Comparative G2(MP2) Study of H_3NBX_3 and H_3PBX_3 (X = H, F, and Cl) Donor−Acceptor Complexes

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The structural parameters, nature of the bonding, and stability of H_3YBX_3 (X = H, F, and Cl; Y = N, P) complexes have been studied at the G2(MP2) level of theory. G2(MP2) results show that the ammonia complexes are more stable than the corresponding phosphine complexes. This stability varies in the same order as the acidity of BX_3 Lewis acids. The NBO partitioning scheme shows that there is a stronger charge transfer from PH_3 to BX_3 than from NH_3. It proves also that the shortening of the P−H bond length upon complexation is due to an increasing "s" character in this bond.

1. Introduction

Boron trihalides are among the most widely used Lewis acids in catalytic reactions. Their ability to form complexes containing electron donor groups plays an important role in these processes.

It is well-known that the Lewis acidities of boron trihalides follow the order $BF_3 < BCl_3$.[1] This trend is the opposite of that expected from electronegativity arguments. The simplest explanation of the unexpected order of the acceptor strength for the boron trihalides involves π-bonding between the boron and halogen atoms. When a boron halide forms a complex with a particular base, its structure changes from trigonal planar (in which the boron atom shows sp^2 hybridization) to trigonal pyramidal (in which the boron atom shows sp^3 hybridization). In this process, energy will be required for (a) orbital rehybridization, (b) overcoming π-bonding in the original molecule, and (c) overcoming increased electron pair repulsion between the halogen atoms due to the decrease in $\angle$XBX angle, although this effect is reduced by the corresponding increase in the B−X bond length as the π-bonding is lost. In addition, the anomalous behavior of boron trihalides has often been attributed to charge back-donation from the pπ orbitals of the halogens to that of the boron.[2−4] The back-donation is viewed as being stronger for the smaller halogens, especially fluorine, owing to a greater degree of pπ−pπ overlap. It has also been argued that the back-donation results in a resonance stabilization of the ground states,[5] which would decrease in the order $BF_3 > BCl_3$ and would be opposed to the formation of Lewis complexes.

Numerous studies have been devoted to the H_3NBX_3 (X = H, F, and Cl) electron donor−acceptor complexes concerning their structural parameters, the nature of the bonding, and other physical properties,[6−17] using different methods for the analyses. In 1989, Hirota et al.[18] have published a theoretical study of H_3NBX_3 and H_3PBX_3 (X = H, F, and Cl) donor−acceptor complexes, using the 3-21G basis set. They found that the H_3NBCl_3 complex is the most stable complex and reported that the H_3PBF_3 complex is stabilized by charge transfer from PH_3 to BF_3. However, in the present work, we will show that the most stable complex is H_3NBH_3, and there is no formation of a complex between PH_3 and BF_3, using G2(MP2) calculations.[19] In the past few years, high-level ab initio calculations yield geometries in very good agreement with the experimental data for H_3NBX_3 (X = H and F) complexes. The ab initio studies on H_3NBX_3 (X = F, Cl) complexes of Brank et al.[8] show that boron trichloride is a stronger Lewis acid than boron trifluoride, in good agreement with the usual Lewis acidity scale. These results have been confirmed by recent studies by Frenking et al.[11] and Branchadell et al.,[14] reporting ab initio and density functional calculations, respectively.

The aim of this work is to do a systematic theoretical study of the structure and the stability of the H_3YBX_3 (X = H, F, and Cl; Y = N, P) donor−acceptor complexes. The electronic structure of these complexes has been analyzed by means of the natural bond orbitals partitioning scheme NBO.[20] To our knowledge, G2(MP2) calculations have not been previously applied to studies of the complexes investigated here.

2. Computational Details

All calculations in this work were performed on IBM RS/6000 workstations of the University of València using the Gaussian 94[21] series of computer programs.

