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Comparative G2(MP2) Molecular Orbital Study of $B_3H_7XH_3$ and H_3BXH_3 Donor−Acceptor Complexes (X = N, P, and As)

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$B_3H_7XH_3$ and H_3BXH_3 (X = N, P, and As) have been studied as donor−acceptor complex type at the G2(MP2) level of theory. Both single- and double-bridged structures of B_3H_7 Lewis acid are taken into account. Although the double-bridged structure is energetically favored in the isolated state, the coordination prefers the single-bridged one. The monoborane adducts adopt the staggered arrangement with C_{3v} symmetry. The energetic analysis by natural bond orbital theory shows that the decrease of hyperconjugative contribution upon complexation in the B_3H_7 moiety has, as consequence, a loss of symmetry for $B_3H_7XH_3$ (X= P and As) complexes. In the two series, the coordination is the result of two opposing interactions. The first one is stabilizing, developed between a' symmetry fragment molecular orbitals, and is mainly of 3MO-4e nature. The second one is destabilizing and developed between occupied molecular orbitals (2MO-4e) of donor and acceptor fragments having a'' symmetry. Furthermore, in the case of BH_3 complexes, the complexation is made along the C_3 axis that joined the two fragments, whereas for B_3H_7, it is mainly centered on the nonequivalent boron atom, but the two other ones are also weakly involved in the coordination through a suitable p orbital even if the donor fragment is not on the three boron triangle center.

1. Introduction

A typical property of electron-deficient boranes is their Lewis acidity, which reflects the fact that boron possesses fewer valence electrons than valence orbitals;[1] they react readily with a range of Lewis bases in both solution and gas phase. However, this property differs from small boranes to higher borane clusters because the boron connectivity increases when the number of borons in the clusters increases. Indeed, the structural chemistry of higher boranes is dominated by deltrahedra, cluster shapes composed of numerous triangles formed with three boron atoms. Thus, it's more interesting to compare the complex stability formed by reaction of monoborane (BH_3) and triborane (B_3H_7) with Lewis bases such as NH_3, PH_3, and AsH_3.

The stability and properties of BH_3L complexes (L = Lewis base) are sufficiently studied[2−18] and carried out. In the case of those Lewis acid−base complexes, it was shown that the stability of the formed donor−acceptor adducts depends on the nature of the ligand and BH_3 acid substituent. Therefore, Anane et al.[17,18] have shown that the complexes formed with BH_3 and XH_3 (X = P and N) are found to be more stable than those obtained with XH_2 (X = O and S) than with XH (X = F and Cl) at the G2 level of theory. They have also shown that H_3BNH_3 is more stable than H_3BPH_3 and that the s character of the B−X bond decreases and p character increases as the electronegativity of X increases. They have concluded that the B−X bond cannot be treated only in terms of a simplest HOMO−LUMO interaction model (two level and two electron model system: 2MO-2e), but the interaction occurs between two molecular orbitals of the acceptor (LUMO and a deeper orbital) and the highest occupied molecular orbital (HOMO) of the donor (a three level and four electron model system: 3MO-4e).

They have also illustrated that the complexation energies depend on the degree of substitution on the acceptor and donor fragments. In recent studies, our group[19,20] has investigated H_3AlXR_3 (X = N, P, and As, R = H and Me) as donor−acceptor complex types at the G2(MP2) level of theory. The stability of these complexes decreases when going from nitrogen to arsenic, and the evolution of the complexation energy of H_3AlXR_3 adducts depends on the coordination mode; this is a result of two interaction types: a stabilizing interaction between a_1 symmetry fragment molecular orbitals and a destabilizing interaction between e ones. The stability of donor−acceptor complexes formed by B_3H_7 borane as Lewis acid and different Lewis bases is not sufficiently studied. However, the stability of isolated B_3H_7 conformations was largely carried out. In fact, Lipscomb et al.[21] have shown that the favored structure is that having two bridged hydrogen atoms (double-bridged: 2102 structure in styx notation[22]) compared to the structure with one bridged hydrogen atom (single-bridged: 1103 structure in styx notation) by above 4.4 kcal/mol. Experimentally, it was shown that the B_3H_7 moiety has only one bridged hydrogen in B_3H_7L (L = NH_3 and CO) compounds.[23−25] Thus, when the ligand is removed, the B_3H_7 unit has a vacant orbital, which can be filled with some strain by conversion of a terminal hydrogen of the single-bridged structure to the double-bridged one. Morokuma et al.[26] have investigated the stability and the structure of both $B_3H_7NH_3$ and B_3H_7CO at the MP2/6-31G level of theory. They have shown that the B_3H_7 species in these complexes prefers the single-bridged arrangement.

