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Hybrid Orbital Force Field Vibrational Analyses of Borane Adducts[1]

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Infrared spectra, in the range 4000–250 cm^{-1}, and Raman spectra have been recorded for the following species: BH_3CN^-, BD_3CN^-, BH_3NC^-, BD_3NC^-, BH_3F^-, BD_3F^-. The hybrid orbital force field model has been examined and found to be applicable to these ions and to other borane adducts (BH_4^-, BH_3CO, BH_3PF_3, BH_3PH_3) which have been studied in the past by other force field approximations. There appears to be a rough correlation among donor strength, boron hybridization, and the BH_3 stretching force constant for the A_1 symmetry coordinate. The BX force constants decrease in the following order: $F^- > CN^- > NC^- > H^- > CO > PF_3 > PH_3$. Various comparisons are made among the force constants for the various adducts.

Introduction

It has been shown for the CH_3X series[2–6] that the type of force field approximation used can have a marked influence on the force constants obtained from analysis of vibrational spectra and that, in order to make comparisons between molecules, it is imperative that the results of the same model be used.[5,6] In view of those results for CH_3X, since there have been no reports of force field calculations for the unusual anionic boranes and since there has been no systematic investigation of borane adducts using a uniform force field approximation, we have examined the applicability of Mills' hybrid orbital force field (HOFF)[7] to a series of borane adducts of widely varying donor groups (F^-, CN^-, NC^-, H^-, CO, PF_3, PH_3).

Calculational Methods

The force field analyses were performed on the Kansas State University IBM 360/50 computer system using the programs of Schachtschneider and Snyder.[8,9] In this work the elements W_i of the weight matrix $\mathbf{W}$ were taken as $1/\lambda_i$. Generous allowance was made for errors in the frequency assignments. For BH_3NC^-, where textbook quality spectra cannot be obtained at present (*vide infra*), the force constant analyses were performed with an error of 10% of the assigned energy of each mode. As a consequence of these large assumed errors for BH_3NC^- the frequencies used in the analyses were rounded to the nearest 5 cm^{-1}. For BH_3CN^- and the other adducts high-quality spectra were available and errors of ± 5 cm^{-1} were assigned to each band.

Because of the importance of the matrix $\mathbf{J}^t\mathbf{W}\mathbf{J}$ in the least-squares equations ($\mathbf{J}$ is the Jacobian matrix), $\mathbf{J}^t\mathbf{W}\mathbf{J}\ \delta\mathbf{F} = \mathbf{J}^t\mathbf{W}\ \delta\mathbf{\Lambda}$, the determinant of that matrix was tested after each iteration for singularity by comparing the product of the diagonal elements, $\Pi_u(\mathbf{J}^t\cdot\mathbf{W}\cdot\mathbf{J})_{uu}$, to the determinant, $|\mathbf{J}^t\cdot\mathbf{W}\cdot\mathbf{J}|$. Since $|\mathbf{J}^t\cdot\mathbf{W}\cdot\mathbf{J}|/\Pi_u(\mathbf{J}^t\cdot\mathbf{W}\cdot\mathbf{J})_{uu} < 10$ signals ill-conditioned least-squares equations,[2b] a calculation was terminated and disregarded in the event of this inequality.

The calculations discussed here were formulated in terms of symmetry force constants and symmetry coordinates which are defined in Table I.

In the present calculations a trial force field was initially refined after which the program entered a multiple regression analysis to examine the missing off-diagonal force constants for significance. Those judged to be significant were refined and those deemed insignificant were constrained to zero. A force constant was retained only if its associated error was less than or equal to its magnitude. Usually only one or two additional constants were added by the regression subroutine. It is important to remember that the addition or removal of force constants by the regression analysis is based on a statistical survey of the constants and their errors. In nearly all cases, however, the constants found to be statistically significant corresponded to those which would be expected to be significant on physical grounds. After the regression analysis was completed, the program reentered the perturbation cycle and refined the frequency fit in view of the off-diagonal force constant additions or deletions by the regression subroutine.

In the absence of structural data for BH_3CN^-, BH_3NC^-, and BH_3F^-, tetrahedral geometry has been assumed for the boron atom in those ions. Bond distances were estimated by a survey of related molecules. For BH_4^-,[10] BH_3CO,[11] BH_3PF_3,[12] and BH_3PH_3,[13] the published structural data have been used. The bond angles and bond distances for all species are summarized in Table II.

The molecular orbital calculations were performed on the IBM 360/50 computer system at Kansas State University using the CNINDO program.[14,15] Energies for BH_3CO and BH_3CN^- for 35 C_{3v} structures each were obtained by varying four parameters (the B–H and B–C bond distances and the HBH and HBC bond angles). The bond angles were varied over a 6° range about the equilibrium angle in increments of 1°. The bond distances were varied over 0.06-Å ranges about the equilibrium distances in increments of 0.014 Å. The force constants were calculated from these data by least-squares expansion of the energies as a parabolic function of the symmetry coordinates. A general para-

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[1] Taken from the Ph.D. thesis of J. R. B., Kansas State University, 1970.