G2(MP2) is a theoretical procedure, based on ab initio calculations,[22] for the computation of total energies of molecules at their equilibrium geometries. G2(MP2) procedure uses the 6-311G(d,p) basis set and corrections for several basis set extensions at the MP2 level. Treatment of electron correlation is made through Möller−Plesset perturbation theory and quadratic configuration interaction (QCISD). The final total energies obtained in the G2(MP2) procedure are effectively at the QCISD(T)/6-311+G(3df,2p)//MP2(Full)/6-31G(d) level, making several assumptions about additivity of the corrections. The zero-point vibrational energies, ZPE, are obtained from

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TABLE 1: MP2(Full)/6-31G(d) Optimized Geometries of BX_3 Lewis Acids (X = H, F, and Cl) and Their Complexes with YH_3 Lewis Bases (Y = N and P)[a,b]

	B−Y	B−X	XBX	XBY	ref
BH_3		1.191	120		
		(1.190)			42[c]
BF_3		1.322	120		
		(1.307)			22[c]
BCl_3		1.736	120		
		(1.742)			22[c]
H_3NBH_3	1.661	1.209	113.8	104.6	
	(1.658)	(1.216)	(113.8)		24[c]
H_3NBF_3	1.678	1.376	114.6	103.7	
	(1.601)	(1.360)	(111.0)		26[d]
H_3NBCl_3	1.628	1.819	113.8	104.6	
	(1.579)	(1.830)	(111.5)		13[c]
H_3PBH_3	1.945	1.206	114.4	103.9	
	(1.937)	(1.212)	(114.6)		28[c]
H_3PBF_3	3.089	1.325	114.6	119.8	
	(1.921)	(1.372)	(111.0)	(112.1)	30[d]
H_3PBCl_3	2.008	1.820	113.9	104.6	

[a] Bond length in Å, bond angles in degrees. [b] In parentheses we give the experimental values. [c] Gas-phase structure. [d] Crystal structure.

TABLE 2: The MP2(Full)/6-31G(d) Calculated Y−H Bond Length and ∠HYH Bond Angles of the YH_3 (Y = N and P) Moiety and Their Complexes with BX_3 (X = H, F, and Cl) and the *n* s MP2(Full)/6-31G(d)-NBO Contribution of Y Atoms in the Y−H Bond

	d(Y−H) Å	*n* s (%)	∠HYH
NH_3	1.017	25.15	106.34
PH_3	1.415	16.22	94.61
H_3NBH_3	1.020	21.62	107.84
H_3NBF_3	1.020	23.01	108.46
H_3NBCl_3	1.024	21.34	108.52
H_3PBH_3	1.404	20.44	100.09
H_3PBF_3	1.412	16.67	95.52
H_3PBCl_3	1.400	21.83	103.51

scaled HF/6-31G(d) frequencies (multiplied by the factor 0.893).[23] Finally, a small empirical correction, referred to as the higher-level correction, HLC, is applied to account for the error in the calculated energy of H_2 molecule and the H atom, and it is based on the number of a and b valence electrons. It should be noted that in calculating complexation energies, the empirical correction cancels out and, therefore, the complexation energies are purely ab initio. We did not correct for the basis set superposition errors (BSSE), which should be relatively small with a large basis set such as 6-311+G(3df,2p). Moreover, a recent study by Mikhali et al.,[43] using the G2(+) method, show that the BSSE has little effect on the calculated complexation energies.

3. Results and Discussion

The optimized geometries of BX_3 Lewis acids (X = H, F, and Cl) moieties and their complexes with YH_3 Lewis bases (Y = N and P) at the MP2(Full)/6-31G(d) level are summarized in Table 1. The H_3YBX_3 complexes have C_{3v} symmetry with staggered orientation of the YH_3 (Y = N, P) and BX_3 fragments.

The MP2 values of B−X bond length for the isolated BX_3 Lewis acids are in excellent agreement with the experimental ones. The relative error is smaller than 1%.

