



THE LEWIS ACIDITY OF BORON TRIHALIDES REVISITED

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Dedicated to Professor Enrique J. Baran, a recognized hooligan of the Quilmes Athletic Club, for his outstanding contributions in the field of Inorganic Chemistry.

Abstract

The relative Lewis acidity of boron trihalides is analyzed within the framework of modern density functional theory using larger basis sets that include both polarization and diffuse functions. Concepts such as the strength of the B-X π bonding and vertical electron affinities, as well as geometry and energetic features of complexes formed with ammonia are revisited. Notions often used in Basic Inorganic Chemistry courses to explain the Lewis acidity of boron trihalides are critically reviewed.

Keywords: boron trihalides; Lewis acidity; density functional theory; adducts.

Resumen

La acidez de Lewis relativa de los trihaluros de boro es analizada a la luz de la teoría del funcional de la densidad moderna utilizando además funciones base de calidad triple-zeta

aumentadas con funciones de polarización y difusas. Conceptos como fuerza de enlace entre orbitales atómicos $p\pi$ y afinidades electrónicas verticales de los trihaluros aislados, así como la geometría y energética de los aductos formados con amoníaco son revisados para analizar críticamente las nociones utilizadas frecuentemente en cursos de Química Inorgánica Básica para explicar la mencionada acidez de Lewis relativa.

Palabras clave: trihaluros de boro, acidez de Lewis, teoría del funcional de la densidad, aductos.

Introduction

It is a well known experimental fact that the acid strength of boron trihalides with respect to strong Lewis bases increases in the order $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$ [1]. This ordering, however, is contrary to that expected from electronegativity differences and steric effects arguments, which suggest that boron trifluoride should be the stronger Lewis acid in the series. Much effort, particularly from the theoretical side, was devoted to shed light on this apparent controversy. Partial atomic charges using different charge partitioning methods were calculated for BX_3 [2]. The results show larger positive values for the boron atom when X becomes more electronegative. Thus, the electron deficiency at the boron atom fails to explain the relative Lewis acid strength of boron trihalides as it suggests that BF_3 should be the stronger acid.

It is usually argued in Basic Inorganic Chemistry textbooks that the charge donation from fluorine $2p\pi$ lone pairs into the formally empty boron $2p\pi$ atomic orbital is more efficient and leads to stronger B-X π bonding than the charge donation of chlorine, bromine and iodine $p\pi$ lone pairs due to an apparent poorer overlap of these larger p atomic orbitals with the small boron p atomic orbital. As a consequence of that stronger B-X π bonding in BF_3 , the boron atom exhibits the lowest Lewis acid character in the series. Experimental results on the halogen nuclear quadrupole coupling tensor in boron trihalides seem to suggest that the B-X π bonding is stronger in BF_3 , indeed [3]. It is also clear that the donor-acceptor complex formation involves a partial pyramidalization of the boron trihalide molecule. The energy needed to bring the boron trihalide from its original planar geometry to the final pyramidal structure in the complex should clearly depend on the strength of the π bonding in the planar molecule. In other words, the unwillingness of BX_3 toward pyramidalization must be larger when the B-X π bonding in the planar molecule is stronger. These facts suggest that BF_3 should be the weaker acid in the series in agreement with experimental evidence. On the other hand, some theoretical results have shown that the overlap between the more diffuse $p\pi$ orbitals of the heavier elements of group 17 and the boron $p\pi$ orbital has a similar size or may even be larger than the overlap involving both fluorine and boron $p\pi$ orbitals [4]. In particular, the overlap between the boron and halogen $p\pi$ orbitals is larger in BCl_3 than in BF_3 [4a]. Furthermore, a theoretical study of the π -donor strength of the halogens in planar AX_3 and BX_3^+ (A = B-Tl; B = C-Pb) showed clearly that the order is always $\text{F} < \text{Cl} < \text{Br} < \text{I}$ [2]. These facts are in disagreement with respect to the relative strength of the B-X π bonding and, most important, they introduce some uncertainty about the relationship between pyramidalization and the strength of the B-X π bonding to describe the relative acidity of boron trihalides.

