.84	546.18		516.78	
$[HNP]^+$	$C\infty v$	771.98	791.42	789.4	759.48	757
$[NPH]^+$	$C\infty v$	443.36	443.45(*)		411.38(*)	
$[NPH]^+$	Cs	–	444.96		417.93	
$[HAlPHH]^+$	Cs	941.10	892.31		861.19	
$[HSiSiH–H]^+$	$C2(\pi)$	828.19	830.48		798.56	
$[HHSiSi–H]^+$	$Cs(\pi)$	868.49	869.94		839.85	
$[HSiP–H]^+$	$Cs(\pi)$	755.20	766.82		739.24	
$[HHSiP]^+$	$C2v$	653.30	690.57		662.35	
$[PP–H]^+$	$C2v(\pi)$	641.87	659.92		632.72	
$[PPH]^+$	$C\infty v$	606.27(*)	619.17(*)		588.59(*)	

* These structures are not minima at the corresponding computational level

[23], specially in the case of the CCSD(T) where the larger deviation is 15 kJ/mol, while in the rest of the cases is less than 6 kJ/mol. The gas-phase basicities are the protonation free-energies, and they have been calculated because these may be at variant with respect to PAs due to entropic effects (see Table 2). In those cases when the experimental basicity was available, a very good agreement with the computed values is found. The difference between the PAs and the gas-phase basicities is very similar in all cases (between 27.03 and 32.12 kJ/mol) indicating that the same happens for the entropic contribution.

In the case of HBNH, protonation took place either at the N or at the B atom (Fig. 1a and b, respectively). However, the $[HHBNH]^+$ structure could be better described as a H_2 molecule (H–H distance of 0.88 Å) symmetrically interacting with the B atom. This was evident when mapping the electron density of this cationic system (Fig. 1c), because bond critical points (bcp), where found between these H atoms, and the molecular graph indicate as well a T shape interaction with the remaining atoms of the molecule (HNB). This $[HHBNH]^+$ cation has a much smaller PA than $[HBNHH]^+$ but really, it cannot be considered a protonated derivative of the triple bonded neutral molecule.

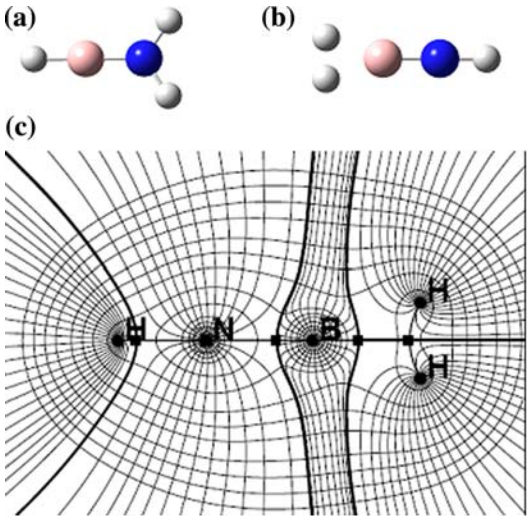


Fig. 1 **a** $[HBNHH]^+$ and **b** $[HHBNH]^+$ structures optimised at CCSD(T) level of theory and **c** MP2 electron density map of $[HHBNH]^+$

In the case of the HCCH, the only protonated structure obtained was that over the π system and the calculated PA at CCSD(T) level is very similar to the experimental one

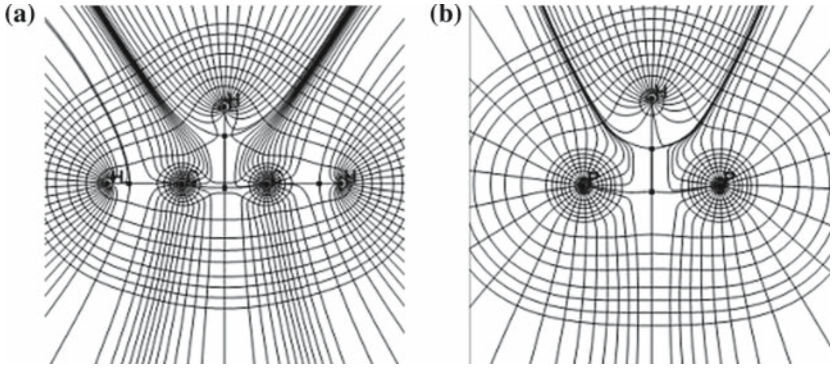


Fig. 2 Electron density maps of the protoanted structures $[HCCH–H]^+$ and $[PP–H]^+$, as examples of "conflict catastrophic systems"

(Table 2). Interestingly the linearity of the molecule is not perturbed upon protonation. Similarly, the N_2 and P_2 molecules present only one protonated minima. However, the minimum of the N_2H cation is linear ($[NNH]^+$) and that of the P_2H cation shows a C_2v symmetry ($[PP–H]^+$) as an indication of the interaction of the proton with the PP triple bond. The experimental PA value for the protonation of N_2 is reproduced very accurately at CCSD(T) level (see Table 2) confirming the linear structure of this system.