The calculated B−N bond length value of 1.661 Å for H_3NBH_3 is close to the experimental one (1.658 Å)[24] and to previous calculations.[10−12,14,15] For the H_3NBF_3 and H_3NBCl_3 complexes, the experimental data included in Table 1 correspond to the crystal structure, which is not necessarily a good reference for theoretical results. Legon and Warner[25] have reported a B−N bond length of 1.59 Å for the H_3NBF_3 complex from the gas-phase microwave spectra. This value is nearly the same that in the solid state (1.601 Å).[26] This result has been discussed by Jonas and Frenking.[10] Moreover, Leopod et al.[27] showed that donor−acceptor complexes exhibit usually shorter donor−acceptor bonds in the solid state than in the gas phase. Previous ab initio calculations at different levels[8−12,14,18] give a value of 1.68 Å for the B−N bond length in the H_3NBF_3 complex instead of the gas-phase experimental value of 1.59 Å as reported by Legon and Warner.[25] The MP2(Full)/6-31G(d) calculated value of 1.628 Å for the B−N bond length in the H_3NBCl_3 complex is in very good agreement with these other accurate calculations: 1.628 Å (BAC-MP4(SDTQ)),[16] 1.618 Å (MP2/6-31+G(2d,p)),[8] 1.62 Å (NL-SCF),[14] and 1.61 Å (MP2/TZ2p).[11] However, all these values are longer by about 0.04 Å than the X-ray experimental value of 1.579 Å, reported in 1995 by Avent et al.[13]

The theoretically predicted geometrical parameters for H_3PBH_3 complex are in very good agreement with the experimental gas-phase values and with previous predictions.[9,28] The B−P bond length is nearly 0.008 Å longer than the experimental value (1.937 Å) reported by Graham et al.[29]

The calculated value for the B−P bond length in the H_3PBF_3 complex is a very interesting case. The MP2(Full)/6-31G(d) optimized value differs by 1.168 Å from the experimental value obtained from the X-ray structure analysis.[30] The experimental P−B bond length of this complex in solid state is even 0.32 Å shorter than that of the H_3NBF_3 complex.

For the H_3PBCl_3 complex, we have neither experimental nor theoretical data for comparison, except the RHF/3-21G value (2.029 Å) reported by Hirota et al.,[18] which is longer by 0.021 Å than the MP2(Full)/6-31G(d) one.

The calculated B−X bond lengths in the H_3NBX_3 and H_3PBX_3 (X = H, F, and Cl) complexes are much longer than in isolated BX_3 moieties. Upon complexation, the lengthening of the B−X bonds increases when going from BF_3 to BCl_3. This is because in the isolated BX_3 (X = F, Cl) strong π donation from the halogen lone pairs into the formally empty p(π) orbital at boron stabilizes the molecule, yielding shorter B−X bonds.[8] In addition, complexation in H_3YBCl_3 (Y = N, P) involves stronger pyramidalization than in the corresponding fluorine complexes. The value of 119.8° for the ∠FBP bond angle, calculated at the MP2(Full)/6-31G(d) level, shows that the H_3PBF_3 complex does not exhibit a tetrahedral arrangement around the boron center. Thus, we can reclaim that there is probably no complex formation upon coordination between PH_3 and BF_3 moieties in the gas phase. This same result has been obtained experimentally by Durig et al.[31] from the ^1H and ^{11}B NMR spectra analysis. They have reported that the attempted synthesis of H_3PBF_3 was unsuccessful because the compound was found to be completely dissociated in the gas phase. For all other complexes the ∠XBY bond angles show that the BX_3 moieties have a tetrahedral structure since the calculated ∠XBY bond angle values are 104−105° (see Table 1). Furthermore, the distortion of BX_3 groups in the H_3PBX_3 complexes is less important than in the H_3NBX_3 ones, as the values of the B−X bond lengths show (see Table 1). This distortion decreases in the same order that the acidity of Lewis acids does.

