Theoret. chim. Acta (Berl.) 28, 103—110 (1973)

Commentationes

Ab initio Calculations of Small Hydrides Including Electron Correlation

VIII. Equilibrium Geometry and Harmonic Force Constants of BH_3

M. Gelus

Laboratoire de chimie générale, Université scientifique et médicale de Grenoble

W. Kutzelnigg

Institut für Physikalische Chemie und Elektrochemie der Universität Karlsruhe

Received August 16, 1972

The harmonic force constants and vibration frequencies of BH_3 (which is not directly accessible to experimental studies) are calculated both in SCF approximation and including correlation in the IEPA–PNO scheme, using a Gaussian basis set. The results are compared with those of related molecules like BH and BH_2.

Die harmonischen Kraftkonstanten und Schwingungsfrequenzen des BH_3 (das experimentellen Untersuchungen nicht unmittelbar zugänglich ist) werden sowohl in der SCF-Näherung als auch unter Einschluß der Elektronenkorrelation in der IEPA-PNO-Näherung mit einer Basis von Gaußfunktionen berechnet. Die Ergebnisse werden mit denen verwandter Moleküle wie BH und BH_2 verglichen.

Les constantes de force et frequences de vibration harmoniques de la molecule BH_3 (qui est inaccessible a des etudes experimentales directes) sont calculées dans le cadre des methodes SCF et IEPA–PNO utilisant une base d'orbitales Gaussiennes. On compare les resultats avec ceux obtenus recemment pour des molecules comme BH et BH_2.

1. Introduction

BH_3 is, like BeH_2 [1], one of the simplest "normal" molecules, yet information from experiment about the properties of BH_3 (like of BeH_2) are virtually nonexistent. The reason for this lack of information is probably that whenever BH_3 is formed in a chemical reaction it readily dimerizes to B_2H_6 (like BeH_2 polymerizes). The experimental values of the dimerization energy of BH_3 is rather uncertain [2], but theoretical calculations [3] suggest that it is close 35 kcal/mol.

In a previous note [3] (see also [4]) we have already reported our results concerning the binding energy of BH_3 with respect to B + 3H. To get more knowledge of this molecule we decided to compute its harmonic force constants and vibration frequencies and to study to which extent they are influenced by electron correlation [5].

In the literature one finds two references to the vibration frequencies of BH_3. Shepp and Bauer [6] proposed an estimate of the normal frequencies of BH_3 based on an assumed geometry of BH_3, on data of compounds such as BH_3CO, on Badger's rule [7] and on an extrapolation in the series BBr_3, BCl_3, BF_3. The vibration frequencies given in the same paper are partially inconsistent with the force constants.

Morrey *et al.* [8] have studied the thermolysis of B_2H_6 by means of IR spectroscopy and found some absorption frequencies that they tentatively assigned to BH_3. The values of the two references [6, 8] do not agree at all.

2. Method

The computational method used is the same as in our previous studies [3–5], the IEPA-PNO method (IEPA = independent electron pair approximation, PNO = pair natural orbitals), the first step of which is always a conventional molecular Hartree-Fock-calculation. Then the canonical Hartree-Fock orbitals are transformed to localized ones and the pair correlation energies both for two electrons in the same orbital (intrapair correlation energy ε_{ii}) and for two electrons in different localized orbitals (interpair correlation energy ε_{ij}) are calculated independently. The sum of these pair correlation energies is regarded as an approximation to the total correlation energy. In this study we have not calculated the contributions to the correlation energy that involve the K-shell, since previous calculations (e.g. [5]) indicate that they remain invariant upon changes in geometry.

For BH_3 in D_{3h} or C_{3v} geometry there is only one type of localized valence-shell orbital, corresponding to one BH bond, and hence only one intrapair and one interpair correlation energy has to be calculated. In the case of an in-plane deformation the BH-bonds are no longer equivalent and several different intrapair and interpair correlation contribution have to be considered. Since the effect of correlation is small anyway we renounced on this extra labour and computed the in-plane deformation in Hartree-Fock approximation only.