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[7] I. M. Mills, *Spectrochim. Acta*, **19**, 1585 (1963).

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[9] J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules. V and VI," Reports 231-64 and 57-65, Shell Development Co., Emeryville, Calif., 1964 and 1965.

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[14] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); J. A. Pople, and G. A. Segal, *ibid.*, **44**, 3289 (1966).

[15] Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind., Program No. 141.

TABLE I[a,b]

SYMMETRY COORDINATE DEFINITIONS FOR BH_3X MOLECULES

A_1 class	E class
$X = CN^-, CO, NC^-$	
$S_1 = \frac{1}{\sqrt{3}}(\Delta r_1 + \Delta r_2 + \Delta r_3)$	$S_5 = \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r_3)$
$S_2 = \frac{1}{\sqrt{c}}[(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - b(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]$	$S_6 = \frac{1}{\sqrt{2}}(\Delta\alpha_2 - \Delta\alpha_3)$
$S_3 = \Delta R$	$S_7 = \frac{1}{\sqrt{2}}(\Delta\beta_2 - \Delta\beta_3)$
$S_4 = \Delta D$	$S_8 = \frac{1}{\sqrt{2}}(\Delta\gamma_1 - \Delta\gamma_2)$
$X = H^-, F^-$	
$S_1 = \frac{1}{\sqrt{3}}(\Delta r_1 + \Delta r_2 + \Delta r_3)$	$S_4 = \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r_3)$
$S_2 = \frac{1}{\sqrt{c}}[(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - b(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]$	$S_5 = \frac{1}{\sqrt{2}}(\Delta\alpha_2 - \Delta\alpha_3)$
$S_3 = \Delta R$	$S_6 = \frac{1}{\sqrt{2}}(\Delta\beta_2 - \Delta\beta_3)$
$X = PH_3, PF_3$	
$S_1 = \frac{1}{\sqrt{3}}(\Delta r_1 + \Delta r_2 + \Delta r_3)$	$S_6 = \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r_3)$
$S_2 = \frac{1}{\sqrt{c}}[(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - b(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]$	$S_7 = \frac{1}{\sqrt{2}}(\Delta\alpha_2 - \Delta\alpha_3)$
$S_3 = \Delta R$	$S_8 = \frac{1}{\sqrt{2}}(\Delta\beta_2 - \Delta\beta_3)$
$S_4 = \frac{1}{\sqrt{3}}(\Delta d_1 + \Delta d_2 + \Delta d_3)$	$S_9 = \frac{1}{\sqrt{2}}(\Delta d_2 - \Delta d_3)$
$S_5 = \frac{1}{\sqrt{c}}[(\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3) - b(\Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3)]$	$S_{10} = \frac{1}{\sqrt{2}}(\Delta\gamma_2 - \Delta\gamma_3)$
	$S_{11} = \frac{1}{\sqrt{2}}(\Delta\delta_2 - \Delta\delta_3)$

[a] Redundant coordinate omitted from A_1 class and only one component of E class listed. $c = 3(b^2 + 1)$; $b = -\sqrt{3}\cos\beta/[\cos(\alpha/2)]$. [b] See Table II for the definitions of r, R, D, α, β, and γ.

TABLE II

STRUCTURAL PARAMETERS FOR BH_3X MOLECULES

BH_3CN^-, BH_3NC^-, BH_3F^-, BH_4^-

$r_{BH} = 1.25$ Å $= r$
$r_{BC} = 1.54$ Å $= R$
$r_{BN} = 1.60$ Å $= R$
$r_{BF} = 1.40$ Å $= R$
$r_{CN} = 1.16$ Å $= D$
HBH $= 109.5° = \alpha = \beta$
BCN $=$ BNC $= 180° = \gamma$

BH_3PH_3	BH_3CO	BH_3PF_3
$r_{BH} = 1.20$ Å $= r$	$r_{BH} = 1.194$ Å $= r$	$r_{BH} = 1.2066$ Å $= r$
$r_{PH} = 1.42$ Å $= d$	$r_{BC} = 1.54$ Å $= R$	$r_{PF} = 1.5378$ Å $= d$
$r_{BP} = 1.93$ Å $= R$	$r_{CO} = 1.31$ Å $= D$	$r_{BP} = 1.8359$ Å $= R$
HBH $= 115° = \alpha$	HBH $= 113.87° = \alpha$	HBH $= 115.08° = \alpha$
HPH $= 92° = \gamma$	HBC $= 104.60° = \beta$	FPF $= 99.83° = \gamma$
HBP $= 103.13° = \beta$	BCO $= 180° = \gamma$	HBP $= 103.13° = \beta$
HPB $= 123.8° = \delta$		FPB $= 117.93° = \delta$

bolic equation including linear terms was used

$$V = V_0 + F_1S_1 + F_2S_2 + F_3S_3 + \frac{1}{2}F_{12}S_1S_2 + \frac{1}{2}F_{23}S_2S_3 + \frac{1}{2}F_{11}S_1^2 + \frac{1}{2}F_{22}S_2^2 + \frac{1}{2}F_{33}S_3^2$$

The F's were determined by least-squares refinement.