On complex formation, the calculated geometrical parameters show both a lengthening of the N−H bonds by about 0.003 Å and a shortening of the P−H bond (Table 2), which has also been confirmed experimentally,[32] as well as an opening of ∠HPH bond angles. In 1974, Durig et al.[31] discussed the shortening of the P−H bond by using the force constants

TABLE 3: Comparison of Our G2(MP2) Complexation Energies with Experimental and Other Accurate Theoretical Calculation for H_3NBX_3 (X = H, F, and Cl) Complexes (kcal/mol)[a]

	BH_3	BF_3	BCl_3	ref
G2(MP2)	−25.97	−19.16	−22.60	this work
MP2/TZ2P	−28.30	−17.4	−21.0	11
NL-SCF[b]	−26.80	−16.0	−18.2	14
CCSD(T)(cc-pVTZ)[c]	−26.5	−19.2		12
DFT(BLYP/6-31G(d))	−28.50	−23.1		15
MP2/6-31+G(2d,p)		−19.81	−24.08	8
BAC-MP4(SDTQ)[d]	−31.3		−25.3	16

[a] The complexation energies value are calculated at 0 K and include ZPE correction. [b] Local density approximation with nonlocal corrections to the correlation and exchange potentials. [c] CCSD(T)/correlation-consistent polarized-valence triplet-ζ calculations. [d] Bond additivity corrections for the MP4(SDTQ) level of theory; the calculated complexation energies were obtained at 298 K.

TABLE 4: G2(MP2) Complexation Energies E_c (in kcal/mol),[a] MP2(Full)/6-31G(d)-NBO Net Charges q(Y) and q(B), and Transferred Charges (Q_t) from Donor YH_3 (Y = N, P) to Acceptor BX_3 (X = H, F, Cl)

	E_c	q(Y)	q(B)	Q_t
NH_3		−1.12		
PH_3		0.05		
BH_3			0.32	
BF_3			1.46	
BCl_3			0.31	
H_3NBH_3	−25.97	−0.94	−0.16	−0.35
H_3NBF_3	−19.16	−1.03	1.35	−0.28
H_3NBCl_3	−22.60	−1.01	0.29	−0.36
H_3PBH_3	−20.10	0.59	−0.65	−0.63
H_3PBF_3	−2.96	0.03	1.45	−0.02
H_3PBCl_3	−5.38	0.52	−0.08	−0.67

[a] $E_c = E_{tot}(H_3YBX_3) - [E_{tot}(YH_3) + E_{tot}(BX_3)]$. The E_c values include ZPE correction.

determined from infrared and Raman spectra. They have reported that the P−H force constant values are higher than the 3.24 mdyn/Å obtained for the isolated PH_3 moiety. Therefore, they suggested that this increase is consistent with a shorter P−H bond upon complex formation. To explain this result, we have applied the natural bond orbital (NBO) analysis. MP2(Full)/6-31G(d)-NBO calculations show that in isolated PH_3 moiety the lone pair on P has lower "s" character than in H_3PBH_3, H_3PBF_3, and H_3PBCl_3 complexes. Therefore, we can deduce from these results that this change alone would imply a shortening of the P−H bond length owing to an increased "s" character in these bonds. Moreover, Table 2 shows that the 3s atomic orbital (AO) contribution of P in the P−H bond length is more important in H_3PBX_3 complexes than in isolated moiety PH_3. In contrast, the contribution of the 2s AO of ammonia is more important in an isolated moiety than in the H_3NBX_3 complexes.

Table 3 presents our G2(MP2) computed complexation energies for the H_3NBX_3 (X = H, F, and Cl) complexes along with previous theoretical calculations. The complexation energies are calculated as the energy differences between the complexes and the respective donor−acceptor moieties.