In continuation of our work, we now report our investigation of the $B_3H_7XH_3$ (X = N, P, and As) donor−acceptor complexes

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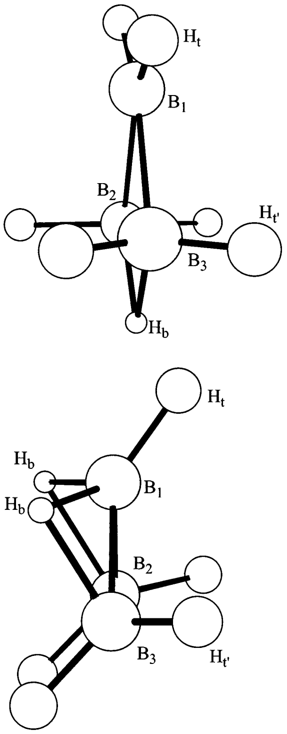

Figure 1. Optimized single- and double-bridged structures of isolated B_3H_7 borane.

compared to the H_3BXH_3 (X = N, P, and As) ones. The relative stability of these complexes is examined with respect to the qualitative molecular orbital analysis (QMOA).[27,28] To the best of our knowledge, no comparative study of these complexes has been carried out.

2. Computational Details

Ab initio calculations were performed using the Gaussian 98 series of computer programs[29] on the IBM RS/6000 workstations at the University of València. 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).[30] For improved energy, the G2(MP2) energies[31] were computed. The electronic structures have been done using the natural bond orbital (NBO)[32] partitioning scheme at the MP2(full)/6-31G(d) level. NBOs are the localized set of easily recognizable Lewis-like (σ and π bond, lone pair, and core) and non-Lewis (σ^* and π^* antibond and Rydberg) orbitals, which are optimal in the sense of orthonormality and maximum occupancy of the Lewis set. 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 significantly affect the result.[32] On another hand, 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 study by Mikhali et al.,[33] using the G2(+) method, and more recently a study by Mo and Gao[34] show that the BSSE has little effect on the calculated complexation energies.

3. Results and Discussion

3.1. Geometries. First, we proceeded to the structural study of the series of $B_3H_7NH_3$, $B_3H_7PH_3$, and $B_3H_7AsH_3$ compounds. Taking into account both C_{2v} and C_s structural conformations of the B_3H_7 fragment (Figure 1), we made two corresponding approaches by imposing the C_s symmetry. Let us remember that the double-bridged structure of isolated B_3H_7 is more stable than the single-bridged one.[35,36] In this work, we have reexamined this stabilization; it is about 3.7 kcal/mol at the G2(MP2) level of theory.

TABLE 1: G2(MP2) Total Energies (in au) of $B_3H_7XH_3$ Complexes

	single-bridged		double-bridged	
	C_s	C_1	C_s	ΔE^a
$B_3H_7NH_3$	−134.971 627		−134.958 355	8.33
$B_3H_7PH_3$	−421.174 055	−421.174 532	−421.154 637	12.44
$B_3H_7AsH_3$	−2314.561 041	−2314.563 113	−2314.545 038	14.29

[a] ΔE (kcal/mol) is the difference in energy above the minimum energy conformation.