Experimental Section

The infrared spectra of BH_3CN^-, BH_3NC^-, BH_3F^-, and the d_3 adducts were recorded in the region 4000–250 cm^{-1} on Perkin-Elmer No. 421 and 457 grating spectrophotometers using standard techniques (KBr pellets, Nujol mulls, THF, and nitromethane solutions). The vibrational frequencies used in the normal-coordinate analyses of BH_3CN^-, BH_3NC^-, and BH_3F^- are those obtained with the pellet technique. Corrections for spectrophotometer wavelength errors were made for all bands used in the analyses. The Raman data were obtained on a Spex Industries Model 1400 double-grating spectrometer equipped with a He–Ne source using polycrystalline samples and 2 M aqueous solutions. Polarization data were taken from the aqueous solutions. The normal and deuterated samples of BH_3CN^- and BH_3NC^- were prepared and purified by published methods.[16] The samples of BH_3F^- and BD_3F^- were prepared by Muetterties' method.[17]

Results

Band Assignments.—The spectra for the BH_3 adducts of CN^-, NC^-, and F^- have been collected and interpreted in this work. The observed infrared and Raman frequencies for several BH_3CN^- and BD_3CN^- salts have been reported by us in earlier papers.[16] Some of those tentative assignments were found to require revision in the course of this work. All minor differences between these numbers and previous numbers are the result of more accurate frequency measurements and corrections for spectrometer wavelength corrections. Table III summarizes the data used for the vibrational analyses of BH_3CN^- and BH_3NC^-. The band assignments for BH_3CN^- and BH_3NC^- have been made on the basis of Raman polarization data and by use of the Teller–Redlich product rule (Table IV).

The region 2500–2000 cm^{-1} contains the BH stretching vibrations and the CN stretch for both BH_3CN^- and BH_3NC^-. The BH stretching vibrations are easily identified; however, the true maxima of the E and A_1 fundamentals are somewhat uncertain due to the proximity of certain BH bending overtones and the possibility of Fermi resonance between the fundamentals and those overtones. It appears that there is definitely a Fermi resonance shifting of ν_1 and $2\nu_3$ in BH_3CN^-, as $2\nu_3$ is observed about 25 cm^{-1} below its calculated position (harmonic approximation) and has an inordinately large intensity for an overtone. Therefore, a correction of -20 cm^{-1} has been made to ν_1 for use in the force constant analysis. The interaction between ν_5 and $2\nu_6$ in BH_3CN^- is less pronounced and

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(17) V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **83**, 2471 (1961).

TABLE III

FREQUENCIES (CM^{-1}) FOR ISOTOPIC BH_3CN^- AND BH_3NC^- [a]

		$^{11}BH_3CN^-$	$^{11}BH_3NC^-$	$^{10}BH_3CN^-$		$^{11}BD_3CN^-$	$^{11}BD_3NC^-$	$^{10}BD_3CN^-$
ν_1	$\nu^{a_1}_{BH}$	2285[b]	2290	2290	$\nu^{a_1}_{CN}$	2180	2075	. . .
ν_2	$\nu^{a_1}_{CN}$	2179	2070	. . .	$\nu^{a_1}_{BH}$	1661	1640	1671
ν_3	$\delta^{a_1}_{BH}$	1135	1105	1145	$\delta^{a_1}_{BH}$	906	940	926
ν_4	$\nu^{a_1}_{BC}$; $\nu^{a_1}_{BN}$	890	760	(910)[c]	$\nu^{a_1}_{BC}$; $\nu^{a_1}_{BN}$	800	665	. . .
ν_5	ν^{e}_{BH}	2350	2350	2365	ν^{e}_{BH}	1761	1745	1775
ν_6	δ^{e}_{BH}	1197	1175	(1205)[c]	δ^{e}_{BH}	870	855	. . .
ν_7	ρ^{e}_{BH}	872	645	(880)[c]	ρ^{e}_{BH}	675	525	(690)[c]
ν_8	δ^{e}_{BCN}; δ^{e}_{BNC}	335	330	355	δ^{e}_{BCN}; δ^{e}_{BNC}	330	300	. . .

[a] Values for BH_3NC^- and BD_3NC^- are uncertain to within 5 cm^{-1} because of the necessity of recording spectra of samples which contained BH_3CN^-. See text. [b] Observed at 2305 cm^{-1} and corrected (20 cm^{-1}) for Fermi resonance. [c] Assignment uncertain, see text.

TABLE IV

PRODUCT RULE RATIOS (D_3:H_3) FOR BH_3X

A Class		Isotope	E Class	
Theoret	Exptl	pair	Theoret	Exptl
0.518	0.526	BH_3CN^-	0.399	0.404
0.518	0.534	BH_3NC^-	0.398	0.400
0.522	0.536	BH_3F^-	0.420	0.434

may be completely negligible. $2\nu_6$ is observed exactly at its calculated position ($2\nu_6 > \nu_5$) and this suggests only a small amount of Fermi resonance shifting of ν_5 and $2\nu_6$. These same comments are applicable to the isocyanide adduct although the extent of resonance interaction for that ion is less certain. The difficulty is that only samples contaminated with BH_3CN^- can be studied at present and the overlap of many of the bands makes precise frequency assignments difficult.