The basis set of gaussian lobes is essentially the same as used in our study of B_2H_6 [3]. It consists of a 9s, 2p-Huzinaga basis with the contractions (5, 1, 1, 1, 1) and (2, 1) for boron and a 5s-Hoyland basis with the contraction (4, 1) for hydrogen. In each of three directions (x, y, z) on each hydrogen atom a p-group with $\eta = 0.65$ was added.

This basis is rather small, but supposed to be sufficient for the present purpose.

3. Potential Field and Force Constants

We first calculated the energy of BH_3 in D_{3h} geometry and varied the BH bond length (Table 1). The minimum was found for $R_0 = 2.248\, a_0 = 1.190$ Å in Hartree-Fock-approximation and for $R_0 = 2.253\, a_0 = 1.192$ Å if one includes

Table 1. Energy of BH_3 in D_{3h} geometry as function of the BH bond distance

R(in a_0)	2.05	2.15	2.25	2.35	2.45
$-E_{HF}$	26.36353	26.37779	26.38206	26.37813	26.36792
$-\varepsilon_{ii}$	0.02806	0.02802	0.02828	0.02836	0.02860
$-\varepsilon_{ij}$	0.00804	0.00794	0.00787	0.00784	0.00783
$-E$	26.47183	26.48567	26.49051	26.4867	26.47721

Table 2. Energy of BH_3 for $R = 2.25\ a_0$ as a function of the in plane – deformation of one BH bond

α	0^0	5^0	10^0
$-E_{HF}$	26.38206	26.38131	26.37908

Table 3. Energy of BH_3 for $R = 2.25\ a_0$ as a function of a simultaneous out-of-plane deformation of the three BH bonds (keeping C_{3v} symmetry)

γ	0°	5°	10°	15°
$-E_{HF}$	26.38206	26.37911	26.37016	26.35522
$-\varepsilon_{ii}$	0.02828	0.2826	0.02843	0.02872
$-\varepsilon_{ij}$	0.00787	0.00789	0.00799	0.00817
$-E$	26.49051	26.48756	26.47942	26.46588

correlation. Keeping R fixed at $2.25\ a_0$ we have then studied both an in-plane deformation (Table 2) and an out-of plane deformation (Table 3). In either case the minimum of the energy was found for the planar molecule with trigonal symmetry, i.e. BH_3 has in fact the symmetry group D_{3h}.

The potential hypersurface V of a planar AX_3 – molecule of this type can, in the neighbourhood of its equilibrium geometry, up to terms of 2nd order in the internal displacement coordinates be expressed as

$$\begin{aligned}
2V = {} & 2E_0 + f_r(r_1^2 + r_2^2 + r_3^2) + 2f_{rr'}(r_1 r_2 + r_2 r_3 + r_1 r_3) \\
& + f_\alpha R_0^2(\alpha_{12}^2 + \alpha_{23}^2 + \alpha_{13}^2) + 2f_{r\alpha} \cdot R_0(r_1 \cdot \alpha_{12} \\
& + r_2\alpha_{12} + r_2\alpha_{23} + r_3\alpha_{23} + r_3\alpha_{13} + r_1\alpha_{13}) \\
& + 2f_{r\alpha'} \cdot R_0(r_1\alpha_{23} + r_2\alpha_{13} + r_3\alpha_{12}) \\
& + 2f_{\alpha\alpha'} \cdot R_0^2(\alpha_{12}\alpha_{13} + \alpha_{12}\alpha_{23} + \alpha_{13}\alpha_{23}) \\
& + f_\gamma \cdot R_0^2(\gamma_1^2 + \gamma_2^2 + \gamma_3^2) + 2f_{\gamma\gamma'} R_0^2(\gamma_1\gamma_2 + \gamma_2\gamma_3 + \gamma_1\gamma_3) .
\end{aligned}$$