The formation of donor-acceptor complexes could be also rationalized in terms of the ionization potential of the former and the electron affinity of the latter as it is governed by a charge transfer process from the donor moiety to the acceptor moiety. It is known experimentally that the electron affinities of boron trihalides increase in the order $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ [5]. This fact helps in understanding the experimental acidity scale. However, the difference in electron affinities does not seem enough to explain the large differences in complexation energies [6]. It has been suggested by means of calculations performed at different levels of theory, the higher one being MP2/6-31G*, that the increase in acidity when going from BF_3 to BBr_3 can be interpreted as a consequence of the increase in the electron affinity and the simultaneous decrease in the ionic and double-bond

character of the boron-halogen bonds [7]. The relative Lewis acidity scale of group 13 trihalides and trihydrides was also studied by means of gradient-corrected density functional theory using a triple-zeta basis set of Slater orbitals augmented with polarization functions [8]. An energy partitioning scheme, in which the energy is divided into steric, orbital and preparation terms, is used in that work to show that the role of the preparation energy is relevant in the relative acidities of boron trihalides when ammonia complexes are formed. The preparation energy could be thought of as a sort of pyramidalization energy that could in turn be associated to X-X repulsions due to the negative charges on halogen atoms that arise as a consequence of electronegativity differences. More recently, both density functional theory and post Hartree-Fock calculations using large basis sets were accomplished on BCl_3 and BF_3 [9]. The authors found that the distortion of those molecules from the equilibrium geometry to the pyramidal form in the complexes requires nearly the same energy. Moreover, the stronger bond in the $\text{Cl}_3\text{B-NH}_3$ complex is explained in terms of the energetically lower lying LUMO (Lowest Unoccupied Molecular Orbital) of BCl_3 .

In the present contribution, those concepts developed to understand the relative Lewis acidity of boron trihalides are reviewed utilizing the density functional theory with a large basis sets and, moreover, BI_3 is included in the overall analysis.

Methods and computational details

Geometry optimization of isolated boron trihalides and ammonia was accomplished with the Becke's three parameters hybrid density functional [10] using the gradient-corrected correlation functional due to Lee, Yang, and Parr [11] as implemented in the Gaussian 03 package [12]. A 6-311G** basis set was used for all the atoms [13].

In order to verify whether the critical points found are local minima or saddle points on the potential energy surface of the molecules, the eigenvalues of the Hessian matrix were determined. The statistical data obtained as side-product of the matrix diagonalization were used to obtain some thermodynamic functions at 298.15 K and 1 atm.

To acquire vertical electron affinities SCF calculations using aug-cc-pVTZ basis sets for B, F and Cl [14], and aug-cc-pVTZ-PP basis sets for Br and I [15] were performed. Equilibrium geometries are those obtained at the B3LYP/6-311G* level of theory.

Visual inspection of molecules and molecular orbitals as well as the drawings shown in the present work were done with the help of gOpenMol [16].

Results and discussion

The overall $p\pi$ overlap between the $2p\pi$ atomic orbital (AO) of boron and the $n\pi$, $n = 2-5$, AO's of halogen atoms was obtained for the BX_3 series from the atomic overlap integrals calculated by the Gaussian 03 package. The order in the overall $p\pi$ overlap was found to be $\text{BF}_3 < \text{BI}_3 < \text{BBr}_3 < \text{BCl}_3$ [17], in good agreement with previous work [2, 4a]. That ordering, however, is contrary to the empirical Lewis acidity scale. On the other hand, a careful visual inspection to the molecular orbitals (MO) of the optimized geometries of BX_3 shows only one occupied orbital, the HOMO - 5 (HOMO, Highest Occupied Molecular Orbital), in which the $p\pi$ AO of every atom contributes appreciably. Figure 1 depicts the HOMO - 5 for the whole BX_3 series. It can be seen from the figure that the HOMO - 5 of BF_3 is the only MO with an appreciable bonding character, whereas the MO clearly presents a non bonding character for heavier trihalides, with an increasing contribution of the $2p\pi$ AO of boron. This result suggests that the strength of the B-X π bonding is in the order $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3 > \text{BI}_3$, in good agreement with nuclear quadrupole coupling tensor measurements [3]. Thus, the overlap between the $p\pi$ AO's seems not to be an adequate guide to establish the strength of the B-X π bonding in boron trihalides. The bonding character of occupied π MO's, which is related to the MO-LCAO expansion coefficients, should be used instead. It is important to

stress that neither the strength of the B-X π bonding nor the bonding character of occupied π MO's should be directly related to the Lewis acidity of boron trihalides as that behavior should involve an empty MO with the ability to accept an electron pair.