As we will show below, the LUMO that confers the Lewis acid property to B_3H_7 is localized on the B_1 boron atom in both single- and double-bridged conformations. Nevertheless, this latter structure would be a bad acceptor via the B_1 atom. In fact, if we compare these two structures, we note that B_1 is not as accessible in the C_s double-bridged triborane as in the C_{2v} single-bridged one. In the C_{2v} conformation, the B_1 atom is practically in a similar neighborhood to the BH_3 simple system. Thus, we should expect a less-stable complexation when B_3H_7 adopts the double-bridged form than when it is in the single-bridged one. Effectively, the collected energetic data (Table 1) confirm it. We notice that for the three complexes, the single-bridged structure is more stable than the double-bridged one. Therefore, the energetic deviations are 8.33, 12.48, and 14.29 kcal/mol for $B_3H_7XH_3$ (X = N, P, and As, respectively) at the G2(MP2) level of theory. In previous works, only the single-bridged structure has been taken into account; the double-bridged one has been omitted for spectral[24,25] and energetical[26,37] considerations. In this work we also considered only the single-bridged structure.

We then reoptimized the three single-bridged complexes $B_3H_7XH_3$ (X = N, P, and As) without symmetry constraints. In Figure 2, we have reported the favored conformations, which are all minima. In Table 2, we present selected bond lengths in isolated and complexed B_3H_7 borane. We remark that there are no important effects of the ligand coordination on the geometry of B_3H_7 Lewis acid. We notice that only the $B_3H_7NH_3$ compound keeps C_s symmetry, whereas for the two other ones, the XH_3 (X = P and As) ligand is out of the symmetry plane.

What are the factors behind these structural preferences? To answer this question, we have undertaken a NBO energetic analysis by carrying out interfragments zeroing interactions and Fock matrix elements deletions on B_3H_7 free and coordinated fragment. On another hand, the thorough examination of fragments' donor and acceptor structural, and orbital interactions and coordination energy evolution within this series will permit, as we will see hereafter, us to confirm factors behind the choice of such geometrical preferences.

3.2. NBO Energetic Analysis. We considered free B_3H_7 and $B_3H_7XH_3$ (X = N, P, and As) compounds taken in their symmetries (C_{2v} for free B_3H_7 and C_s for the others). We took only the symmetrical structures with the aim to know factors responsible for the fragment symmetry maintenance of the B_3H_7 fragment. This last could be regarded as being formed by a BH_2 (Frag1) fragment and a $H_2B(H)BH_2$ (Frag2) one (Scheme 1).

However, slight rotations of the Frag1 unit around the B_1−H_b C_2 axis (bisector axis of HB_1H angle) cause a symmetry loss. This symmetrical breaking is avoided thanks to, among other things, an electronic delocalization between B−H bonds (σ) of Frag1 unit and antibond lone pairs (LP*) of B_1 and B_2

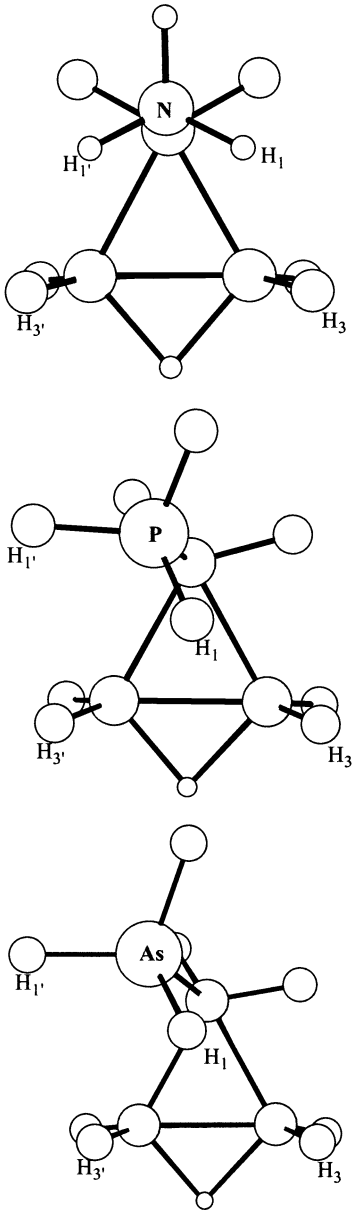

Figure 2. Optimized structures of $B_3H_7XH_3$ (X = N, P, and As) complexes.

