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Ab initio molecular orbital study of the substituent effect on ammonia and phosphine–borane complexes

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Abstract

The complexation energies of $H_3BXH_{3-n}F_n$ ($X=N$, P; $n=0$–3) and the proton affinities of $XH_{3-n}F_n$ compounds have been investigated at the G2(MP2) level of theory. The G2(MP2) results show that the phosphine complexes are more stable than the corresponding ammonia ones. Increasing fluorine substitution on nitrogen atom reduces both the basicity of $NH_{3-n}F_n$ and the stability of ammonia complexes. For the phosphine complexes, the successive fluorine substitution on the phosphine increase the stability of $H_3BPH_{3-n}F_n$ complexes although the reduction of the basicity of the $PH_{3-n}F_n$ ligands with this substitution. The NBO partitioning scheme shows that the stability of the phosphine complexes was related to the hypeconjugation effect. It also proves that the shortening of the P–H and X–F bond lengths, upon complexation, is due to an increasing 's' character in these bonds.
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Keywords: Ammonia–borane; Phosphine–borane; Donor–acceptor complexes; NBO analysis; Substituent effect

1. Introduction

Chemical bonds are usually classified as electrostatic, covalent, or metallic [1]. Weakly bound molecules exhibit yet another type of bonding, which is characterised by Van der Waals interactions [2]. Most compounds can be identified as belonging to one of these classes by the nature of the chemical bonds in the molecule. However, there is one type of compounds, which makes such a difficult assignment. The class of donor–acceptor complexes comprises molecules that may be bound by electrostatic, covalent or Van der Waals interactions. The present understanding of this important class of molecules is based on the epochal work of Lewis [3], who introduced the concept of electron-pair donor–acceptor complexes. A popular qualitative model for the interpretation of donor–acceptor interactions is the theory of hard and soft acids and bases (HSAB) suggested by Pearson [4]. A quantitative evaluation and prediction of donor–acceptor interactions haves been made by Drago [5]. The Drago's model has been applied to understand solvent effects and the reactivity in chemical and biological systems [6]. Although much work has been done to puzzling features of donor–acceptor complexes that are not completely understood, as compounds containing boron, nitrogen and phosphorus. In fact, these compounds play an important role in synthetic chemistry and have received extensive attention in the chemical literature [7–9]. Accurate knowledge of the thermodynamics of complexation energies would serve as a useful framework from which to build a detail and quantitative understanding of borane reactivity and mechanism.

Numerous study have been devoted to these type of compounds concerning their structural parameters, the nature of the bonding, their stability and other physical properties [10–20], where the methods used for analyses differ but no systematic comparison of the substituent effect on ammonia–borane and phosphine–borane has been reported. In 1996, Skancke [10] have reported that the increasing fluorine substitution on nitrogen, using DFT method, reduces the stability of H_3BNH_3, H_3BNH_2F, H_3BNHF_2 and H_3BNF_3 complexes. The same trend has been obtained for $H_3BNH_{3-n}Cl_n$ ($n=0$–3) ones [21]. In 1997, Durig and Shen have published a theoretical study

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at the MP2 level of theory of the H_3BPH_3, H_3BPHF_2 and H_3BPF_3 complexes using various basis sets [11]. They have shown that the substituting the hydrogen atoms on the phosphine group by fluorine atoms increases the stability of the corresponding complexes. They have also obtained that the difluorophosphine–borane complex is more stable than the trifluorophosphine–borane one. From these results one can see that upon fluorination on ammonia the stability decreases while upon successive fluorination on phosphine this stability increases and can see also that the order of stability at the phosphorus complexes is broken with the degree of the substitution. Contrary what was expected for the methyl effect? Recently, we have reported that the successive methylation on XH_3 (X=N, P) increases the basicity of $XH_{3-n}Me_n$ (n=1–3) and therefore favours their coordination with BH_3 [12–14]. We have also found that the first substitution, on XH_3, stabilises the complex by 5.91 kcal/mol, whereas the second substitution stabilises the complex by 9.19 kcal/mol and the third one by 10.26 kcal/mol for ammonia complexes, and by 6.72, 12.16, and 16.05 kcal/mol for phosphine complexes. In short, we have shown that the stability of the $H_3BXH_{3-n}Me_n$ (X=N, P; n=0–3) increase with the degree of substitution. In continuation of our work, we present in this paper a comparative study of the substituent effect on ammonia–borane ($H_3BNH_{3-n}F_n$; n=0–3) and phosphine–borane ($H_3BPH_{3-n}F_n$; n=0–3) donor–acceptor complexes at the G2(MP2) level of theory. We give clarification of the comportment of each series of complexes. The electronic structure of these complexes has been analysed.