Our G2(MP2) results are in agreement with all previous predictions. The experimental value for the complexation energy of the H_3NBH_3 complex is −31.1 kcal/mol,[33] which is an extrapolation based on the measured bond strengths of the set of methylamine−BH_3 and methylamine−BMe_3 complexes. This value differs from the G2(MP2) one by about 5.13 kcal/mol. Recently, Gurvich et al. yield a B−N complexation energy of −37.5 kcal/mol,[34] which is significantly more negative than any of the predicted values and also than Haaland's estimation.[33] Bearing in mind that the complexation energy is based on a single experimental study and is thus not firmly established, these comparisons suggest that the complexation energy determined by Gurvich et al. is too negative.

Table 4 lists the G2(MP2) computed complexation energies for the H_3YBX_3 (Y = N, P and X = H, F, Cl) donor−acceptor complexes, the MP2(Full)/6-31G(d)-NBO net charge on donor atom (q(Y)) and acceptor atom (q(B)), and the charge transfer from YH_3 Lewis bases to BX_3 Lewis acids (Q_t).

The NH_3 complexes with BX_3 (X = F and Cl) Lewis acids are calculated to be more strongly bound than the respective PH_3 complexes. In fact, the complexation energies of H_3NBF_3 and H_3NBCl_3 are −19.16 and −22.60 kcal/mol, respectively, while the complexation energies of H_3PBF_3 and H_3PBCl_3 are −2.96 and −5.38 kcal/mol, respectively. For H_3NBH_3 and H_3PBH_3 complexes, one can observe that the complexation energy deference between these two complexes is small (5.87 kcal/mol). This result comes from both the small back-donation from BH_3 to PH_3 and the effect of hyperconjugation present in the H_3PBH_3 complex. The hyperconjugation is reflected by the change in the net charge at the boron hydrogens, since it is negative in the isolated BH_3 moiety (−0.11e) and becomes positive upon the formation of the complex (0.01e). Moreover, the greater stability of the H_3NBX_3 complexes is obvious since the complexation energies were related to the basicity of Lewis bases.[35−37] The experimental proton affinities of NH_3 (203.4 kcal/mol)[38] and PH_3 (188 kcal/mol)[39] show that NH_3 is a stronger base than phosphine. Therefore, the strongest bonding to a given acceptor appears to be formed by nitrogen donors.

The G2(MP2) calculations predict that the H_3NBH_3 complex is more stable than the other ones. Also, the H_3PBF_3 complex is calculated as a weakly bound van der Waals complex (−2.96 kcal/mol). Finally, the H_3PBCl_3 complex is calculated as a weak donor−acceptor bond (−5.38 kcal/mol).

The calculated donor−acceptor bond strengths of the YH_3 (Y = N and P) complexes shown in Table 4 indicate that BH_3 appears as a marginally stronger Lewis acid than BCl_3, which is significantly stronger than BF_3. They also show that, in NH_3 complexes, the substitution of hydrogen by fluorine and by chlorine at boron in borine complexes seems to have little effect upon the complex formation. In fact, complexation energies decrease by 6.81 and 3.37 kcal/mol in going from BH_3 to BCl_3, respectively. However, in PH_3 complexes, the substitution of hydrogen by halogen atoms as F and Cl leads to a decrease in the values of complexation energies of 17.14 and 14.27 kcal/mol for H_3PBF_3 and H_3PBCl_3, respectively. Table 4 shows also that the bond strengths of H_3NBCl_3 and H_3PBCl_3 are higher than those of the respective BF_3 complexes. We can explain this result by the qualitative model of hard and soft acids and bases (HSAB) developed by Pearson.[40] We know that BF_3 is a hard acid (η = 9.7 eV)[41] and BCl_3 is a soft one (η = 5.64 eV),[41] while NH_3 and PH_3 are soft bases in the terminology of the HSAB model. This model makes it plausible that the YH_3 (Y = N and P) coordination with BCl_3 be more favored than with BF_3. In addition, our calculated structures for H_3NBX_3 and H_3PBX_3 (X = F and Cl) complexes show that the BCl_3 moiety is more pyramidal than BF_3, the XBX angles being 113.8 and 114.6°, respectively. Thus, we can arrive at the same conclusion as presented before, i.e., that H_3NBX_3 complexes are more stable than the corresponding H_3PBX_3 complexes.