Here R_0 is the equilibrium BH-bond distance, r_i means the change in the length of the bond between B and the i-th H atom, the α_{ij} refer to in-plane deformation and γ_i to the out-of-plane deformation of the i-th BH-bond with respect to the original molecular plane. Due to reasons of symmetry (D_{3h}) and redudancy $\left(\sum_{i<j} \alpha_{ij} = 0\right)$ the different coefficients are not independent, but the following relations hold

$$f_\alpha = -2f_{\alpha\alpha'}$$
$$f_{r\alpha'} = -2f_{r\alpha}$$
$$f_\gamma = f_{\gamma\gamma'} .$$

An alternative expression of $2V$ is in terms of the symmetry-coordinates S_i

$$2V = 2E_0 + F_1 S_1^2 + F_2 S_2^2 + F_3 (S_3^2 + S_3'^2) + 2F_{34}(S_3 S_4 + S_3' S_4') + F_4 (S_4^2 + S_4'^2)$$

with

$$S_1(A') = \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3),$$

$$S_2(A'') = \frac{1}{\sqrt{3}} R_0(\gamma_1 + \gamma_2 + \gamma_3),$$

$$S_3(E') = \frac{1}{\sqrt{2}}(r_1 - r_2),$$

$$S_3'(E') = \frac{1}{\sqrt{6}}(r_1 + r_2 - 2r_3),$$

$$S_4(E') = \frac{1}{\sqrt{2}} R_0(\alpha_{13} - \alpha_{23}),$$

$$S_4'(E') = \frac{1}{\sqrt{6}} R_0(2\alpha_{12} - \alpha_{13} - \alpha_{23}).$$

The force constants F_i for symmetry coordinates are related to the f_i for internal coordinates through

$$F_1 = f_r + 2f_{rr'},$$

$$F_2 = 3f_\gamma,$$

$$F_3 = f_r - f_{rr'},$$

$$F_{34} = 3f_{r\alpha},$$

$$F_4 = \tfrac{3}{2} f_\alpha.$$

The F_i constitute the elements of the Wilson F-matrix [9], in terms of symmetry coordinates, the corresponding G-matrix [9] elements are

$$G_1 = \frac{1}{m_H},$$

$$G_2 = \frac{1}{R_0^2}\left(\frac{1}{m_H} + \frac{3}{m_B}\right),$$

$$G_3 = \frac{1}{m_H} + \frac{3}{2m_B},$$

$$G_{34} = -\frac{3\sqrt{3}}{2R_0 \cdot m_B},$$

$$G_4 = \frac{3}{R_0^2}\left(\frac{1}{m_H} + \frac{3}{2m_B}\right).$$

S_1 and S_2 are automatically normal coordinates of A' and A'' symmetry respectively. The corresponding force constants F_1 and F_2 are obtained directly from the dependence of $2V$ on either of their symmetry coordinates (Tables 1 and 3).

The vibration frequencies ν_1 and ν_2 are given as

$$2\pi\nu_1^2 = \frac{F_1}{m_\mathrm{H}},$$

$$2\pi\nu_2^2 = F_2\left(\frac{1}{m_\mathrm{H}} + \frac{3}{m_\mathrm{B}}\right).$$

The vibration frequencies ν_3 and ν_4 of E' symmetry are obtained from the eigenvalues $\lambda_i = 2\pi\nu_i^2$ of the product matrix

$$\begin{pmatrix} F_3 & F_{34} \\ F_{34} & F_4 \end{pmatrix} \cdot \begin{pmatrix} G_3 & G_{34} \\ G_{34} & G_4 \end{pmatrix}.$$

In order to calculate ν_3 and ν_4 one ought to compute first F_3, F_{34} and F_4 or alternatively f_r, f_{rr}, $f_{r\alpha}$ and f_α. Previous calculations on BeH_2 [1] and BH_2 [10] indicated that the off-diagonal stretching force constants of molecules of this kind are very small in absolute value, namely