2. Computational details

All calculations in this work were performed on IBM RS/6000 workstations of the University of València using the GAUSSIAN 98 [22] series of computer programs. Geometry optimizations were performed at the MP2(full)/6-31G(d) level; the zero-point vibrational energies (ZPE) are obtained from scaled HF/6-31G(d) frequencies (scaled by the factor 0.893) [23]. For improved energy, the G2(MP2) energies [24] were computed. The electronic structure have been done using the natural bond orbital (NBO) [25] partitioning analysis at the MP2(full)/6-31G(d) level. An important feature of the NBO method is that, unlike other charge partitioning schemes, the presence of diffuse functions in the basis sets does not affect the result [25].

3. Results and discussion

Table 1 lists the most important geometrical parameters of $XH_{3-n}F_n$ (X=N, P; n=0–3) moieties and their complexes with BH_3. It can be seen that a small changes

Table 1
MP2(Full)/6-31G(d) calculated d_{X-Y}^a bond lengths (in Å)

	X–H	X–F	B–X	Reference
NH_3	1.017			
NH_2F	1.023	1.433 (1.433)		[26]
NHF_2	1.029	1.406 (1.400)		[29]
NF_3		1.383 (1.371)		[30]
PH_3	1.415			
PH_2F	1.419	1.626		
PHF_2	1.421	1.608 (1.582)		[31]
PF_3		1.593 (1.570)		[32]
H_3BNH_3	1.020		1.661 (1.657)	[33]
H_3BNH_2F	1.023	1.416	1.609	
H_3BNHF_2	1.027	1.388	1.594	
H_3BNF_3		1.366	1.623	
H_3BPH_3	1.404		1.945 (1.937)	[34]
H_3BPH_2F	1.401	1.603	1.873	
H_3BPHF_2	1.399	1.582 (1.552)	1.852 (1.832)	[35]
H_3BPF_3		1.568 (1.538)	1.857 (1.836)	[36]

a In parentheses we give the experimental bond lengths (in Å).

in the X–H and X–F bond distances result from fluorine substitution in XH_3. In fact, we observed a lengthening of the X–H bond lengths and a shortening of the X–F ones. For ammonia compounds, the bond distances of N–H and N–F pass, respectively, from 1.017 to 1.029 Å and from 1.433 to 1.383 Å. For the phosphine species the P–H and P–F bonds changes by about 0.006 Å and 0.033 Å, respectively. The experimental values of X–F (X=N, P) bond lengths, reported in Table 1, are in agreement with our optimised ones. These values are 1.433, 1.4, 1.371, 1.582, and 1.570 Å for NH_2F, NHF_2, NF_3, PHF_2 and PF_3, respectively. Thus, the experimental results predict the same trend as our calculations.

It has been suggested [26,10] that the bond length changes discussed above are caused by the rehybridisation of donor atom 'X' upon fluoration and also due to a reversion of polar effects as the partial charge on the donor atom change. It becomes very positive with increasing fluorine substitution on XH_3. The net charge on N, obtained from MP2-NBO level, are −1.12, −0.45, 0.15, and 0.69 electron for NH_3, NH_2F, NHF_2 and NF_3, respectively. For the phosphine species PH_3, PH_2F, PHF_2 and PF_3, the net charges on P atom are, respectively, 0.05, 0.75, 1.3, and 1.75 electron. With reference to our NBO analysis, it may be claimed that the contribution rate of the 's' character in the X–H and X–F bonds also play an important role in this context (see below).

The theoretically predicted donor–acceptor bond lengths for H_3BNH_3, H_3BPH_3, H_3BPHF_2 and H_3BPF_3 complexes are in agreement with the experimental values and with previous predictions [10,11]. However, for H_3BPHF_2 and H_3BPF_3, the bond distances of B–P are 1.852 and 1.857 Å, respectively, 0.02 and 0.021 Å longer than the corresponding experimental values obtained from the microwave study (Table 1). The calculations predict that the B–X bond lengths for $H_3BXH_{3-n}F_n$ (X=N, P; n=1–3) are shorter than for H_3BXH_3. Furthermore, the successive fluoration at

donor atom 'X' decreases the B–X distances except for H_3BXF_3 where the distance is longer than in H_3BHF_2. Geometries of the $H_3BXH_{3-n}F_n$ complexes show a tetrahedral arrangement around the boron centre. The $\angle XBH$ bond angle is 104–105° and 101–103° for X=N an P, respectively. The B–H bond is slightly longer in complexes than in isolated BH_3. These values are reasonable because the hybridisation changes from sp^2 in BH_3 to sp^3 in complexes.