The CN stretching frequencies, on the other hand, are very accurately known because they appear as the sharp, isolated bands typical for this mode. Also, the CN stretch bands do not measurably shift upon deuteration. Similar results have been obtained with CH_3CN.[1] The 110-cm^{-1} difference in ν_{CN} for BH_3CN^- (2179 cm^{-1}) and BH_3NC^- (2070 cm^{-1}) is typical for cyanides and isocyanides.

The E and A_1 BD stretching vibrations for BD_3CN^- and BD_3NC^- are located in the 2000–1600-cm^{-1} region. The E stretch is assigned to the highest energy depolarized band at 1761 cm^{-1} for BD_3CN^- and 1745 cm^{-1} for BD_3NC^-. The A_1 stretch mode in BD_3CN^- is somewhat more difficult to assign since there are two remaining polarized bands, one at 1661 cm^{-1} and one at 1700 cm^{-1}. A comparison with similar molecules and the product rules indicate that the 1661 cm^{-1} band is the correct assignment for the A_1 fundamental. Furthermore, the band at 1700 cm^{-1} can be readily assigned to the combination band $\nu_3 + \nu_4$ (1710 cm^{-1}), whereas no combination band or overtone closely corresponds to the 1661-cm^{-1} band. The ν_2 vibration for BD_3NC^- is assigned similarly at 1640 cm^{-1}.

All of the remaining fundamentals except for the linear bending modes are found between 1600 and 500 cm^{-1}. The BH bending vibrations are easily assigned to the two prominent bands at 1197 and 1135 cm^{-1} in BH_3CN^- and 1175 and 1105 cm^{-1} for BH_3NC^-. The polarization data indicate that the E fundamental is at higher energy than the A_1. The assignment of the BH rock and the BC stretch in BH_3CN^- presents a most intractable problem since these two fundamentals are nearly degenerate at 890 and 872 cm^{-1}. The Raman data do not resolve the assignment ambiguity even though the vibrations are of different symmetry (the weak intensity of these vibrations has prevented accurate polarization data from being obtained). Reversing the assignments of these two frequencies has little effect on the force field calculations. This problem does not exist for the BH rock and BN stretch of BH_3NC^-. These vibrations are conveniently assigned, with the help of the product rule, to the bands at 645 and 760 cm^{-1}, respectively.

The assignment of the frequencies of the deuterated compounds which fall in this (1600–500 cm^{-1}) region of the spectrum is now described. Again the most prominent features are the two bands which are assigned to the BD bending vibrations. Interestingly, upon deuteration the E bending mode becomes the lower energy vibration of the two bending modes. This reversal is well documented for a number of similar molecules[18] and the Raman polarization data confirm this assignment. Therefore, ν_3 and ν_6 in BD_3CN^- are assigned to the bands at 906 and 870 cm^{-1}, respectively. In the isocyanide these vibrations are assigned at 940 and 855 cm^{-1}. Finally, the BC stretch, the BN stretch, and the BD rock are assigned to the remaining bands. Note that upon deuteration of BH_3CN, the initially nearly degenerate BH rock and BC stretch split apart. The product rules are used to make the assignments ν_{BC} at 800 cm^{-1} and ρ_{BH} at 675 cm^{-1}. Again, neither of these vibrations was intense enough in the Raman spectrum to allow accurate polarization measurements.

TABLE V

INFRARED FUNDAMENTALS FOR KBH_3F

ν(KBH_3F), cm^{-1}	Assignment	ν(KBD_3F), cm^{-1}	ν(KBH_3F), cm^{-1}	Assignment	ν(KBD_3F), cm^{-1}
2291 s	$\nu^{a_1}_{BH}$	1673 s	2380 m	ν^{e}_{BH}	1748 ms
1125 s	$\delta^{a_1}_{BH}$	824 m	1177 m	δ^{e}_{BH}	921 m
1081 s	$\nu^{a_1}_{BF}$	1059 s	802 w	ρ^{e}_{BH}	597 mw

TABLE VI

SUMMARY OF CALCULATED FREQUENCY ERRORS

	Av error in calcd freq, cm^{-1}		Max error, cm^{-1}	
Compd	A_1	E_1	A_1	E
BH_3CN^-	2.9	2.5	8.4	−6.1
BH_3NC^-	6.5	0.2	−10.5	−0.4
BH_3F^-	0.5	4.4	1.5	7.8
BH_3CO	1.0	1.9	2.0	3.8
BH_4^-	4.0	4.5	4.5	10.4
BH_3PF_3	2.4	3.3	9.5	8.2
BH_3PH_3	0	0	0	0

The remaining fundamental, the linear bend, is found at 360 cm^{-1} in BH_3CN^- and at 330 cm^{-1} in the isocyanide. These vibrational modes shift to 330 and 300 cm^{-1}, respectively, in the deuterated compounds.

