Ab initio Calculations of the Nuclear Quadrupole Coupling Constants of $BH_{n=2,4}X^+$ ($X = NH_3, PH_3, H_2O, H_2S$)

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The electronic structure and strength of acid-base bonding in the protonated boron-Lewis complexes $BH_{n=2,4}X^+$ ($X = NH_3$, PH_3, H_2O, H_2S) and their neutral parents were studied. The results showed that in the H_2BX^+ monocations the electron releasing from the donor atom in X to BH_3 is significant and more complete than in the other studied complexes. Therefore the bonding between the donor and acceptor in H_2BX^+ is strongest. To obtain these data, the electric field gradient (EFG) at the quadrupolar nuclei in each complex was calculated. The EFG's of the boron atom and other quadrupolar nuclei were calculated by the Gaussian 98 program, using the MP2/6-31G** method.

Key words: Ab initio Calculations; Acid-Base Lewis; Boron; EFG; NQR.

1. Introduction

Donor-acceptor complexes between Lewis acids and bases play an important role in many catalytic reactions. In particular, donor-acceptor complexes of BH_3 have been the subject of many theoretical studies [1]. In 1997, a G2 molecular orbital study of a series of donor-acceptor complexes of BH_3, including BH_4X^+ ($X = NH_3$, PH_3, H_2O, H_2S), was reported [2]. Furthermore, Rasul and Olah calculated the structure and energy of the parent hexa-, hepta- and octa coordinate boronium ions, $BH_6{}^+$, $BH_7{}^{2+}$ and $BH_8{}^+$ [3]. In [4] they extended their investigation to the structure and energy of protonated BH_4X^+ ($X = NH_3$, PH_3, H_2O, H_2S).

Knowing the structure and properties of these complexes is a necessity for understanding the mechanism of their catalytic processes. One way to investigate the electronic structure of compounds is to study the charge distribution around the nuclei composing the complexes.

The quantum mechanical approach is very effective in the determination of the charge distribution in a molecule and/or a complex [5]. It permits to estimate the electric field gradient (EFG) at any point in the molecule [6]. The calculation of the EFG is possible for the nuclei with spins greater than $\frac{1}{2}$. These nuclei possess a nuclear electric quadrupole moment which interacts with the molecular electric field gradient tensor [7, 8]. This interaction can be measured by nuclear quadrupole resonance (NQR) spectroscopy. Quadrupolar nuclei have the nuclear quadrupole coupling constant (NQCC)

$$\chi = \frac{e^2 q_{zz} Q}{h}, \tag{1}$$

where e is the charge of an electron, Q the electric quadrupole moment of the nucleus, q_{zz} the z component of the EFG tensor in the principal axes system, and h Planck's constant [9]. χ is a measure of the interaction of the nuclear electroric quadrupole moment with the molecular EFG tensor.

In this work, the electronic structure of BH_3 Lewis acid-base complexes, especially their acid-base bonding strength, is investigated by means of the calculated NQCCs of their boron nuclei. Some of these complexes have not yet been treated experimentally.

2. Computational Details

All calculations were performed at the MP2/6-31G** level of the theory [10], using the Gaussian 98 package [11]. The optimized structures were characterized by minima based on the calculated vibrational frequencies (NIMAG = 0). EFG's and NQCC's were also calculated. The results reported in Table 1 lead to rather acceptable qualitative NQCCs. It is evident that

Table1. Comparison of calculated NQCCs using the MP2/6-31G** level and experimentally measured NQCCs of some available molecules.

	NH_3		OH_2		SH_2	
	χ_N^{calc}	$\chi_N^{exp\ a}$	χ_O^{calc}	$\chi_O^{exp\ a}$	χ_S^{calc}	$\chi_S^{exp\ a}$
MHz	4.571	4.084	11.593	9.830	39.818	40.000

[a] The experimental values of NQCCs from [10].

Table 2. Calculated NQCCs of N, O and S atoms in X[a].

	χ_N (MHz)		χ_O (MHz)		χ_S (MHz)
H_3BNH_3	2.654	H_3BOH_2	9.603	H_3BSH_2	34.941
$H_4BNH_3{}^+$	1.395	$H_4BOH_2{}^+$	11.023	$H_4BSH_2{}^+$	28.153
$H_2BNH_3{}^+$	1.379	$H_2BOH_2{}^+$	10.247	$H_2BSH_2{}^+$	27.322
NH_3	4.571	OH_2	11.593	SH_2	39.818

[b] Phosphorus atom has a quadrupolar nucleus ($I_P = 1/2$).

Table 3. Calculated asymmetry parameters (η), NQCCs of boron (χ_B) and B-X bond lengths using the MP2/6-31G** method.