Upon complexation, the MP2 calculation shows a small distortion of the N–F and P–F bond lengths (1.75 and 2.4%, respectively). Moreover, this calculation predicts both a lengthening of N–H and a shortening of N–F, P–H and P–F bond lengths (Table 2), which has been observed experimentally for H_3BPH_3, H_3BPF_3 [27] and justified theoretically [20]. To explain this result, we have applied the NBO analysis. MP2-NBO calculations show that in isolated $XH_{3-n}F_n$ (X=N, P; n=0–3) moieties the lone pair on donor atom 'X' has lower 's' character than in complexes. Hence, we can deduce from these results that this change alone would imply a shortening of the P–H and X–F bond lengths owing to an increased 's' character in these bonds. Even, Table 2 shows that the 3s atomic orbital (AO) contribution of P in the P–H bond length is more important in $H_3BPH_{3-n}F_n$ (n=1–3) complexes than in isolated moiety PH_3. In contrast, the contribution of the 2 s AO of ammonia is more important in an isolated moiety than in the $H_3BNH_{3-n}F_n$ (n=1–3) complexes. Then, we can understand why we had an elongation of the N–H bond length and a shortening of the P–H one.

By successive fluorine substitutions on nitrogen atom, the highest occupied molecular orbital-lowest unoccupied molecular orbital HOMO–LUMO gap increases (0.468, 0.512, 0.555, and 0.604 au for NH_3, NH_2F, NHF_2 and NF_3, respectively, obtained at the MP2/6-311+G(3df,2p) level of theory). Moreover, the energy of HOMO is lowered from

Table 2
MP2(Full)/6-31G(d) calculated X–H and X–F bond lengths (in Å), 2s and 3s MP2-NBO contributions of nitrogen and phosphorus atoms, respectively, in the X–H and X–F (X=N,P) bonds (in %).

	X–H	X–F	$ns_{(X–H)}$	$ns_{(X–F)}$
NH_3	1.017		25.15	
NH_2F	1.023	1.433	24.39	12.70
NHF_2	1.029	1.406	23.85	12.57
NF_3		1.383		12.35
PH_3	1.415		16.22	
PH_2F	1.419	1.626	14.73	11.85
PHF_2	1.421	1.608	13.58	10.86
PF_3		1.593		10.00
H_3BNH_3	1.020		21.62	
H_3BNH_2F	1.023	1.416	22.18	13.26
H_3BNHF_2	1.027	1.388	22.83	15.75
H_3BNF_3		1.366		16.92
H_3BPH_3	1.404		20.44	
H_3BPH_2F	1.401	1.603	21.12	17.71
H_3BPHF_2	1.399	1.582	22.18	18.16
H_3BPF_3		1.568		18.89

Table 3
G2(MP2) complexation energies E_c of $H_3BXH_{3-n}F_n$ (X=N, P; n=0–3) complexes and proton affinities PA of $XH_{3-n}F_n$ ligands (in kcal/mol), the MP2-NBO transferred charge Q_t.(in electron)

Complex	E_c	PA	Q_t
H_3BNH_3	−25.97	202.5	0.35
H_3BNH_2F	−24.15	181.12	0.32
H_3BNHF_2	−18.89	158.16	0.29
H_3BNF_3	−8.67	132.18	0.25
H_3BPH_3	−21.10	186.84	0.63
H_3BPH_2F	−27.50	182.41	0.68
H_3BPHF_2	−28.88	174.92	0.73
H_3BPF_3	−22.90	158.78	0.73

−0.431 to −0.567 au on going from NH_3 to NF_3. This indicates that NH_3 is a soft base and NF_3 is a hard one. This is in good agreement with the calculated hardness 'η' values of $NH_{3-n}F_n$ bases[1] (7.2, 7.7, 8.3, and 9.3 eV for NH_3, NH_2F, NHF_2 and NF_3, respectively). Referring to the Pearson's qualitative theory of hardness and softness in chemistry [28,4c] the coordination of BH_3 with NH_3 will be more favored than with $NH_{3-n}F_n$ (n=1–3). Therefore, we can predict qualitatively that the stability of $H_3BNH_{3-n}F_n$ complexes decreases as well as the degree of substitution decreases. Arguing along the same line for fluorine-substituted PH_3 species, we find that the HOMO–LUMO gap increases by successive fluorine substitutions (0.423, 0.436, 0.455, and 0.511 au for PH_3, PH_2F, PHF_2, and PF_3, respectively). This is consistent with a corresponding increases in the hardness 'η' of the $PH_{3-n}F_n$ bases (6.1, 6.2, 6.5, and 7.3 eV for PH_3, PH_2F, PHF_2, and PF_3, respectively). According to the above reasoning, we would expect a decrease in complexation energies from H_3BPH_3 to H_3BPF_3. However, this qualitative results is not in agreement with our calculated G2(MP2) complexation energies of $H_3BPH_{3-n}F_n$ (n=0–3) (see below).