Protonation of the HSiSiH system yielded two different cations. One was the actual protonated system of the HSiSiH molecule on the triple bond ($[HSiSiH–H]^+$) whereas the other one had two H atoms on one of the Si atoms ($[SiSiHH–H]^+$), while the third proton was interacting with the π system. This last one was around 40 kJ/mol more stable.

Analysing the topology of the electron density in the symmetric π-protonated complexes of HCCH, N_2, P_2 and HSiSiH, it can be observed that there is an interaction line between the proton and the bcp at the midpoint of the bond between the heavy atoms of the molecule, that is, all the configurations found correspond to "conflict catastrophe structures" (Fig. 2). Thus, from the point of view of the electron density these *complexes* are unstable because a small displacement of the proton out of the symmetry axes causes the molecular graphs to change radically. Similar examples have been described for hydrogen bonded complexes with π-systems [24,25].

Protonation of HCP showed two minima at the MP2 level, one seemed to have the proton over the π cloud ($[HCP–H]^+$) and another with the proton attached to the carbon atom ($[HHCP]^+$). In fact, at the CCSD(T) level with the basis set used here, the first minima collapsed to the second one. We have already shown that the presence of these two structures is very dependent on the methods and basis set used [1]. Considering the experimental PA of this protonated system and that calculated at the CCSD(T) level (699.0 and 683.90 kJ/mol, respectively, see Table 2) it seems likely that the actual experimental structure of the cation is that with the proton attached to the C atom. Likewise, the HSiP molecule showed two protonated systems, one with the proton over the π cloud, and the other with the proton on the Si (planar trigonal), being the first structure the most stable one. In the electron density molecular graph of the π-complexes of the previous three unsymmetrical cases (H_2SiSi, HCP and HSiP) the interaction line observed between the proton and the rest of the system goes not to the π bond but to one of the heavy atoms [$(H_2)Si$, C and P, respectively]. In all the cases, the bond is established with the most electronegative group (Fig. 3).

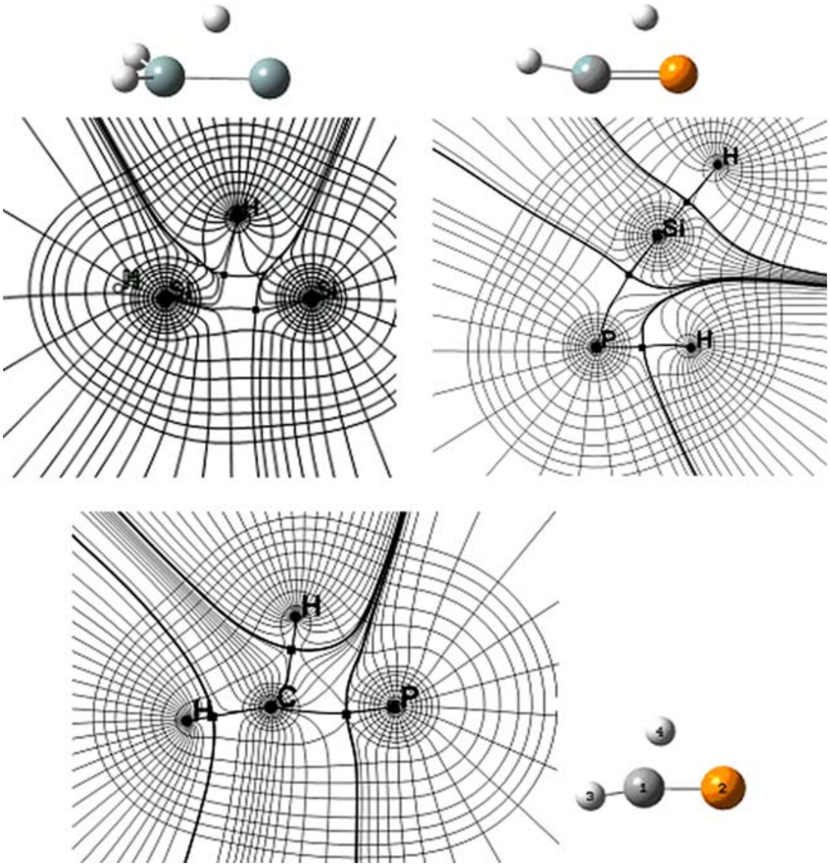
In the case of the triple bonded molecules HCN and HNAlH only one protonated system was obtained as a minimum with the proton added on the N atom in a linear ($[HCNH]^+$) and planar trigonal ($[HHNAlH]^+$) disposition respectively (Fig. 4). The experimental PA obtained for the protonation of HCN is very similar to that obtained using CCSD(T) calculations (see Table 2).