TABLE 2: Selected Optimized Bond Lengths (Å) in Isolated and Complexed Single-Bridged B_3H_7 Borane

distances	isolated B_3H_7	$B_3H_7NH_3$[a]	$B_3H_7PH_3$[a]	$B_3H_7AsH_3$[a]
B_1-B_2	1.78	1.84	1.84	1.84
B_2-B_3	1.73	1.71	1.73	1.73
B_1-H_t	1.19	1.20	1.20	1.20
$B_2-H_{t'}$	1.20	1.19 1.20	1.19 1.20	1.19 1.20
B_2-H_b	1.34	1.32	1.31	1.31

[a] The second value corresponds to equivalent hydrogen atoms.

SCHEME 1

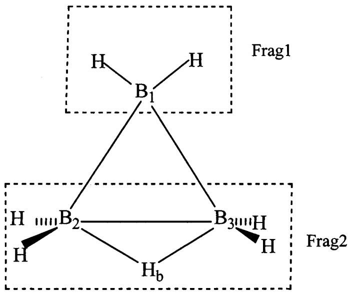

TABLE 3: HF/6-311G(d,p)//MP2(full)/6-31G(d) Deletion Energies (kcal/mol)

compound	Frag1−Frag2 zeroing	$LP(B_3)-LP^*(B_{1,2})$ deletion	$\sigma(B_3-H)-LP^*(B_{1,2})$ and $\sigma(B_{1,2}-H)-LP^*(B_3)$ deletion
B_3H_7	510	408	54
$B_3H_7NH_3$	475	323	41
$B_3H_7PH_3$	515	265	9
$B_3H_7AsH_3$	513	275	9

atoms or between $\sigma(B_{1,2}-H)$ NBOs and LP (or LP*) ones of B_1 atom. Those delocalizations are as much best as Frag1 B−H bonds are in the three-boron atoms plane. Two qualitative deletions have been considered. The first one is the Frag1 and Frag2 zeroing interaction. The corresponding energies could be considered close at this level of theory (Table 1). This interaction is a result of Lewis−Lewis and Lewis−non-Lewis Frag1 and Frag2 NBOs mixtures. The second deletion is the elimination of two Fock-matrix element sets that have a significant role in the Frag1−Frag2 interaction. However, the elimination of elements corresponding to $LP(B_1)-LP^*(B_{1,2})$ shows that the corresponding interaction does not control the symmetry maintenance of the B_3H_7 moiety although its energy represents about 80%, 70%, and 50% of the total energy of the Frag1−Frag2 interaction for B_3H_7, $B_3H_7NH_3$, and $B_3H_7XH_3$ (X = P and As), respectively (Table 3). In fact, it is not too sensitive to the symmetry breaking by turning the Frag1 unit around the C_2 axis. This interaction contributes to the three-centers two-electron (3c-2e) bonding.[1] The second deletion corresponds to sets of elements that ensure the σ(B−H) of one fragment and LP (or LP*) NBOs of boron atom of the other one. However, because this interaction implies out of three boron's ring B−H bonds, its relative energy values give an idea of its capability to control the symmetry loss. The corresponding energy is about 54, 41, and 9 kcal/mol for free B_3H_7, $B_3H_7NH_3$, and $B_3H_7XH_3$ (X = P and As), respectively and represents 11%, 9%, and 2% of the total Frag1−Frag2 interaction (Table 3). Starting from these values, we can already conclude that $B_3H_7PH_3$ and $B_3H_7AsH_3$ compounds are more likely to lose their symmetry than free B_3H_7 and $B_3H_7NH_3$ ones. On the other hand, because the interacting NBOs are vicinal, we can also conclude that the symmetry breaking can be related, among other things, to the decrease of the hyperconjugative energetic contribution of Frag1−Frag2 interaction. A weak electrostatic or steric perturbation caused by the ligand could be sufficient to cause a symmetry breaking.

