



## HOMO-LUMO, INFRARED FREQUENCIES AND MOLECULAR GEOMETRY COMPARISON STUDY OF THE STRENGTH OF BORON TRIHALIDES ACIDITY USING AM1 MOLECULAR MODELING

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### Abstract

AM1 Molecular Modeling has been used in the comparison of Lewis acid strength of Boron Trihalide using available opportunities in this method such as HOMO-LUMO gap , infrared frequencies and molecular geometry. HOMO-LUMO separation was employed to evaluate acid strength of  $BX_3$ , and results show that  $BI_3$  is more acidic than others and acidity has decreased up to halogen group. When complex formation between  $BX_3$  and dimethylamine was made , N—H bond stretching alters to red shift ( lower frequency) .It was found that  $I_3BNH(CH_3)_2$  has the lowest frequency for this bond .Geometry for these complexes , B—N bond length and degree of X-B-X angle of all mentioned complexes were also studied and pyramidal structure for complexed  $BX_3$  were observed.

### دراسة HOMO-LUMO وترددات أطيف الاشعة تحت الحمراء والشكل الهندسي للمقارنة بين قوة حامضية مركبات ثلاثي هاليد البورون باستخدام الحسابات الجزيئية بطريقة AM1

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### الخلاصة

استخدمت تقنية الحسابات الجزيئية (Molecular Modeling) وتحديدًا طريقة AM1 في دراسة المقارنة بين مجموعة هاليدات البورون الموصوفة بأنها أحماض لويس لتعيين درجة قوتها باستخدام الإمكانيات المتاحة في هذا البرنامج مثل الفرق بين HOMO-LUMO ، ترددات الاهتزاز والشكل الهندسي . استخدم الفرق بين HOMO-LUMO لتقييم طبيعة التدرج في قوة الحوامض من صنف  $BX_3$  وقد بينت النتائج ان  $BI_3$  يمتلك قيمة الحد الأدنى من هذا الفرق وهذا يعني انه الأكثر فعالية (الحامض الأقوى) من بين مجموعة الأصناف الحامضية المدروسة وان قوتها تقل صعودًا باتجاه أعلى مجموعة الهالوجينات . و فيما يخص قيم ترددات الاهتزاز ، فان تشكل معقدات بين ثنائي مثيل أمين و ثلاثي هاليد البورون أفضل حسب نتائج البحث الى نقصان في قيمة تردد الاصرة N—H ، اذ بينت النتائج ان أوطأ قيمة لهذه الترددات كانت للمعقد  $I_3BNH(CH_3)_2$  ، واخيرًا وفيما يخص الشكل الهندسي ، فقد تم دراسة اطوال الاواصر B—N لهذه المعقدات وكذلك الزوايا X—B—X و X—B—N ولوحظ من هذه القيم ان معقدات  $BX_3$  قد تحولت من المثلث المستوي الى الهرمي .

## Introduction

Elements in group 3A, especially boron and aluminum form three coordinate Lewis acids capable of accepting an electron pair. Some of the most common used Lewis acids are the boron trihalides  $BX_3$ [1].

It is well known as experimental fact that the Lewis acid strength of boron trihalides with respect to strong Lewis bases increases in the order  $BF_3 < BCl_3 < BBr_3 < BI_3$  however this order is reverse as expected on the basis of electronegativity and steric effect of halogens. This sequence must be in the opposite direction and boron trifluoride should be the stronger Lewis acid in the series.[2,3]. Experiments show the opposite, the bromide complex is more stable, for example,  $\Delta H_f$  for reaction between trimethylamine and boron trihalides become more negative from  $BF_3$  to  $BBr_3$  [4].

This behavior of boron halides has been explained on the basis of tendency of halogen atoms to back donate its electrons to vacant p-orbital of the boron atom[5].

Shortening of B-X bonds in boron trihalides is attributed to the ability of boron to accept electrons from the filled  $P_{\parallel}$  orbitals of the halogens through back donation. The bond is formed using the vacant  $P_{\parallel}$  orbital of boron and this phenomenon is probably most significant in  $BF_3$ .