Two special cases are those of the HBPH and HAlPH protonated systems where the optimised structures present two hydrogen atoms in the π-cloud region. The protonation energy and PA of HBPH at MP2 level seem very high compared to the values obtained with the CCSD(T) method (around 100 kJ/mol in each case, see Table 2). This could probably be explained because, at MP2 level, the neutral molecule is different of that optimised at CCSD(T) level even though it was used as the starting point of the optimisation (see Fig. 5a, b). At both levels of computation, the resulting protonated structure, $[HBP–HH]^+$, has a *Cs* symmetry where two protons are interacting at the same time with the π system of the triple bond, forming a H–π–H angle of 97.70° (Fig. 5c).

In the same way, protonation of HAlPH yielded only one protonated structure, $[HAlPHH]^+$, which shows two protons on the P atom forming H–P–π angles of 86.85° and H–P–H angles of 93.26°. Therefore, the protons are almost under the influence of the π cloud.

When analysing the electron density topology, it was found that, in the case of $[HBP–HH]^+$, the bond paths are very curved. In a slightly non symmetrical way, in this structure one of the bond paths goes from the proton to the P atom and the

Fig. 3 MP2 electron density molecular graph for the protonated $[HHSiSi–H]^+$, $[HSiP–H]^+$ and $[HCP–H]^+$ systems. The corresponding CCSD(T) optimised structures are also shown



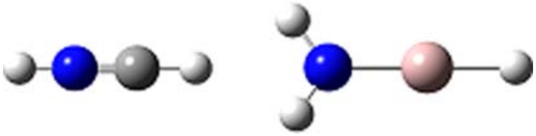


Fig. 4 CCSD(T) optimized structures of $[HCNH]^+$ and $[HHNAlH]^+$ cation systems

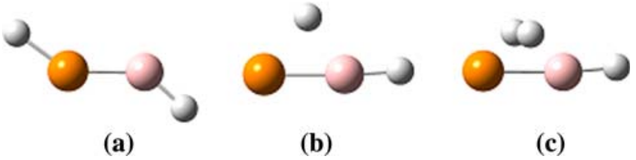


Fig. 5 Neutral [**a** MP2 level, **b** CCSD(T) level] and protonated [**c** CCSD(T) level] structures of the HBPH triple bonded molecule (B is represented in *pink* and P in *orange*)

other to the B, as an indication of the low stability of the electron density description (Fig. 6a). Re-optimising the totally symmetric protonated system it was found that both protons interact with the triple bond (Fig. 6b). In the second case, the $[HAlPHH]^+$ cation, the two hydrogen atoms are connected to the Al, probably since they are much closer to it than to the P atom (Fig. 6c).

Regarding the HCSiH and NSiH molecules, they show two different protonated structures, one with the proton attached to the C or N atoms and the other to the Si atom. In terms of energy the protonation on the C/N atom is much more favourable than that on the Si atom (Fig. 7).

Finally, in the case of the NP triple bonded molecule no π protonation was observed. At MP2 level, two linear cations were formed, one with the proton on the N atom and another, with smaller E_{prot} and PA, protonated on the P atom. However, this last one, which was a minimum at MP2 level with an N–P–H angle of 180°, showed two imaginary frequencies at CCSD(T) level. When optimised at this higher level the $[NPH]^+$ evolved to a *Cs* system almost linear. The $[HNP]^+$ cation has much larger E_{prot} and PA than the other one at any level of computation. Moreover, the experimental PA for the NP molecule is very similar tot hat calculated for the $[HNP]^+$ cation at CCSD(T), an indication that the experimental protonation occurs at the N atom (see Table 2).

3.3 Comparison of neutral and protonated molecules

Triple bond distances of the neutral and protonated species, calculated with MP2 and CCSD(T) methods, are shown in Tables 1 and 3, respectively.