3.3. Structural Analysis. As we will show below, the complexation becomes weaker on going from NH_3 to AsH_3 fragments. However, the central atom of the donor fragment becomes increasingly bulky. This has the consequence of an increasing long distance B−X, so the donor fragment becomes increasingly mobile. Thus, small electrostatic or steric interactions could move it to one or the other side of its medium position. In Table 4, we have reported the net charges of the hydrogen atoms that are likely to interact with each other and distances that separate them. However, we note that, from the geometrical point of view, the distance d_{B1-X} increases on going from N to As (1.63, 1.93, and 2.00 Å, respectively). This is normal because the atomic radius of the donor central atom increases in the even feel (0.74, 1.1, and 1.21 Å for N, P, and As, respectively).[38]

This has an effect on the distances between $H(XH_3)$ and $H(B_3H_7)$ atoms, which increase, and thereafter, their interactions decrease. To illustrate this, we take d_{H1-H3} distance as an

TABLE 4: MP2(full)/6-31G(d) B−X Bond Lengths (Å) and NBO Charges (e) of Interacting Hydrogens in Single-Bridged $B_3H_7XH_3$ (X = N, P, and As) Complexes

	$B_3H_7NH_3$	$B_3H_7PH_3$		$B_3H_7AsH_3$	
	C_s	C_s	C_1	C_s	C_1
		NBO Charges			
H_1	0.446	0.032	0.038	−0.020	0.026
$H_{1'}$	0.446	0.032	0.035	−0.020	0.018
H_3	−0.010	0.003	0.003	−0.024	0.007
$H_{3'}$	−0.010	0.003	−0.004	−0.024	−0.008
		Distances			
d_{H1-H3}	2.21	2.66	2.76	2.70	2.97
$d_{H1-H3'}$	3.16	3.71	2.88	3.81	2.65
$d_{H1'-H3'}$	2.21	2.66	2.73	2.70	2.71

TABLE 5: G2(MP2) Energies (au), Complexation Energies (kcal/mol), and MP2(full)/6-31G(d) B−X Bond Lengths (Å) of Single-Bridged $B_3H_7XH_3$ and BH_3XH_3 Complexes, and Charge Transfer Q_c (electron)

complexes	energies	E_c	d_{B-X}	Q_c
$B_3H_7NH_3$	−134.971 627	−31.80	1.63	0.400
$B_3H_7PH_3$	−421.174 532	−22.90	1.93	0.734
$B_3H_7AsH_3$	−2314.563 113	−14.80	2.00	0.740
BH_3NH_3	−83.022 744	−25.96	1.66	0.354
BH_3PH_3	−369.232 050	−21.10	1.94	0.630
BH_3AsH_3	−2262.623 433	−14.67	2.05	0.598