Complex		η	χ_B (MHz)	bond length (Å)	
H_3BNH_3	1a	0.000	2.668	B-N	1.659
$H_4BNH_3{}^+$	1b	0.998	3.181		1.585
$H_2BNH_3{}^+$	1c	0.711	5.401		1.558
H_3BPH_3	2a	0.000	2.224	B-P	1.949
$H_4BPH_3{}^+$	2b	0.797	2.884		1.951
$H_2BPH_3{}^+$	2c	0.557	5.562		1.846
H_3BOH_2	3a	0.038	3.986	B-O	1.730
$H_4BOH_2{}^+$	3b	0.601	3.927		1.532
$H_2BOH_2{}^+$	3c	0.903	5.069		1.401
H_3BSH_2	4a	0.038	3.463	B-S	2.034
$H_4BSH_2{}^+$	4b	0.809	3.192		1.945
$H_2BSH_2{}^+$	4c	0.786	5.267		1.893

for any nucleus in a series of homologous compounds, a special level of the theory will be proper to obtain quantitative NQCC results, and therefore, using of the same level of the theory for all quadrupolar nuclei, may help to generate qualitative results.

The calculated NQCCs are shown in Tables 2 and 3. The most recent values of nuclear quadrupole moments, $Q(^{11}B) = 40.59$ mb, $Q(^{14}N) = 20.44$ mb, $Q(^{17}O) = 25.58$ mb, and $Q(^{33}S) = 67.8$ mb, reported by Pyykko [12], were used in this study.

3. Results and Discussion

From (1) it is obvious that the NQCC of nuclei is proportional to q_{zz}. There are two factors controlling the value of q_{zz} at a nucleus: the charge density and the symmetry of the EFG at the quadrupolar nucleus. It is evident that an increase of the charge density causes an increase of q_{zz} and consequently χ. If the symmetry of the EFG increases, then q_{zz} and consequently χ will decrease.

The Acid-base bond σ (X-BH_3) between X (= NH_3, PH_3, H_2O, H_2S) and BH_3 is formed through the participation of lone pairs of N, P, O and S atoms in X groups into the unfilled boron orbital. Therefore, the charge density around donor atom in X and consequently its χ decreases. The χ values of N, O and S atoms in the complexes are much smaller than those of free NH_3, SH_2 and OH_2 (Table 2), which may be attributed to the direct participation of electron pairs of N, O and S atoms (in NH_3, H_2O, H_2S) in the formation of a chemical bond with the boron atom.

Our findings showed that χ_B in an H_2BX^+ monocation is greater than its value in all the other studied boron complexes. Since BH_3 is a Lewis acid and the boron atom has an electron deficiency, in order to form an acid-base bonding, the electrons are released from the X part of the complex toward BH_3. For a strong bonding, the mentioned electron releasing must be significant. In the other words, the strength of the acid-base bond in H_2BX^+ is bigger. The shorter values of the optimized distances of B-N, B-P, B-O and B-S bonds in H_2BX^+ monocations (Table 3) confirm this.

B-H protonation of H_3BX (1a, 2a, 3a and 4a) leads to the monocation H_4BX^+ (1b, 2b, 3b and 4b).

3.1. Protonated H_3BNH_3 and H_3BPH_3

Our studies were based on the distortion of the charge distributions around the boron atom. Any charge distributions in any given complex may be interpreted by the EFG.

The χ value of boron (χ_B) in H_3BNH_3 (1a) and H_3BPH_3 (2a) complexes is less than in their monocations; H_4BX^+ and H_2BX^+ (Table 3). In H_4BX^+, the H^+ ion has electron deficiency and causes the charge density on the boron atom to decrease. In the other hand, a five-coordinate boron atom in these complexes with a three-center two-electron (3c-2e) bond (Fig. 1) causes a distortion of the charge distribution from spherical, and therefore a decrease in the symmetry of the EFG at the boron atom. The large values of the asymmetry parameters of B in $H_4BNH_3{}^+$ and $H_4BPH_3{}^+$ relative to their related complexes verify this. These two factors increase q_{zz} of the boron atom and consequently χ_B.

The dissociation of 1b and 2b to 1c and 2c and H_2, leads to the H_2BX^+ monocation. The shorter optimized B-N and B-P bonds in H_2BX^+ monocations (Table 3) can be attributed to the better participation of the electron pairs of the donor atoms (N and P) in the