It is important to note that the ^{10}B frequencies were obtained from the natural abundance of this isotope. For some bands the ^{10}B shifts were sufficiently large to

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(18) J. C. Evans and H. J. Berstein, *Can. J. Chem.*, **33**, 1746 (1955).

TABLE VII[a,b]

A$_1$ SYMMETRY FORCE CONSTANTS FOR BH_3X

	X							
	CO	CN^-	NC^-	H^-[c]	F^-	PF_3	PH_3	Description
F_{11}	3.31 (1)	3.00 (1)	2.99 (3)	2.79 (3)	3.00 (0)	3.34 (1)	3.36 (0)	BH_3 str
F_{12}	0.04 (1)	. . .	. . .	0.02 (2)	. . .	. . .	. . .	
F_{13}	. . .	. . .	. . .	0.16 (1)	. . .	. . .	. . .	
F_{22}	0.53 (0)	0.56 (0)	0.46 (1)	0.45 (0)	0.54 (0)	0.61 (1)	0.52 (0)	BH_3 def
F_{23}	−0.30 (0)	−0.60 (1)	−0.18 (2)	−0.04 (2)	−0.64 (0)	−0.29 (2)		
F_{33}	2.78 (1)	4.56 (2)	3.36 (9)	2.92 (1)	5.68 (1)	2.39 (5)	2.04 (0)	BX str
F_{34}	0.0[d]	0.5 (1)	0.5 (1)	. . .	. . .	. . .	. . .	
F_{44}	17.94 (1)	17.12 (4)	16.03 (13)	. . .	. . .	5.65 (8)	3.21 (0)	CO, CN, PX_3 str
F_{55}	. . .	. . .	. . .	. . .	. . .	1.42 (4)	0.40 (0)	PX_3 def

[a] Units: stretch, mdyn/Å; bend, mdyn Å; stretch–bend, mdyn. [b] Inapplicable constants and those constrained to zero are entered as three dots. [c] From C_{3v} formulation. [d] Best value fixed; see text.

ensure a reasonably accurate assignment; for other bands this was not true. One might ask whether these data should be included in the force field analysis. The calculations have been performed with and without the ^{10}B data and invariably lead to the same force constant values but inclusion of the ^{10}B data reduces their errors. Also, the isocyanide adduct always contained some of the normal cyano adduct and therefore the frequencies for the isocyanide have been given larger error limits to compensate for any uncertainties in the positions of the bands.

The assignment of the bands for BH_3F^- and BD_3F^- are given in Table V. Again, the BH_3 group frequencies are easily distinguished, with one exception. In BH_3F^-, the A$_1$ BF stretch band lies close to that of the A$_1$ and E BH bending vibrations. This presents problems similar to those encountered with the BH rock and the BC stretch in BH_3CN^-, except in this case polarization data would be of limited help because two of the three vibrations are of the same symmetry. However, the force field calculations, discussed below, support the assignment in Table V. All of the assignments in the deuterated analog are easily made by using the product rules and by analogy with the other molecules of the series. There is some uncertainty in the BF stretching frequency of BD_3F^-, however, since several prominent difference bands fall in this region of the spectrum. Most certainly, ν_{BF} is affected by resonance shifts but, due to the number of bands present, it is not possible accurately to measure the anticipated Fermi shift of the BF stretch.

The vibrational frequencies and assignments for BH_3CO,[11] BH_4^-,[10] BH_3PF_3,[12,19,20] and BH_3PH_3[13] were compiled from the literature.

Calculations.—Table VI contains the average error and maximum error in the calculated frequencies for the compounds studied. Symmetry force constants are tabulated, along with their dispersions, in Tables VII and VIII. Force constants which were constrained to zero are omitted. It is important to note that the average errors in calculated frequencies are small, even on an absolute basis. Similarly, the force constant dispersions are certainly acceptable.

The force constants which result from the MO calculations will be presented and discussed at the end of the Discussion. From these calculations, it was possible to obtain molecular parameters for the minimum energy structure. For BH_3CO, these parameters are r_{BH} = 1.20 Å, HBH = 112°, and r_{BC} = 1.44 Å, while for BH_3CN^-, they are r_{BH} = 1.22 Å, HBH = 108.5°, and r_{BC} = 1.52 Å. In the case of BH_3CO, these may be compared with the known parameters given in Table II.