example (Table 4); we note that it increases from NH_3 to AsH_3 (2.21, 2.66, and 2.70 Å, respectively, in C_s symmetry and 2.21, 2.76, and 2.97 Å in C_1 symmetry, respectively). In C_s symmetry, the H_1 and $H_{1'}$ atoms, on one hand, and H_3 and $H_{3'}$ atoms, on the other hand, are of like charge sign in the PH_3 and AsH_3 cases and oppositely charged in the NH_3 one. Indeed, this symmetry imposes to H_1-H_3 and $H_{1'}-H_{3'}$ interactions the same intensities and same natures (repulsive or attractive). The B_3H_7-PH_3 and $B_3H_7AsH_3$ complexes are transition states and the B_3H_7-NH_3 complex is a minimum on the C_s symmetry potential surface. For the $B_3H_7PH_3$ compound, in C_1 symmetry, the rotation of the PH_3 axis group around $P-B_1$ and the P atom output from the median plane lead to a new geometrical repositioning of the H_1 and $H_{1'}$ atoms with respect to the H_3 and $H_{3'}$ ones (Figure 2). In fact, $H_{3'}$ (negatively charged) moves to 2.88 and 2.73 Å from H_1 and $H_{1'}$, respectively, which are both positively charged, whereas H_3 (positively charged) is at 2.76 Å from H_1. Thus lateral double-attraction ($H_1-H_{3'}$ and $H_{1'}-H_{3'}$) and repulsion (H_1-H_3) take place and favor the C_1 structure. We notice that this latter corresponds to a minimum in the total potential energy surface. The same remark can be made concerning the AsH_3 complex (Figure 2 and Table 4). One can thus conclude that the interactions between these hydrogen atoms favor C_1 symmetry for PH_3 and AsH_3 adducts and do not for the NH_3 complex. Being given that, the attractive and repulsive interactions between hydrogen atoms in both cases have a decisive role in the structure choice. Let us note that although these interactions are weak, they affect the structural form solely if the coordination is also weak, that is, when the ligand is not strongly bound to the acceptor and could be easily moved out of its symmetrical position. This is confirmed by the low energy difference between the C_s structure and C_1 one (0.30 and 1.33 kcal/mol at G2(MP2) level of theory for B_3H_7-PH_3 and $B_3H_7AsH_3$, respectively (Table 1)) or by the complexation energy, which decreases from the corresponding NH_3 compound to the AsH_3 one (Table 5).