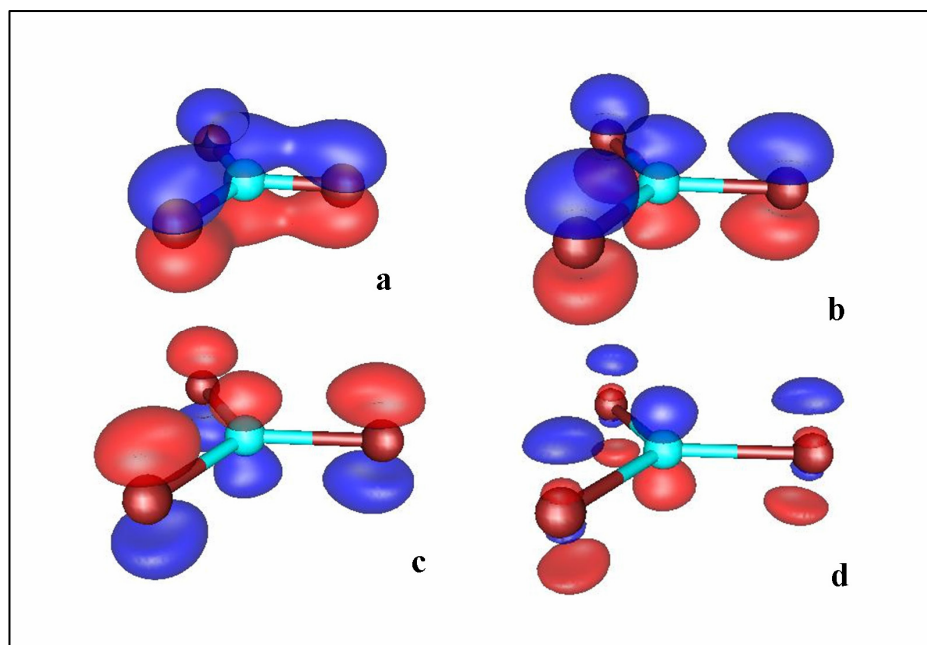


Figure 1. The HOMO – 5 of (a) BF_3 , (b) BCl_3 , (c) BBr_3 and (d) BI_3 . An isovalue of 0.080 a.u. was used to construct the surfaces.

Vertical electron affinities (EA) were calculated as $E^- - E$, where E^- and E are the total electronic energies of BX_3^- and BX_3 , respectively, both at the equilibrium geometry of the neutral species. Results, in eV, are 0.605, 0.046, -0.375 and -0.934 for BF_3 , BCl_3 , BBr_3 and BI_3 , respectively. Although those values are in quantitative disagreement with experimental evidence [5], it is interesting to note that the empirical difference between the EA of BBr_3 and BCl_3 is 0.49 eV [5], whereas present results provide a difference of 0.421 eV, in excellent agreement. Furthermore, the EA increase in the BF_3 - BI_3 series is well reproduced and clearly indicates that the LUMO becomes lower in energy in the same direction. Thus, the increase in the (vertical) EA is parallel to the increase in the Lewis acidity of boron trihalides. Figure 2 shows the LUMO for the whole BX_3 series. It is important to emphasize that the LUMO is the antibonding (or non bonding) counterpart of the bonding HOMO – 5, which features were discussed above. Besides the fact that the LUMO's are quite similar, it is clear from the figure that the contribution of boron $p\pi$ AO is almost constant along the series. On the other hand, the contribution of halogen $p\pi$ AO's decreases in the order $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3 > \text{BI}_3$, indicating that the LUMO becomes a non bonding MO mainly located at the boron center for heavier trihalides. This fact clearly favors the Lewis acid behavior as the atomic number of the halogen atom increases.

The formation of $\text{X}_3\text{B-NH}_3$ adducts was also studied. Table 1 lists the B-N equilibrium distance and some energetic features of the four complexes, including the pyramidalization energy. The pyramidalization energy was obtained by subtracting the total electronic energy obtained through an SCF calculation on the frozen geometry of the boron trihalide in the complex to the total electronic energy of the planar, equilibrium geometry. It is seen from the table that the $\text{F}_3\text{B-NH}_3$ complex shows the larger B-N distance, being the order $\text{F}_3\text{B-NH}_3 > \text{Cl}_3\text{B-NH}_3 > \text{Br}_3\text{B-NH}_3 > \text{I}_3\text{B-NH}_3$.