TABLE VIII[a]

E SYMMETRY FORCE CONSTANTS FOR BH_3X

	X			
	CO	CN^-	NC^-	Description
F_{55}	3.12 (1)	2.92 (2)	2.96 (0)	BH_3 str
F_{56}	0.00 (1)	−0.04 (1)	−0.11 (0)	
F_{57}	0.00 (1)	0.04 (1)	0.11 (0)	
F_{66}	0.34 (0)	0.49 (0)	0.47 (0)	BH_3 def
F_{67}	0.02 (0)	−0.03 (1)	0.00 (0)	
F_{77}	0.31 (0)	0.60 (0)	0.31 (0)	BH_3 rock
F_{78}	−0.19 (0)	0.06 (1)	−0.01 (0)	
F_{88}	0.50 (0)	0.31 (0)	0.31 (0)	BXY def

	X		
	H^-	F^-	
F_{44}	2.65 (2)	3.05 (4)	BH_3 str
F_{45}	0.00 (1)	−0.26 (4)	
F_{46}	0.00 (1)	0.26 (4)	
F_{55}	0.45 (0)	0.48 (1)	BH_3 def
F_{56}	. . .	−0.23 (1)	
F_{66}	0.45 (0)	0.61 (1)	BH_3 rock

	X		
	PF_3	PH_3	
F_{66}	3.16 (1)	3.06 (0)	BH_3 str
F_{687}	−0.05 (5)	. . .	
F_6	0.05 (5)	. . .	
F_{77}	0.34 (0)	0.37 (0)	BH_3 def
F_{88}	0.41 (1)	0.54 (0)	BH_3 rock
F_{99}	5.70 (6)	3.28 (0)	PX_3 str
$F_{10,10}$	1.31 (3)	0.67 (0)	PX_3 def
$F_{11,11}$	0.31 (2)	0.27 (0)	PX_3 rock

[a] Units as in Table VII.

Discussion

Description of the Force Field Approximation.—In the HOFF[7] it is assumed that the sign of stretch–bend interaction constants can be predicted from orbital following considerations. Increase of a bond angle about the central atom leads to an increase in the s character of the central atom hybrids defining the angle due to orbital following in the bending coordinate. If, using BH_3X as an example, we imagine an increase in symmetry coordinate S_2 ($\Delta S_2 > 0$), this would lead to a shortening of the BH bonds, represented by a coordinate S_1 ($\Delta S_1 < 0$), and, since the interaction force constant can be represented by the equation[7] $F_{12} = -(\Delta S_1/\Delta S_2)F_{11}$, the stretch–bend interaction constant is expected to have a positive value. Mills[7] has presented these arguments in a more quantitative form and predicted, for a C_{3v} MH_3X group, that force constants involving stretch–bend interactions will be related as follows (the numbering system is that in Tables VII and VIII for X = CO)

$$\sqrt{2}F_{12} \approx F_{57} = -F_{56} > 0 \qquad (1)$$

$$F_{23} < 0 \qquad (2)$$

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(19) W. Sawodny and J. Goubeau, *Z. Anorg. Allg. Chem.*, **356**, 289 (1968).

(20) R. C. Taylor and T. C. Bissot, *J. Chem. Phys.*, **25**, 780 (1956).

Another interaction constant which orbital-following effects predict to be important[21] is that between in-phase rocking motions of the CH_3 groups of C_2H_6. Molecules in our study which may require inclusion of this constant are BH_3PF_3, BH_3CN^-, BH_3NC^-, and BH_3CO. In the last three cases, the interaction constant is predicted for the BH_3 rock–BXY bend coordinates.

In performing our calculations, we have made use of the experience of Mills[3,4] and Duncan[1,5,22] with the HOFF as applied to a number of CH_3X and SiH_3X molecules. This approximation yields force constants in good agreement with those for the general valence force field for methyl halides.

An important finding by Mills and Duncan is that the A_1 MH stretch–MH bend interaction constant (F_{12}) is not sufficiently well determined by only hydrogen and deuterium isotopic data adequately to test the first inequality given above. Therefore, Mills constrained this force constant to zero in the absence of additional data. It is an interesting point that, of F_{12}, F_{56}, and F_{57}, the first is predicted to be the smallest. Judging from the smallness of F_{56} for these compounds, it is not surprising that F_{12} is difficult to determine. Furthermore, Mills and Duncan have shown that Coriolis interaction and centrifugal distortion constants and heavy-atom isotopic frequency data[5] are often useful in determining the MH_3 stretch–bend interaction constants.

Since the HOFF has not previously been tested with BH_3X compounds, we have included in our study of BH_3CN^-, BH_3NC^-, and BH_3F^- a number of molecules studied by other force field approximations. In carrying out the analyses the only HOFF constraint forced into our calculations is that of (stretch–bend) = −(stretch–rock) in the E block.

Summary of Force Field Data.—Of all the molecules considered, only for BH_4^- and BH_3CO was it possible to determine statistically reliable values for F_{12}. For BH_4^-, a calculation under C_{3v} symmetry gave the results in Table VII. Application[4] of a $T_d \rightarrow C_{3v}$ unitary transformation to the T_d force field results led to a negative value for F_{12}, as a direct result of the positive value for F_{34} in T_d symmetry ($F_{34} = 0.02 \pm 0.02$ mdyn). Thus, our results for the T_d calculation for BH_4^- agree with those of Taylor,[10] but the vibrational data alone are insufficient to determine a reliable value for this constant. Similar difficulties have been recorded for SiH_4.[22] It is interesting that a change in the computational formalism alone allows a change in the sign of the interaction constant. With BH_3CN^-, a large negative a value of F_{12} (−0.11 mdyn) resulted from refinement of the vibrational data. Inclusion of F_{12} also produced a marked lowering of the ratio $|J^tWJ|/\Pi_u(J^tWJ)_{uu}$ from 0.35 to 0.024. Thus, this constant is indeterminant from the vibrational data alone. The same problem arose for the other adducts. The molecular orbital results discussed later support the HOFF in predicting a positive value for F_{12} in BH_3CN^-.