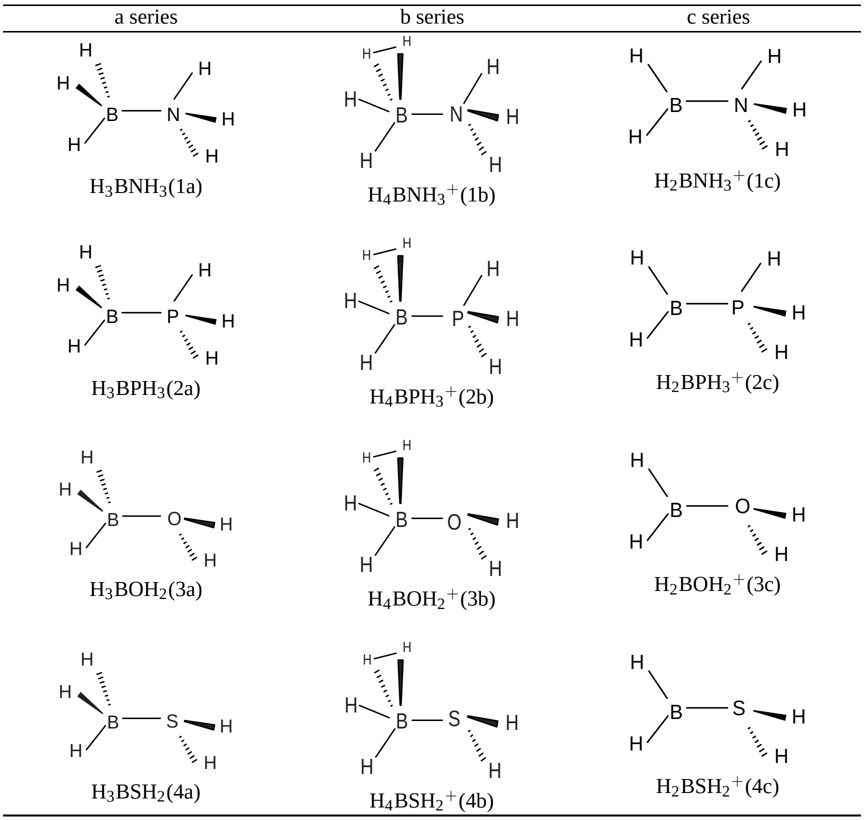

Figure 1. Structures of boron complexes and their monocations.

formation of a stronger acid-base bond with the boron atom of BH_3. Therefore the χ_B values in 1c and 2c are greater than in their related complexes.

These results show that, when X = NH_3 and X = PH_3, the acid-base bonding strength will be in the order

$$\chi_B(H_2BX^+) > \chi_B(H_4BX^+) > \chi_B(H_3BX).$$

3.2. Protonated H_3BOH_2 and H_3BSH_2

We have also calculated the charge distribution at the boron atom in protonated H_3BOH_2 (3a) and H_3BSH_2 (4a). Based on the results reported in Table 3, the values of χ_B in the monocations H_4BX^+ (3b and 4b) are smaller than those of their related complexes. This is different from the above mentioned results for X = NH_3 and X = PH_3.

It is evident that the electric field gradient around a given nucleus arises from the charge distribution of the surrounding atoms, and the contribution of nonbonding electrons is greater than that of bonding ones. The bent structures of SH_2 and OH_2 (due to the presence of the lone pair nonbonding electron in S and O) cause the structure symmetry to be different from that of H_3BNH_3 and H_3BPH_3, where the donors have a pyramidal structures. In the other words, by the presence of H^+ in these complexes the effect of nonbonding electron pairs becomes modest, and therefore q_{zz} and χ_B in 3b and 4b are smaller than in the other complexes.

The results show that the charge density on the boron atom changes with the geometry of the base. Therefore, when X = OH_2 and X = SH_2, the acid-base bonding strength will be in the order

$$\chi_B(H_2BX^+) > \chi_B(H_3BX) > \chi_B(H_4BX^+).$$

Since the q_{ii} values (the components of the electric field gradient tensor at the nuclear site in its system of principal axes) are extremely sensitive to changes in the atomic positions and the chemical bondings in a material, the values of χ and η are excellent parameters to monitor those characteristics.

4. Conclusion

The q_{zz} and consequently the NQCC of quadrupolar nuclei is proportional to the charge density, so that one can determine the strength of the bonding between acceptor and donor by calculating χ for quadrupolar nuclei. The calculated values of χ_B are greater in H_2BX^+ than in all other studied boron complexes, and therefore the electron releasing from X of H_2BX^+ is greater than in the other complexes.

Therefore the determination of the charge distribution around the boron atom in various complexes can be a suitable criterion for the determination of the strength of the bonding between the donor and acceptor. These results are in agreement with the more stable structures obtained by energy calculations [4].

Furthermore, the results show that the NQCCs of the boron atom change with the geometry of the base, and when X = NH_3 and X = PH_3, due to their pyramidal structure and complex symmetry it is expected that electron releasing be such that $\chi_B(H_3BX) < \chi_B(H_4BX^+) < \chi_B(H_2BX^+)$. But, when X = SH_2 and X = OH_2, due to the bent structure of these two bases $\chi_B(H_3BX)$ is greater than $\chi_B(H_4BX^+)$.

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