The reduced tendency among the heavier elements to form multiple bonds may be due to:

- An increase in the size of the central element.
- Less effective overlap of more diffused ( $3p$ ,  $4p$  etc.) orbitals and consequent weaker bonds.
- Repulsion between filled inner orbitals of larger M and X. [3]

Frontier orbital theory tells us that the HOMO (highest occupied molecular orbitals) and the LUMO (lowest unoccupied molecular orbitals) play a predominant role in chemical reactions. Small HOMO-LUMO gap implies low kinetic stability, because it is energetically favorable to add electrons to a high lying LUMO, and/or to extract electrons from a low-lying HOMO[6,7]

The higher HOMO energy corresponds to the more reactive molecule in the reactions with electrophiles, while lower LUMO energy is essential for molecular reactions with nucleophiles [8,9]. According to the frontier molecular orbital

theory, a higher HOMO energy of one reactant molecule and a lower LUMO energy of the other are advantageous to the reaction between the two molecules, because electrons more easily transfer from the HOMO of one reactant to the LUMO of the other in the orbital interaction [10].

All the trihalides of all the boron group elements exist, the normal trihalides are planar molecules which have an empty p orbital in the valence shell make use of this empty orbital, both in the structure of the trihalides and in the formation of complexes of the form  $MX_3 \cdot D$  where D is a lone pair donor[11].

Adduct formation may be considered to be taking place in two stages, the reorganization of the planar  $BX_3$  into pyramidal  $BX_3$ , followed by formation of the addition product. The observed behavior, indicates that the reorganization of  $BX_3$  is the least favorable for  $X=F$  [3].

Bathochromic shift (effect) is one of the important parameters in studying complexation processes, which means "Shift to lower frequencies (longer wavelengths) owing to the presence of substitution or a change in environment, atom involved in coordination will lower frequency due to alteration in electron density[12].

In current work, an attempt has been made to correlate the Lewis acid strength of boron trihalides with geometries of their complexes with dimethylamine and HOMO LUMO gap using AM1 theoretical calculations.

## Calculation method:

AM1 (Austin Model 1)[13] a semi-empirical method for the quantum electronic structure in computational chemistry were performed in this work. It is based on the Neglect of Differential Diatomic Overlap integral approximation. Specifically, it is a generalization of the modified neglect of differential diatomic overlap approximation. Several parameters were used to optimize the calculations, at the first time, MM2 (Molecular Mechanics) geometric optimization calculations were carried out followed by UHF (unrestricted Hartree-Fock) geometric optimization. Force keyword another parameter was used to calculate vibrational frequency.

## Results and Discussion

Due to the high confidence of AM1 method in N—H frequency calculations, this might be

considered as a way to conclude acid strength of boron trihalides.

Results from table (1). show that N—H stretching in free dimethylamine are  $3408\text{ cm}^{-1}$  due AM1 calculations while experimental value is  $3420\text{ cm}^{-1}$ , which refers to very slight deviation of theoretical calculation from experimental data about ( $-12\text{ cm}^{-1}$ ) and this comes in a good agreement between them.

**Table 1: NH frequencies of  $X_3\text{BNH}(\text{CH}_3)_2$  complexes**

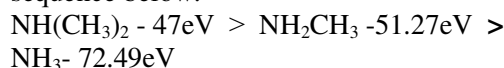
Complex	N—H stretching $\text{cm}^{-1}$	N—H bending $\text{cm}^{-1}$
$\text{I}_3\text{BNH}(\text{CH}_3)_2$	3264	1469
$\text{Br}_3\text{BNH}(\text{CH}_3)_2$	3275	1479
$\text{Cl}_3\text{BNH}(\text{CH}_3)_2$	3293	1492
$\text{F}_3\text{BNH}(\text{CH}_3)_2$	3372	1531

In general, coordination between nitrogen (as Lewis base) and boron trihalide (as Lewis acid) alter these values and shift them to the lower frequency. These differences were due to alteration of N—H dipole moment, if an electron lone pair of a nitrogen atom of a dimethylamine group has a high donation to vacant  $p_z$  orbital in boron, dipole moment become less and frequency move to lower region. So N—H stretching of  $\text{I}_3\text{BNH}(\text{CH}_3)_2$  have lower frequency ( $3264\text{ cm}^{-1}$ ), while this value in  $\text{F}_3\text{BNH}(\text{CH}_3)_2$  complex being ( $3372\text{ cm}^{-1}$ ), means that the vacant  $P_z$  orbital of boron in this complex is partially occupied with back donation from the filled  $p_{\text{II}}$  orbital of the fluorine and becomes weak acceptor, that means it behaves as weak Lewis acid relatively comparable to the others, see the gradual decreasing of frequency down to the halogen group complexes. bending values also agree with this sequence.

As summarized in table (2), gradually energy gap increasing up to the halogen group indicates that boron trifluoride is relatively the more stable acid comparable to the others ( $26.66\text{ eV}$ ) while boron triiodide represents the more reactive acid ( $16.22\text{ eV}$ ).