In SCF-approximation	With correlation	
$f_{rr'} = -0.04$ mdyn/Å	$= +0.12$ mdyn/Å	for BeH_2
$= +0.12$ mdyn/Å	-0.14 mdyn/Å	for BH_2 ($X\,^2A_1$)
$= -0.03$ mdyn/Å	-0.11 mdyn/Å	for BH_2 ($A\,^2B_1$)

compared to $f_r \approx 4$ mdyn/Å. We do not think that the calculated values of $f_{rr'}$ (note the occurence of a change in sign with inclusion of correlation) are really significient (i.e. beyond the error limits of the calculations) so that we decided to put $f_{rr'} = 0$ and consequently $F_3 = f_r = F_1$. Previous calculations [10] also suggest that $f_{r\alpha}$ should be very small

$f_{r\alpha} = 0.041$ mdyn/Å in SCF-approximation for $BH_2(X\,^2A_1)$
$= 0.054$ mdyn/Å with correlation for $BH_2(X\,^2A_1)$.

So we decided to put $f_{r\alpha} = 0$ as well. We calculated f_α from the dependence of the energy of BH_3 upon in-plane deformation of one BH-bond. The assumption $f_{rr'} = f_{r\alpha} = 0$, which seems to be well justified for BH_3 is, of course, known as the simple valence force field approximation. In order to be conform with the notation [12] of the valence force field model we introduce the force constants

$$\tilde{f}_\alpha = \tfrac{3}{2} f_\alpha \quad \text{and} \quad \tilde{f}_\gamma = 3 f_\gamma$$

rather than f_α and f_γ. For ν_3 and ν_4 one then obtains the wellknown [17] expressions

$$2\pi(\nu_3^2 + \nu_4^2) = \left(\frac{1}{m_\mathrm{H}} + \frac{3}{2m_\mathrm{B}}\right)(f_r + 3\tilde{f}_\alpha),$$

$$4\pi^2\nu_3^2\nu_4^2 = 3\left(\frac{1}{m_\mathrm{H}^2} + \frac{3}{m_\mathrm{H} m_\mathrm{B}}\right) f_r \cdot \tilde{f}_\alpha.$$

In our calculation the approximation that consists in neglecting $f_{rr'}$ and $f_{r\alpha}$ has an effect only on the vibration frequencies of the E' species, the A' and A'' frequencies would not be altered if we introduced $f_{rr'}$ and $f_{r\alpha}$ explicitly.

For comparison with experiment, anharmonicity effects have, of course, to be dealt with as well.

4. Discussions of the Results

The calculated equilibrium distances and harmonic force constants of BH_3 (both in SCF approximation and with correlation) are tabulated and compared with previous estimates [6, 8] in Table 4.

The effect of correlation is very small. As it has been observed in other cases [10, 11] correlation increases the bond length slightly and diminishes somewhat the stretching force constant.

A direct comparison of our computed values with their experimental counterparts is not possible (even if they were precisely known) since our calculations refer to harmonic force constants and vibration frequencies, whereas the values deduced from observed spectra contain implicitly anharmonicity effects. Generally "anharmonic" force constants of XH-bonds are about 10% smaller than the corresponding harmonic ones, so our "harmonic" value of 4.1 mdyn/Å would be consistent with an "anharmonic" force constant of about 3.7 mdyn/Å which is in sufficient agreement with the value of 3.5 mdyn/Å generally assumed [12] for the stretching force constant of a terminal bond in B_2H_6.

If one has to choose between the two previous estimates [6, 8] our results would rather support the values of Morrey *et al.* [8].