The MP2(Full)/6-31G(d)-NBO results listed in Table 4 show that the PH_3 complexes have a higher charge transfer from the phosphine to the BX_3 acceptor moiety than the NH_3 complexes, except for the H_3PBF_3 complex, which presents nearly null charge transfer from PH_3 to BF_3 (0.02*e*). However, the negative partial charge at nitrogen (−1.12*e*) is much higher than that of PH_3 (0.05*e*), contrary to the scale of stability between the NH_3 complexes and their homologous PH_3 ones. In fact, the charge transfer from PH_3 to BCl_3 and BH_3 is higher than from NH_3 (the charge transfer for H_3PBCl_3, H_3PBH_3, H_3NBCl_3, and H_3NBH_3 is −0.67, −0.63, −0.36, and −0.35*e*, respectively), while the complexation energies of PH_3 complexes are lower than for ammonia complexes. Moreover, the H_3BNH_3 complex is the most stable (−25.97 kcal/mol) and it shows only a charge transfer of 0.35*e*, whereas the less stable complex is H_3PBCl_3 (−5.38 kcal/mol) and it shows a charge transfer of 0.67*e*. Hence, one can see that from NBO results it follows that there is no correlation between charge transfer and the G2(MP2) complexation energies for H3YBX_3 donor−acceptor complexes, as recently reported.[11,37] Also, the NBO results show that on formation of the PH_3 complexes, the electrons flow mostly from the 3s (0.26, 0.01, and 0.25*e* for H_3PBH_3, H_3PBF_3, and H_3PBCl_3, respectively) and 3p_z (0.35, 0.01, and 0.0.37*e* for H_3PBH_3, H_3PBF_3, and H_3PBCl_3, respectively) AO of phosphorus to the 2p_z AO of boron, whereas in ammonia complexes, the electrons flow only from the 2p_z AO of nitrogen (0.21, 0.18, and 0.22*e* for H_3NBH_3, H_3NBF_3, and H_3NBCl_3 respectively) to the 2p_z AO of boron.

Table 4 shows also that H_3PBH_3, H_3PBCl_3, and H_3NBH_3 complexes differ from the other structures by a much higher change of the partial charge at the acceptor atom (boron) toward more negative values. Furthermore, it reveals that the charge transfer to BCl_3 is higher than for BH_3 and BF_3. It reveals first that the B atom in BH_3 has a truly empty 2p_σ orbital (0.01*e*), while this orbital is almost occupied in BF_3 (0.33*e*) and in BCl_3 (0.50*e*) by charge donation from halogen lone-pair electrons, and second, boron is found to be significantly more positive in BF_3 (1.46) than in BCl_3 (0.31) and in BH_3 (0.32). Also, it is found that the boron 2p_π orbital is more populated in BH_3 (1.70*e*) than in BCl_3 (1.34*e*), which is significantly more populated than in BF_3 (0.72*e*). Thus, this population of the boron 2p_π orbital increases in the same order as both the Lewis acidity of BX_3 (X = H, F, and Cl) and the stability of H_3NBX_3 and H_3PBX_3 complexes.

4. Conclusion

The comparative study between H_3NBX_3 and H_3PBX_3 (X = H, F, and Cl) complexes shows that the NH_3 complexes have shorter donor−acceptor bond lengths and are more stable than the PH_3 ones. Upon formation of the complexes, the P−H bond lengths become shorter than in an isolated PH_3 moiety. This shortening is related to the increasing “s” character in this bond. The NBO results reveal that the phosphine complexes show a stronger charge transfer than their ammonia homologous, although the negative partial charge at nitrogen is much higher than that of PH_3. Moreover, of all complexes the stability decreases when both the Lewis acidity of BX_3 Lewis acids decreases and the population of 2p_π boron orbital increases.

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