NH₃ in agreement with results reported elsewhere [9]. Both the total electronic energy difference and the thermodynamic quantities support in some degree the above trend. The standard enthalpy of reaction, in particular, indicates that BCl₃, BBr₃ and BI₃ react with ammonia with a similar *driven force* as they lie in a range of about 2.4 kcal/mol only, whereas the formation of the F₃B-NH₃ complex is about 3 kcal/mol less exothermic than BCl₃. Not surprisingly, pyramidalization energy is found to exhibit the same order that the B-N equilibrium distance, F₃B-NH₃ > Cl₃B-NH₃ > Br₃B-NH₃ > I₃B-NH₃. Furthermore, the strength of B-X π bonding is in the order BF₃ > BCl₃ > BBr₃ > BI₃, as could be deduced from Figure 1. Thus, present results suggest that the pyramidalization energy is closely related to any attempt to weaken the B-X π bonding.

Table 1. B-N equilibrium bond distance, in Å, for the four X₃B-NH₃ adducts, X = F, Cl, Br, I. Total electronic energy difference with respect to the isolated reactants, standard enthalpy of complex formation reactions, standard Gibbs free energy of complex formation reactions and pyramidalization energy, all in kcal/mol, are also given.

	BF ₃	BCl ₃	BBr ₃	BI ₃
r(B-N)	1.700	1.628	1.615	1.611
ΔE	-22.59	-26.16	-27.23	-28.67
ΔH^0	-20.25	-23.13	-24.10	-25.52
ΔG^0	-10.81	-12.95	-12.92	-14.33
E _{pyr}	23.63	23.40	21.21	18.77

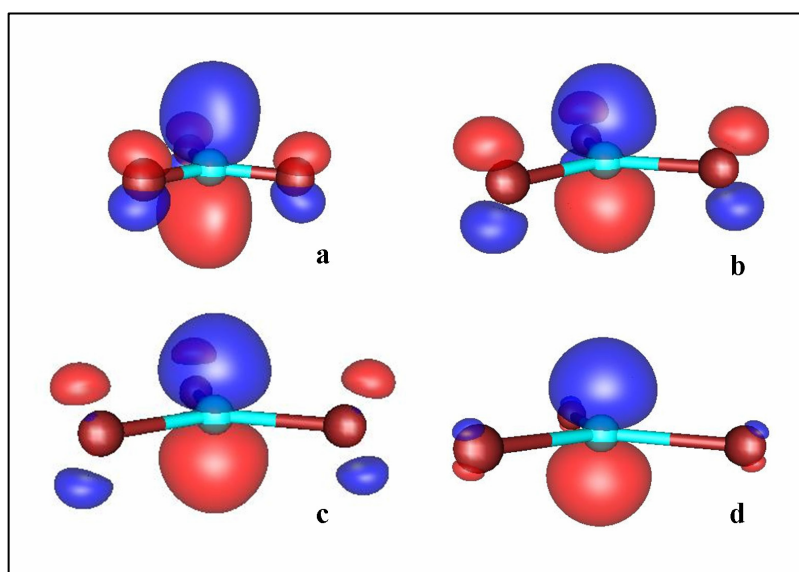


Figure 2. The LUMO of (a) BF₃, (b) BCl₃, (c) BBr₃ and (d) BI₃. An isovalue of 0.080 a.u. was used to construct the surfaces.

Table 2 shows atomic charges and the change in atomic charges upon ammonia complexes formation, calculated through a Mulliken Population Analysis [18]. It can be seen that the charge transferred from ammonia to BX_3 is in the order $BF_3 < BCl_3 \approx BBr_3 \leq BI_3$, a fact that correlates well with the variation in the B-N equilibrium distance, namely, the shorter the B-N distance, the larger the charge transferred to the trihalide. Moreover, the amount of charge transferred to BX_3 also shows a good correlation with the non bonding character of the LUMO. Furthermore, the atomic charges in isolated trihalides follow the trend expected by electronegativity differences, although iodine atoms become positively charged when compared to the less electronegative boron atom, probably due to the arbitrary overlap partitioning in the Mulliken Population Analysis. These results seem to suggest that the pyramidalization energy could be related to strong X-X repulsions arising as halogen atoms approach each other when the interaction with ammonia occurs, as was also argued in [8]. This argument could be criticized, however, by noting that the atomic charges in trihalides listed in Table 2 clearly show that strong X-X repulsions should exist even in isolated trihalides. That repulsion should be stronger in BF_3 as fluorine atoms bear the larger negative charge and they are closer to each other than in heavier trihalides. Nevertheless, the atomization energy (not shown) of isolated trihalides is in the order $BF_3 > BCl_3 > BBr_3 > BI_3$, which, is the same order exhibited by the strength of the B-X π bonding. These facts clearly indicate that the relative stability of BX_3 molecules is mainly influenced both by the strength of the σ skeleton and the strength of the B-X π bonding, whereas X-X repulsions could not play any determinant role. Following the same line it should be expected that X-X repulsions do not play any role during pyramidalization either. It is argued in the present work that the pyramidalization energy is related to the attempts to distort the B-X π bonding and, presumably, to the repulsion of B-X σ bonds, which increases when the σ skeleton distorts from the planar configuration to the pyramidal one.