In Table 3 we give the calculated complexation energies of the $H_3BXH_{3-n}F_n$ (X=N, P; n=0–3) complexes, the proton affinities of $XH_{3-n}F_n$ moieties and the MP2-NBO transferred charge from $XH_{3-n}F_n$ to BH_3. The complexation energies are calculated as the energy differences between the complex and the respective donor–acceptor moieties. The theoretical proton affinities (PA) are taken as the energy difference between the neutral and protonated $XH_{3-n}F_n$ bases. From this table, one can see that, in general, the phosphine complexes are more stable than their homologous ammonia ones. Furthermore, higher complexation energy is predicted for H_3BPHF_2 complex (−28.88 kcal/mol). The theoretical predicted complexation energies of $H_3BPH_{3-n}F_n$ (n=0–3) (−21.1, −27.5, −28.88, and −22.9 kcal/mol for H_3BPH_3, H_3BPH_2F,

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[1] The hardness "η" was calculated as follow: $\eta = -(I-A/2)$ with $I=$ ELUMO and $A=$ EHOMO. The HOMO and LUMO energies were obtained at the MP2/6-311+G(3df,2p)//MP2(full)/6-31G(d) level of theory (for more details see [4c]).

H_3BPHF_2, and H_3BPF_3, respectively) show that the successive fluorine substitution on PH_3 increases the stability of the corresponding complexes. In addition, this stability increases despite the decrease of the basicity of the $PH_{3-n}F_n$ species, with the degree of substitution, which reflected by their G2(MP2) proton affinities (186.84, 182.41, 174.92, and 158.78 kcal/mol for PH_3, PH_2F, PHF_2, and PF_3, respectively). This result comes from both the back-donation from BH_3 to $PH_{3-n}F_n$ and the effect of hyperconjugation present in the $H_3BPH_{3-n}F_n$ complexes. The hyperconjugation is put in evidence by the change in the net charge at the boron hydrogens, since it is negative in isolated BH_3 moiety (-0.11 e) and becomes positive upon the formation of the complex (<0.06 e). Moreover, the MP2-NBO analysis show both that the back-donation from BH_3 to $PH_{3-n}F_n$ (0.36, 0.42, 0.54, and 0.54 electron) and the transferred charge from $PH_{3-n}F_n$ to BH_3 (0.63, 0.68, 0.73, and 0.73 electron) increase as the stability of the corresponding complexes except for H_3BPHF_2 and H_3BPF_3 complexes. In short, in the series with the fluorinated phosphorus there is also a general trend of increasing complexation energies upon fluorination, but in this case the trend is broken as H_3BPHF_2 has larger complexation energy than its congenial H_3BPF_3. It seems that the interaction between BH_3 and PHF_2 is energetically more favourable than the one with the most fluorinated PF_3 involved. We suggest that the destabilisation of the H_3BPF_3 complex due to F–F repulsion, since the F–F distance becomes smaller in going from H_3BPHF_2 (2.435 Å) to H_3BPF_3 (2.406 Å).

On the other hand, the H_3BNH_3 complex is more bounded (-25.97 kcal/mol) than the $H_3BNH_{3-n}F_n$ ($n= 1$–3) complexes (-24.15, -18.89, and -8.67 kcal/mol for H_3BNH_2F, H_3BNHF_2, and H_3BNF_3, respectively). It has been found that the introduction of the first fluorine atom on ammonia destabilises the complex by 1.82 kcal/mol, the second by 7.08 kcal/mol and the third by 17.3 kcal/mol. Therefore, the calculations show that the successive fluorine substitution on NH_3 reduces the stability of the corresponding complexes. The basicity of $NH_{3-n}F_n$ and the transferred charge 'Q_t' from $NH_{3-n}F_n$ to BH_3 were also decreased upon fluorination (see Table 3). Hence, one can see that the stability of the $H_3BNH_{3-n}F_n$ complexes was related to the basicity of the $NH_{3-n}F_n$ species.

4. Conclusion

The substitution effect on ammonia–borane and phosphine–borane complexes was investigated at the G2(MP2) level of theory. The G2(MP2) results show that the stability of $H_3BPH_{3-n}F_n$ ($n=0$–3) complexes increases with the degree of the fluorine substitution at the phosphorus atom although that this substitution decrease the basicity of the $PH_{3-n}F_n$ bases. This result has been attributed to the back-donation from BH_3 to $PH_{3-n}F_n$. For ammonia complexes the introduction of the fluorine atom on the NH_3 reduces

the stability of $H_3BNH_{3-n}F_n$ ($n=0$–3) complexes as the basicity of $NH_{3-n}F_n$ bases. Upon complexation, the MP2 theoretical structural parameters of $H_3BXH_{3-n}F_n$ ($X=N$, P; $n=0$–3) complexes show a lengthening of N–H and a shortening of P–H and X–F bonds. The analysis of the electronic structure using the NBO partitioning scheme shows that this change was related to the contribution rate of the 's' character in these bonds.

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