Rather interesting is the comparison (Table 5) of BH_3 with BH [5], BH_2^+ [13] and BH_2 [11] for which quite reliable calculations are available (even if one has to bear in mind that the basis sets for the different molecules were of different quality). The decrease in bond length on going from BH to BH_2^+ can to a first approximation be understood in terms of hybridisation. The hybrid-AO of boron in BH is nearly a pure *p*-AO, in both BH_2 ($X\ ^2A_1$) and in BH_3 it is roughly

Table 4. Harmonic force constants and vibration frequencies for $^{11}BH_3$

	R_0	f_r	$\tilde{f}_\alpha$	$\tilde{f}_\gamma$	$\nu_1(A')$	$\nu_2(A'')$	$\nu_3(E')$	$\nu_4(E')$
	in a_0	in mdyn/Å			in cm^{-1}			
Hartree Fock	2.248	4.26	0.30	0.80	2680	1310	2860	1300
With correlation	2.253	4.10	–	0.75	2620	1270	2810	1300
Ref. [6][a]	2.19	3.38	0.13	0.30	2384	801	(2976)	(1735)
Ref. [8]	–	3.41	0.25	1.13	2400	1560	2560	1190
		±0.78	±0.04	±0.04	± 300	± 50	± 100	± 10

[a] The frequencies in parentheses are inconsistent with the force constants given by the same authors.

Table 5. Comparison of the harmonic force constants in different boron hydrides (the first entry is always without, the second with correlation)

	R_0	f_r	$\tilde{f}_\alpha$	$\tilde{f}_\gamma$
	(in a_0)	in mdyn/Å		
BH	2.311; 2.316	3.33; 3.19	–	
$BH_2(X^2A_1)$	2.234; 2.276	3.96; 3.70	0.32; 0.27	–
BH_3	2.248; 2.253	4.26; 4.10	0.30;	0.80; 0.75
$BH_2\,(A^2B_1)$	2.196; 2.223	4.65; 4.57	0.28; 0.25	
BH_2^+	; 2.221	; 4.17	; 0.27	

sp^2 and in both BH_2 ($A\,^2B_1$) and BH_2^+ it is sp. In the order $p \rightarrow sp^3 \rightarrow sp^2 \rightarrow sp$ the bond strength is known to increase which implies a decrease in bond length and an increase in the force constant. In fact the stretching force constants behave in the expected way. The bending force constants are almost the same for BH_3 and the lowest state of BH_2 ($X\,^2A_1$, with an equilibrium angle of 129°). The force constant (~ 0.8 mdyn/Å) for an out-of plane deformation in BH_3 is rather large.

It is hard to give error estimates for the calculated values. There are too many sources for possible errors. The neglect of $f_{rr'}$ and $f_{r\alpha}$ is probably the least harmful. More serious is the limatation of the basis set. There is some evidence that with small basis sets, configurations of high symmetry are represented more poorly than those of lower symmetry. So extension of the basis may lower the energy more strongly for the equilibrium than for distorted geometry and hence increase the force constants for angular deformation. Another source of error is the fact that IEPA is only an approximation and that the deviations from additivity of the pair correlation energies may depend on geometry. This point has recently been stressed by Meyer [14]. A really refined calculation of the vibrational spectrum should also consider the cubic and quartic terms in the potential and their influence on the vibration frequencies. We do not think that (except for diatomic molecules) the present state of numerical quantum chemistry is such as to encourage one to do the extra labour.

5. The Zero-Point Energy

The original motive for this study was the need for a reliable value of the zero point of BH_3 to calculate the dimerization energy to B_2H_6 [3]. From the harmonic vibration frequencies we obtain 17.3 kcal/mole which is very close to the value of 18 kcal/mole estimated by us [3] on more heuristic grounds.

Acknowledgement. The work reported here has been sponsored in part by Deutsche Forschungsgemeinschaft and by Fonds der Chemie.

Most of the computations were performed at the IBM 360/75 of C.I.R.C.E. (Orsay) with grants given by CNRS to the laboratoire de chimie generale in Grenoble. Some computation was carried out at the UNIVAC 1108 of the University of Karlsruhe.

The authors are grateful to R. Ahlrichs and V. Staemmler for contributions and comments.

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Dr. W. Kutzelnigg
Institut für Physikalische Chemie
und Elektrochemie der Universität Karlsruhe
D-7500 Karlsruhe
Kaiserstr. 12
Federal Republic of Germany