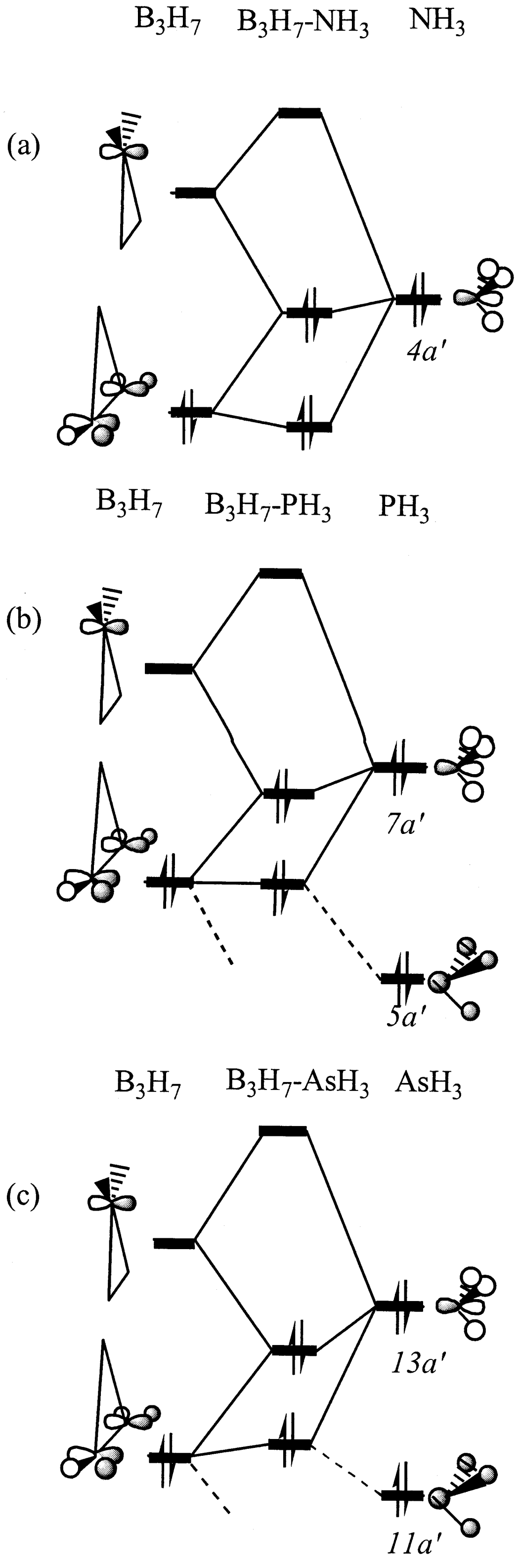

Figure 3. Fragmental analysis of the “*a′*” symmetry molecular orbitals of (a) $B_3H_7NH_3$, (b) $B_3H_7PH_3$, and (c) $B_3H_7AsH_3$.

Concerning the analogous compounds having BH_3 as the acceptor, the staggered conformation is energetically favored with a perfect C_{3v} symmetry. According to our reasoning and compared to B_3H_7 compounds, we would expect that there would be no change concerning the symmetrical properties. This is especially controlled by atomic interactions between hydrogens. Indeed, each hydrogen atom of one fragment is exactly in the same geometrical environment as the two others, consequently the H(acceptor)−H(donor) interactions have the same intensity and the same nature. Contrary to B_3H_7 cases, this does not favor the symmetry reduction; thus all corresponding complexes kept the staggered C_{3v} symmetry.

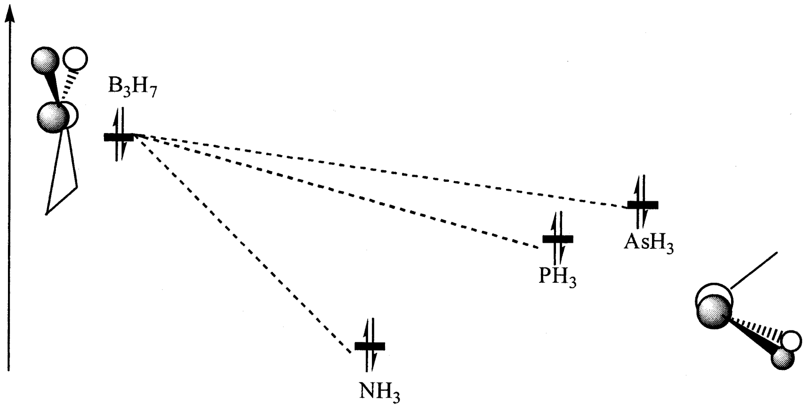

Figure 4. "a''" symmetry MO energy level diagram for B_3H_7 and XH_3 (X = N, P, and As).

3.4. Qualitative Molecular Orbitals Analysis. As we have mentioned in the Introduction, we showed that there are two interaction types that manage the AlH_3 complexation with NH_3, PH_3, and AsH_3.[19] In the present work, the same remarks have been noted for the BH_3XH_3 (X = N, P, and As) complexation. The first one is stabilizing and occurs between the higher a' molecular orbitals of both donor and acceptor fragments, whereas the second one occurs between a'' ones. This latter has a destabilizing character because its interacting orbitals are occupied. The coordination is a mixture of these two interactions but is globally stabilizing, and the evolution of the complexation energy is decreasing along the donor central atom column of the periodic table from N to As.

Similarly to the BH_3 adducts case, the $B_3H_7XH_3$ (X = N, P, and As) coordination is governed by stabilizing and destabilizing interactions. The first one is the seat of a mixture between a' molecular orbitals of both acceptor and donor fragments. In this interaction, the acceptor fragment principally participates in the LUMO. Another orbital is also concerned by this interaction; it is that developed on both p atomic orbitals implying in the four B−H bonds of BH_2 bridged fragments (Figure 3). However, although the coordination of the two Lewis acids (BH_3 and B_3H_7) is almost the same from the energetic point of view, their coordination mode is different because B_3H_7 involves the three boron atoms. In fact, for the BH_3 Lewis acid, the complexation is made perfectly along the C_3 axis that joins the two fragments, whereas for the B_3H_7 one, while it is mainly centered on B_1 boron atom, the two, B_2 and B_3, others also are involved through a suitable p orbital. Nevertheless, the donor fragment is not on the $B_1B_2B_3$ triangle center (Figure 2).