Lewis base in the same table(2) clears that amine compounds become more reactive when substituted with alkyl groups instead of hydrogen

atom due to the electron donating of alkyl group behaviors toward nitrogen atom, and this phenomenon made  $\text{NH}(\text{CH}_3)_2$  the most reactive Lewis base between the others and follow the sequence below:



**Table 2: HOMO-LUMO energy gap of Lewis acid boron trihalides and Lewis base substituted amines**

Type	Homo	Lumo	Homo/Lumo -gap
Lewis acid			
$\text{BF}_3$	-18.09	8.57	26.66
$\text{BCl}_3$	-10.96	10.92	21.88
$\text{BBr}_3$	-10	8.47	18.47
$\text{BI}_3$	-7.8	8.42	16.22
Lewis base			
$\text{NH}_3$	-14.37	58.12	72.49
$\text{NH}_2\text{R}^*$	-11.97	39.3	51.27
$\text{NHR}_2$	-10.4	36.6	47.00

\*  $\text{R} = -\text{CH}_3$

It has been shown in (Figure 1) that the compression of the HOMO of  $\text{BF}_3$  and  $\text{BCl}_3$  indicates that  $\text{BF}_3$  molecule appears clear HOMO interaction and electron cloud expand between boron and fluorine due to  $P\pi$  back bonding, while the heavier chlorine seems to have a non bonding character.

Correlator between geometries and acid strength was also carried out. This correlation include bond lengths, bond angles and pyramidalization phenomenon were found.

As is shown in table (3), there are significant differences between B—N bond lengths in the mentioned complexes, shortening of this bond reflects an increasing amount of pyramidal degree due to the repulsion between electron density (donated from nitrogen) and electron lone pairs of halogens attached to boron.

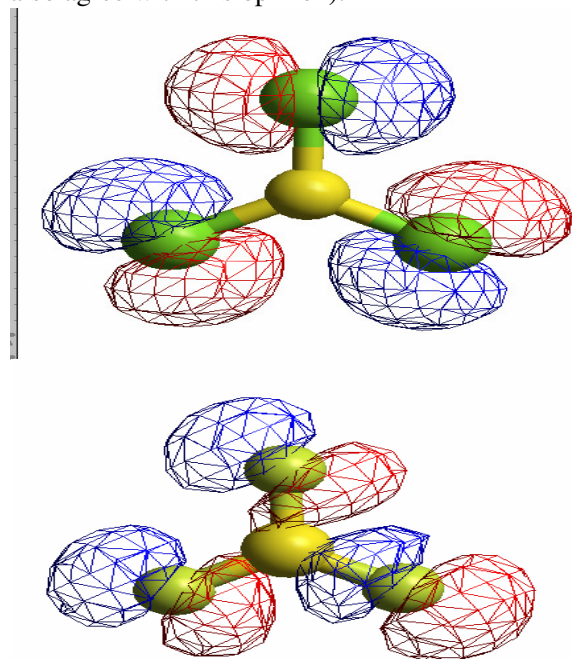
It was also found that the degree of bond angles reveal significant opinion about the correlation nature between acid strength and the structure of complex due to the following points:

- 1- a low degree of X-B-X angle means high Pyramidal Geometry.
- 2- shorter B—N bond length means strong interaction between nitrogen electron pair and vacant p orbital on boron.

3- longer B—N bond length means strong p $\pi$  back bonding donation.

Thus, the obtained results suggest that the pyramidalization is closely related to B-N length and the strength of B-X p $\pi$  back bonding that reflects the magnitude of pyramidalization.

It has been found that the observed results showed a little differences between angles in the same complex, one of three angles of each complex was different from the other two which have the same degree. The explanation of these phenomena is due to the steric effects and the presence of two bulky CH<sub>3</sub> groups which tend to show strong repulsion with halogen atom in the same side and this difference increased with increased halogen atom size down the group (note that X-B-N angle also agree with this opinion).