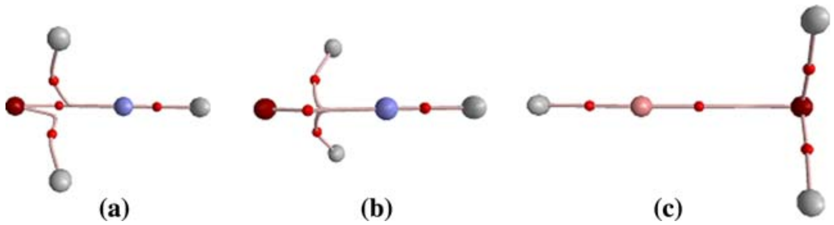


Fig. 6 Bond paths and bcp found for the slightly unsymmetrical **a** and symmetrical **b** structures of the [HBP–HH]$^{+}$ cation and for the [HAlPHH]$^{+}$ cation

Fig. 7 Most stable CCSD(T) optimized protonated structures of HCSiH and NSiH over the C or N atoms

Table 3 Triple bond distances (Å) of all protonated molecules calculated at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels

System	Sym.	MP2 d($X \equiv Y$)	CCSD(T) d($X \equiv Y$)
[HHBNH]$^{+}$	$C2v$	1.232	1.229
[HBNHH]$^{+}$	$C2v$	1.320	1.322
[HBP–HH]$^{+}$	$Cs(\pi)$	1.751	1.756
[HCCH–H]$^{+}$	$C2v(\pi)$	1.229	1.230
[HCNH]$^{+}$	$C\infty v$	1.144	1.140
[HHCSiH]$^{+}$	Cs	1.694	1.745
[HCSiHH]$^{+}$	$C2v$	1.725	1.729
[HCP–H]$^{+}$	$Cs(\pi)$	1.580	*
[HHCP]$^{+}$	$C2v$	1.608	1.622
[NN–H]$^{+}$	$C2v(\pi)$	1.137(*)	1.154(*)
[NNH]$^{+}$	$C\infty v$	1.108	1.099
[HHNAlH]$^{+}$	$C2v$	1.724	1.724
[HNSiH]$^{+}$	Cs	1.541	1.544
[NSiHH]$^{+}$	$C2v$	1.708	1.706
[HNP]$^{+}$	$C\infty v$	1.483	1.475
[NPH]$^{+}$	$C\infty v$*	1.560	1.516(*)
[NPH]$^{+}$	Cs	*	1.534
[HAlPHH]$^{+}$	Cs	2.281	2.295
[HSiSiH–H]$^{+}$	$C2(\pi)$	2.138	2.162
[SiSiHH–H]$^{+}$	$Cs(\pi)$	2.287	2.291
[HSiP–H]$^{+}$	$Cs(\pi)$	2.018	2.023
[HHSiP]$^{+}$	$C2v$	2.122	2.129
[PP–H]$^{+}$	$C2v(\pi)$	1.967	1.965
[PPH]$^{+}$	$C\infty v$	1.913(*)	1.903(*)

* These structures are not minima at the corresponding computational level

In most of the cases, protonation of triple bonded molecules induces an elongation of the bond between the heavy atoms between 0.083 and 0.008 Å. When protonation takes place perpendicular to the π system, the triple bond becomes longer by 0.017 and 0.050 Å. However, in the case of most of the molecules containing N atoms, protonation on this N atom produces a shortening of the triple bond by 0.085 and 0.005 Å. There are two exceptions to this, protonation on the N atom of HBNH and HNAlH produces an elongation of the triple bond of 0.077 and 0.066 Å, respectively. These two cases are the only ones involving both one N atom (group 15 of the P.T., five valence shell electrons) and one atom from the group 13 of the P.T. which contains only three electrons in the valence shell. Thus, if we consider only the Lewis rule, after protonation on the N atom with the formation of an extra N–H bond there is not enough electrons between the valence shells of both heavy atoms to contribute to a triple bond and the molecules appear to be evolving towards the double bonded systems.

In the particular cases of [HSiSiH–H]$^{+}$, [HHSiP]$^{+}$ and [HAlPHH]$^{+}$ the elongation of the bond between the heavy atoms produced after protonation is so large (around 0.138–0.184 Å) that really corresponds to a double bonded molecule.

In the case of [HBP–HH]$^{+}$ where two protons are simultaneously interacting with the π system, the B≡P distance is much larger, 0.4–0.5 Å, than in the other HBPH protonated systems (see Table 3).

4 Conclusions

We have studied the protonation of all possible triple bonded molecules formed by B, C, N, Al, Si and P atoms, the effect of this protonation on their structure and their corresponding PAs and gas-phase basicities.

In general, no clear preference for protonation over the π system has been observed and many structures were protonated on one of the atoms participating in the triple bond. However, those molecules containing a Si atom are preferable protonated over the π cloud, and, in fact, the only Si containing system protonated on one of the heavy atoms, [HHSiP]$^{+}$, corresponds more to a double bonded structure (Si–P distance of 2.13 Å).

Several interesting protonated structures have been found such as [HHBNH]$^{+}$ which can be described as an H_2 molecule interacting with the B end of the BNH cation. Regarding cations with H–π interaction, it is rather interesting the structure of [HBP–HH]$^{+}$ with two protons simultaneously interacting, at a 90° angle, with the triple bond.

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