For the adducts BH_3CN^-, BH_3NC^-, and BH_3CO[23,24] we included the interaction constant F_{34} in the refinement procedures. With the former, the refinement oscillated about values of F_{34} from 0.35 to 0.5 mdyn/Å on successive cycles. A value of $F_{34} = 0.5$ mdyn/Å was arrived at by manually varying the constant from 0.1 to 0.8 mdyn/Å in steps of 0.1 mdyn/Å to give the best overall fit of frequencies and best standard errors in force constants. This value can be compared with that for CH_3CN, which has been reported to be from 0.25 to 0.8 mdyn/Å by various workers.[1,6] The other constants are affected by less than 10% by varying F_{34} from 0.1 to 0.8 mdyn/Å. A similar procedure was necessary for BH_3CO, which, interestingly enough, gave the best results for $F_{34} = 0.0$ mdyn/Å. The value for BH_3CN^- was transferred directly to BH_3NC^-.

A not-unusual situation arose for BH_3F^-. The near degeneracy of the a_1 BH_3 bending and a_1 BF stretching modes is reflected in mixing of the corresponding symmetry coordinates which, in turn, produced strong oscillations in the refinement cycles. Convergence was finally achieved by reducing the force constant corrections on each cycle to one-fourth of the computed correction. The same final solution was obtained from various starting force constants. The assignment in Table V corresponds to that based on the computed potential energy distributions.

The E symmetry calculations for BH_3PF_3 gave less reliable results than for the other BH_3X molecules mainly because of the missing frequency, ρ_{BD}. Calculations have been done both by omitting the BD rock frequency and by giving it a value of 570 cm^{-1}, a value based on the expected shift of the hydrogen rocking frequency upon deuteration. There is a strong band in this region (ν_{BP}), which might obscure the BD rock. Both calculations gave essentially identical results. Even when ρ_{BD} is approximated as 570 cm^{-1}, the frequencies are not fit very well in spite of the inclusion of a $\delta^e_{BH}-\rho^e_{BH}$ interaction constant (F_{78}). Thus, the location of the BD rocking frequency is still open to question. Consequently, while the values of F_{67} and F_{68} are found to be in line with the other calculations and the HOFF, they are poorly defined because of the missing frequency. Interestingly, and in spite of the limited data, the regression procedure attempts to include the PF_3 rock–BH_3 rock interaction constant, which is permitted by orbital following and found in C_2H_6, but the data are simply too restricted to evaluate the constant meaningfully.

With regard to BH_3PH_3, we find Goubeau's assignments[19] more satisfactory than those of Parry.[25] Since frequencies from only one isotopic species are available, only a diagonal force field can be calculated. The omission of F_{23} is estimated to produce a value of F_{33} which is probably ~5% low. This estimate is based on the finding that inclusion of F_{23} raises F_{33} by this amount in the other members of this series.

From the data reported here it is possible to make some generalizations about the force fields in BH_3X adducts. First, the hybrid orbital force field concept is as useful for BH_3X molecules as it is for the CH_3X and SiH_3X series. Second, the wide variations in F_{11} (0.57 mdyn/Å) and in F_{22} (0.16 mdyn/Å) observed in these compounds caution against citing a nominal, transferable force field for the borane group.

One of the similarities between the borane and methyl series is the sensitivity of the interaction constants in-

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(21) M. Davies, Ed., "Infrared Spectroscopy and Molecular Structure," Elsevier, New York, N. Y., 1963, p 195.

(22) J. L. Duncan, *Spectrochim. Acta*, **20**, 1807 (1964).

(23) G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26**, 1118 (1957).

(24) S. Sundaram and F. F. Cleveland, *ibid.*, **32**, 166 (1960).

(25) R. W. Rudolph, R. W. Parry, and C. F. Farran, *Inorg. Chem.*, **5**, 723 (1966).

volving the MH_3 group to isotopic molecule frequency data. We find a sensitivity to isotopic substitution in the BH_3X molecules like Mills and Duncan have found in CH_3X and SiH_2X—in spite of the smaller size of these interaction constants for BH_3X. Summarizing very briefly, F_{12} is virtually indeterminant with only H and D isotopic data and is best constrained to zero. The inclusion of *accurate* heavy-atom isotopic data, such as those of boron-10, generally permits F_{12} to be entered into the least-squares refinement of the force field without a significant deterioration of the equations. In such cases, F_{12} is found to be positive. With regard to the necessity of often ignoring F_{12}, in those cases where *both* general harmonic and hybrid orbital approximate calculations have been performed,[4] it is found that $F_{12} = 0$ has little effect on the other constants. F_{23} is always found to be negative and requires only H and D data. In the E block, F_{56}, F_{57}, and F_{67} are usually sufficiently sensitive to H and D frequencies to determine their value accurately, even though they appear to be generally small, and the HOFF constraint of $F_{56} = -F_{57} > 0$ leads to acceptable force fields.