**Figure 1 : difference for HOMO interaction between BCl<sub>3</sub> and BF<sub>3</sub>**

**Table 3: molecular geometry data for different complexes**

Complex	B-N A <sup>o</sup>	X-B-X			X-B-N		
		Angle 1	Angle 2	Angle 3	Angle 1	Angle 2	Angle 3
BF <sub>3</sub> NH(CH <sub>3</sub> ) <sub>2</sub>	1.882	114.0 <sup>o</sup>	114.6 <sup>o</sup>	114.6 <sup>o</sup>	103.5 <sup>o</sup>	103.5 <sup>o</sup>	104.8 <sup>o</sup>
BCl <sub>3</sub> NH(CH <sub>3</sub> ) <sub>2</sub>	1.644	110.4 <sup>o</sup>	112.1 <sup>o</sup>	112.1 <sup>o</sup>	106.7	106.8 <sup>o</sup>	108.5 <sup>o</sup>
BBr <sub>3</sub> NH(CH <sub>3</sub> ) <sub>2</sub>	1.64	109.4 <sup>o</sup>	111.3 <sup>o</sup>	111.4 <sup>o</sup>	107.5	107.5 <sup>o</sup>	109.5 <sup>o</sup>
BI <sub>3</sub> NH(CH <sub>3</sub> ) <sub>2</sub>	1.599	107.4 <sup>o</sup>	110.2 <sup>o</sup>	110.1 <sup>o</sup>	108.9	108.9 <sup>o</sup>	111.3 <sup>o</sup>

## Conclusions

The present results demonstrate the ability of AM1 calculations to better estimate the relative relativities of boron trihalides and the gradual strength of Lewis acidities of these compounds. All studied parameters such as HOMO-LUMO energy gap, vibrational frequencies and molecular geometries agree to provide the order of BI<sub>3</sub> > BBr<sub>3</sub> > BCl<sub>3</sub> > BF<sub>3</sub> for Lewis acid strength. (Figure 2). refers to pyramidal structure of complexed trihalide which convert from uncomplexed trigonal planer BX<sub>3</sub>. These structures clearly reflects more pyramidal of complexed heavier halogens and this is very clear in I<sub>3</sub>BNH(CH<sub>3</sub>)<sub>2</sub>. The molecular point group of all mentioned complexes are C<sub>s</sub> except I<sub>3</sub>BNH(CH<sub>3</sub>)<sub>2</sub>.

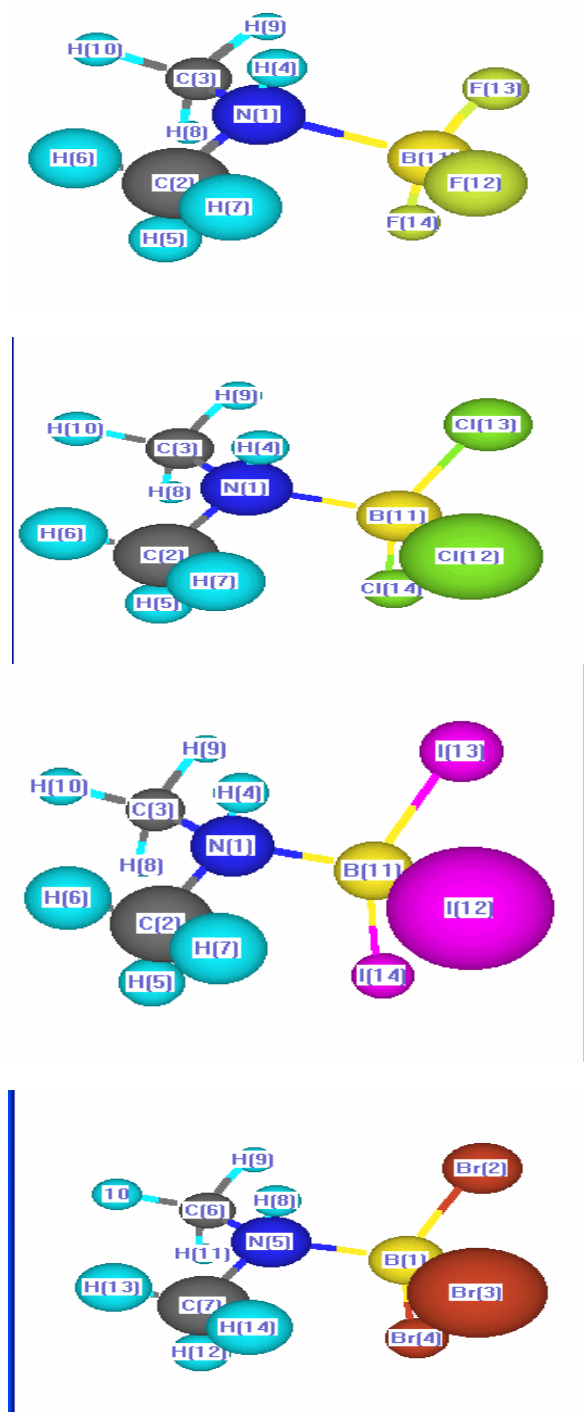


Figure 2: pyramidalization phenomenon of boron trihalides after complexation with secondary amine

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