The donor molecular orbital analysis brings out a weak difference concerning a' MOs, which is implied in the stabilizing interaction. This difference has an important consequence on the complexation energy evolution along the column of the periodic table corresponding to the central atom of the donor fragment. In fact, the NH_3 donor participates only by the $4a'$ HOMO, whereas PH_3 and AsH_3 participate by the na' HOMO and $(n-2)a'$ ($n = 7$ and 13, respectively). This latter MO is so much energetically deeper in the NH_3 fragment that it does not affect the 3MO-4e stabilizing mixture of $B_3H_7NH_3$ interaction, whereas in the two other compounds, its energy position enables it to intervene in this interaction. Having a perturbational role (destabilizing), these molecular orbitals unfavorably act in the coordination process and have a consequence on the complexation energy evolution despite the similarity of the coordination mode within this series.

Concerning the second interaction, it occurs between the occupied a'' MO of both fragments. Having 2MO-4e character, this interaction is destabilizing and disfavors the coordination (Figure 4). The energetic position of the XH_3 donor fragment a'' molecular orbital becomes closer to those of the acceptor and, consequently, the destabilizing interaction becomes stronger with the series (N, P, and As). Nevertheless, the destabilizing interaction is lower than the first stabilizing one because the complexation is energetically confirmed.

As we have mentioned before, those two mixtures have an influence on the coordination energy variation within the two series of $B_3H_7XH_3$ and BH_3XH_3 (X = N, P, and As). In Table 5, we notice that for B_3H_7, as for BH_3 acceptor compounds, the complexation energy decreases on going from NH_3 to AsH_3 adducts. This evolution does not agree with the HOMO of one of the donors, which becomes energetically close to the vacant orbital of the acceptor, which would lead one to believe that the coordination becomes strong in this direction. The destabilizing interaction increases more quickly, within these two sets from NH_3 to AsH_3, than the stabilizing one. This results therefore in a decreasing and no regular evolution of the complexation energy.

Finally, by analyzing NBO charge evolution (Table 5), we can conclude that generally, there is no correlation between the complexation energy and the charge transfer for the same Lewis acid. Nevertheless, we notice that the increase of the transferred charge contributes to the stability of $B_3H_7XH_3$ (X = N, P, and As) complexes according to their homologous BH_3XH_3, respectively.

4. Conclusion

Both B_3H_7 and BH_3 borane Lewis acid complexes with electron donors such as XH_3 (X = N, P, and As) depend on two types of interaction (stabilizing and destabilizing). The first one is ensured by the HOMO(donor)−LUMO(acceptor) mixture, which is weakly perturbed by an occupied a' molecular orbital intervention of the acceptor, leading to a 3MO-4e system. The latter perturbation acts unfavorably to the coordination. Another occupied a' molecular orbital of the donor also acts against the formation of the complex especially in the PH_3 and AsH_3 cases. With regard to the strongly destabilizing mixture between the occupied a'' orbitals, it becomes increasingly strong on going from NH_3 to AsH_3 because the corresponding interacting orbitals become energetically close. The complexation is a result of those four interactions of which the stabilizing one is the prevailing. The decreasing evolution of the complexation energy is due to the increased variation of the destabilizing interactions in comparison with the stabilizing one.

Furthermore, the complexation of B_3H_7 is mainly made on the nonequivalent boron atom, and the two others also are weakly implied, but the acceptor–donor bond is not on the axis of the three boron atom ring. Confirmed by the NBO energetic analysis and NBO charge calculations, the interaction of any hydrogen atoms of both fragments and the lowering of hyperconjugative contribution in B_3H_7 fragment are responsible for the symmetry breaking in $B_3H_7PH_3$ and $B_3H_7AsH_3$ adducts.

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