With regard to trends in force constants, it is possible to divide the BH_3X series into two groups which are differentiated by the magnitude of F_{11}. The adducts with strong donors (H^-, F^-, CN^-, NC^-) have a BH stretching force constant in the range 2.8–3.0 mdyn/Å, while the weaker donors (CO, PF_3, PH_3) have values of F_{11} in the range 3.3–3.4 mdyn/Å. These results are consistent with the argument that the stronger donors force greater boron p character into the BH bonds than do the adducts of the weaker donor group. It is disappointing that differences in hybridization within each group apparently do not give rise to calculable differences in the BH stretching force constants. A possible reason for this may lie in the necessity of constraining $F_{13} = 0$.

Although F_{11} gives qualitative information on the boron hybridization, it is F_{33} (the B–X stretching force constant) that is most informative about the actual stiffness of the B–X bond and presumably its energy. Ordering of the F_{33}'s for these adducts implies the order of B–X bond stiffness: $F^- > CN^- > NC^- > H^- > CO > PF_3 > PH_3$. While this order might correlate fairly well with the (unknown) gas-phase adduct bond dissociation energies ($BH_3X \rightarrow BH_3 + X$), it does not correlate well with hydrolytic or redox stabilities (BH_3F^- and BH_3NC^- are more reactive with H_2O than with BH_3CN^-). Hydrolytic stability is not a good criterion for adduct bond strengths because of the wide variations possible for hydrolysis mechanism over this widely varying donor series.

Probably more meaningful comparisons can be made among common donor atoms. When values of F_{33} for BH_3 adducts which contain a common donor atom are compared, it is found that F_{33} reflects the expected stability of the adduct to dissociation into acid and base: for carbon, $CN^- > CO$; for phosphorus, $PF_3 \gtrsim PH_3$.

Examination of the values for F_{22} indicates there is apparently no general correlation between the value of F_{22} and boron hybridization (F_{11}) or B–X bond stiffness (F_{33}). However, when common donor atoms are compared, one sees a tendency for decreasing F_{22} with decreasing F_{33}.

The CN^- force constants (all in mdyn/Å) are interesting to compare. In BH_3CN^-, F_{44} (the CN stretch force constant) is intermediate (17.2) between the values found for CH_3CN (18.1) and free CN^- (16.4) and is consistent with the observation that CN force constants tend to increase on coordination of the carbon lone pair.[26] On the other hand, in BH_3NC^-, F_{44} has a value of 16.0, which is less than that of free CN^-; by contrast, in CH_3NC the value of F_{44} is 16.7. The value for BH_3NC^- is most certainly dependent on the assumption that $F_{34} = 0.5$. However, a lower value for F_{34} results in an even lower value for F_{44}. On the other hand, increasing F_{34} would increase F_{44}, but F_{34} would have to have a value of ~1.0 to raise F_{44} to 16.4—the value in free CN^-. Consequently, it seems that BH_3NC^- is one case where F_{CN} decreases upon nitrogen coordination.

Molecular Orbital Calculations.—As mentioned in the vibrational analysis section, the sign of F_{12} in BH_3CN^- was found to be at odds with the predictions of the HOFF. To test whether or not this is real or merely another instance of the difficulty in defining F_{12} with only H and D frequencies, CNDO calculations on BH_3CN^- and BH_3CO were done to calculate the *sign* of F_{12}. It has been shown that semiempirical calculations generally give stretch–bend interaction and bending force constants of the correct sign and magnitudes.[14,27] The objective of this work was to determine whether some electronic effect could cause a reversal in the sign of F_{12} on going from BH_3CO to BH_3CN^-.

The results, summarized in Table IX, bear out the predictions of the HOFF, and, furthermore, all experimentally observed trends between corresponding BH_3CO and BH_3CN^- constants are held by the MO calculations. This is true even for the stretching force constants which are characteristically too large by such methods. From these calculations and the previously given arguments, we feel that it is safe to conclude that there is no theoretical reason for F_{12} in BH_3CN^- to have a sign different from that predicted by orbital-following arguments.

TABLE IX[a]
COMPARISON OF CNDO AND VIBRATIONAL ANALYSIS RESULTS

	BH_3CN^-		BH_3CO	
F_{ij}	CNDO	Vibrational analysis	CNDO	Vibrational analysis
F_{11}	8.09	2.98	8.75	3.30
F_{22}	0.864	0.557	0.647	0.529
F_{33}	10.95	4.56	9.06	2.79
F_{12}	0.069	0.0	0.037	0.044
F_{23}	−0.140	−0.600	−0.115	−0.290

[a] Units as in Table VII.

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