Table 2. Atomic charges, in $|e|$, for B and X = F, Cl, Br, I. $Q(X)$ is the atomic charge of the halogen atom in isolated BX_3 , $\Delta Q(B)$ and $\Delta Q(X)$ are the change in the atomic charge after ammonia complexes are formed, and ΔQ_{tot} is the amount of charge donated by NH_3 to BX_3 after complexation. Negative values indicate an increase in negative charge.

	BF₃	BCl₃	BBr₃	BI₃
Q(X)	-0.165	-0.081	-0.005	0.091
$\Delta Q(B)$	-0.014	-0.003	0.014	0.043
$\Delta Q(X)$	-0.110	-0.145	-0.149	-0.161
ΔQ_{TOT}	-0.344	-0.438	-0.433	-0.440

Conclusions

The Lewis acidity of boron trihalides, BX_3 , was revisited using modern density functional theory and larger basis sets. The most outstanding conclusions reached in the present work can be summarized as follows.

Both total electronic energy differences and basic thermodynamic quantities agree to provide the order $F_3B-NH_3 < Cl_3B-NH_3 < Br_3B-NH_3 < I_3B-NH_3$ for the relative stability of the

complexes formed. This trend is parallel to the increase in the non bonding character of the LUMO in isolated trihalides, which in turn favors their Lewis acid behavior.

The strength of the B-X $p\pi$ bonding, measured as the bonding character in the HOMO – 5, was found to be in the order $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3 > \text{BI}_3$ showing that the argument usually found in basic Inorganic Chemistry books stating that the lowest acidity in BF_3 is mainly due to the strongest $p\pi$ bonding in the series is partially correct. Furthermore, the pyramidalization energy, the energy necessary to bring boron trihalides from their original planar geometry to the final pyramidal structure in the complexes, is in the order $\text{BF}_3 \approx \text{BCl}_3 > \text{BBr}_3 > \text{BI}_3$. Thus, the strength of the B-X $p\pi$ bonding seems to be related to the magnitude of the pyramidalization energy. It is quite plausible that the strength of the σ skeleton will be also related to the energy needed to distort the planar geometry of trihalides during complexation. Comparison of atomization energies seems to indicate that the pyramidalization energy is mainly related both to the repulsion of B-X σ bonds, which increases when the pyramidal geometry is adopted, and to any attempt to distort the $p\pi$ bonding.

The vertical electron affinities of boron trihalides follow a trend that is parallel to their Lewis acidity. As the electron affinity can be related to the energy of the LUMO, through the well-known Koopman's theorem, it is clear that the relative acidity of boron trihalides can be understood in terms of the strength of the donor-acceptor interaction, in which the key quantities are the ionization potential of the former and the electron affinity of the latter. As stated above, the non bonding character of the LUMO of isolated trihalides should play an important role in their acceptor behavior.

In summary, the relative Lewis acidity of boron trihalides can be better understood and explained in terms of properties that arise after donor-acceptor complexes are formed. This is in line with Mulliken, who stated in 1952 that "it must be kept in mind that the strength of a (Lewis) acid is not quite a unique absolute quantity, but depends appreciably on specific features of its interaction with the base with which it is paired." Nevertheless, some properties of isolated boron trihalides such as the (vertical) electron affinity, or the energy of the LUMO within the framework of Koopman's theorem; the non bonding character and localization of the LUMO at the boron atom, and the $p\pi$ bonding character of the HOMO – 5 arise as useful quantities to teach the acidity of boron trihalides in any advanced Inorganic Chemistry course.

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- [17] The B-X $p\pi$ overlap *per halogen atom* is 1.28, 1.56, 1.44 and 1.39 for BF₃, BCl₃, BBr₃ and BI₃, respectively. It should be noted that the triple- ζ basis sets used in the present work involves the calculation of nine overlap integrals between contracted functions for every B-X pair. Thus, the overall overlap could be greater than the unity.
- [18] Atomic charges calculated with more sophisticated algorithms, such as Natural Bond Orbitals, lead to the same qualitative conclusions.