Table V

Physical Constants of the Methyl(phosphino)silanes and -germanes

Compound	Mp, °C	Bp,[a] °C	ΔHv,[b] kcal mol^{-1}	Trouton constant	Vapor pressure equation constants[c] *A*	*C*	Temp range, °C
$(CH_3)_3GePH_2$	−97.2	95.8	7.762	21.0	−1696.2	7.4784	0–45.9
$(CH_3)_2Ge(PH_2)H$	−106.5	74.2	8.526	24.5	−1863.3	8.2458	−17.0–19.8
$(CH_3)_2Si(PH_2)_2$	−108.0	117.9	9.766	25.0	−2134.1	8.3384	0.0–54.6
$(CH_3)_2Si(PH_2)H$	−116.6	54.7	7.519	22.8	−1643.0	7.8491	−30.7–14.3
$(CH_3)_2Ge(PH_2)_2$[d]	−100.2	...	...	...	...	...	...

[a] Calculated from the vapor pressure equation. [b] Calculated from the slope of a log P_{mm} *vs.* t^{-1} plot. [c] For the equation log $P_{mm} = [A/(t + 273.16)] + C$. [d] Too unstable for a vapor pressure *vs.* temperature determination.

samples with anhydrous HCl. The calculated ratio of $(CH_3)_2SiH_x(PH_2)_{2-x}:PH_3:(CH_3)_2SiH_xCl_{2-x}$ according to the reaction

$$(CH_3)_2SiH_x(PH_2)_{2-x} + (2 - x)HCl \longrightarrow (2 - x)PH_3 + (CH_3)_2SiH_xCl_{2-x} \qquad (x = 0, 1)$$

is as follows: for $(CH_3)_2Si(PH_2)H$: calcd, 1.00:1.00:1.00; found, 1.00:0.97:0.94; for $(CH_3)_2Si(PH_2)_2$: calcd, 1.00:2.00:1.00; found, 1.00:1.92:0.95. The PH_3,[11,20] $(CH_3)_2SiCl_2$,[27,28] and $(CH_3)_2SiHCl$[29,30] which formed in the reactions were confirmed by ir spectra and vapor tension data.

Vapor Pressure Data.—Vapor pressures of the phosphinosilanes and -germanes are given in Table IV. Melting points and the physical constants obtained from the vapor pressure data are given in Table V. Data were not obtained for $(CH_3)_2Ge(PH_2)_2$ since decomposition to yield PH_3 and uncharacterized solids was too rapid in the temperature range required for vapor tension measurements.

Mass Spectra.—Mass spectra were obtained at an ionizing voltage of 70 eV. All spectra were obtained after the sample inlet chamber has been pretreated with the desired phosphinosilane or -germane for a period of 10–15 min.

All of the compounds characterized in this study exhibited the expected mass spectral fragmentation patterns. Fundamental spectral data for the compounds are: $(CH_3)_2Si(PH_2)H$, highest mass peak at *m/e* 94 (relative intensity 0.7% of the major peak at *m/e* 59) assigned to the $(CH_3)_2{}^{30}Si(PH_2)H^+$ molecular ion; $(CH_3)_2Si(PH_2)_2$, highest mass peak at *m/e* 126 (relative intensity 0.6% of the major peak at *m/e* 91) assigned to the $(CH_3)_2{}^{30}Si(PH_2)_2{}^+$ molecular ion; $(CH_3)_3GePH_2$, highest mass peak at *m/e* 154 (relative intensity 0.8% of the major peak at *m/e* 119) assigned to the $(CH_3)_3{}^{76}GePH_2{}^+$ ion; $(CH_3)_2Ge(PH_2)H$, highest mass peak at *m/e* 140 (relative intensity 6.4% of the major peak at *m/e* 105) attributed to the $(CH_3)_2{}^{76}Ge(PH_2)H^+$ ion; and $(CH_3)_2Ge(PH_2)_2$, highest mass peak at *m/e* 172 (relative intensity 1.7% of the major peak at *m/e* 137) attributed to the $(CH_3)_2{}^{76}Ge(PH_2)_2{}^+$ molecular ion.

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The Electronic Energies and Structure of Difluoroborane

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The electronic energy and distribution of difluoroborane, HBF_2, are examined by molecular quantum chemical calculations using Gaussian-type atomic orbitals. The structure of HBF_2 is investigated and excellent agreement with the experimental parameters is obtained. The π-localization and reorganization energies of difluoroboranes are calculated to be 35.7 and 24.4 kcal/mol, respectively.

Introduction

The preparation of difluoroborane (HBF_2) was first reported in 1964.[1] It has since been subjected to a thorough physical examination by infrared,[2-6] nuclear magnetic resonance,[7,8] and microwave[9] spectroscopy. There is very little information, however, concerning the electronic structure and energy of this compound. In this publication the results of calculations on this compound are reported giving details of the electronic structure and energy.

Results and Discussion

Calculations.—The calculations have been performed within the framework of LCAO-MO-SCF theory using Gaussian orbitals[10] as the basis set. The

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Gaussian orbital exponents were taken from the work of Csizmadia, *et al.*[11] The various bond angles and bond lengths were obtained from the microwave spectroscopy work of Kasuya, *et al.*[9] These values are $l_{B-F} = 1.311$ Å, $l_{B-H} = 1.189$ Å, and ∠FBF = 118.3°. The molecular plane of HBF_2 was defined to be in the xy plane with the B–H bond along the y axis.

The orbital energies and total energy of HBF_2 calculated using a (7, 3, 3) basis set are presented in Table I. (A basis set (l, m, n) is defined as l orbitals of s-type symmetry and m orbitals of p-type symmetry on the boron and fluorine atoms and n orbitals of s-type symmetry on the hydrogen atom.) The (7, 3, 3) basis set is reasonably large for the total energy to be approaching the Hartree–Fock limit and hence the dissociation energy will have a realistic value. The simple binding energy calculated as the difference between the energies of the molecule and its individual atoms is 292.1 kcal/mol. The correlation energy for HBF_2 is estimated to be 122.2 kcal/mol (40.72 kcal/mol for each of the three bonds formed[12]). Therefore, the calculated dissociation energy ignoring relativistic terms is the sum of the above terms equaling 414.3 kcal/mol. The experimental value for the dissociation energy is unknown; however a value of 377.4 kcal/mol obtained as a sum of the energies of the individual bonds ($E_{B-F} = 150.4$ kcal/mol and $E_{B-H} = 76.6$ kcal/mol[13]) is a reasonable estimate and is in satisfactory agreement with the calculated value. The highest occupied orbital is a σ-type orbital whose major component is the hydrogen s orbitals. Invoking Koopmans' theorem[14] the ionization potential is calculated to be 15.4 eV.

TABLE I

ORBITAL ENERGIES AND TOTAL ENERGY OF HBF_2 (IN AU)

2*	0.2322 (a_1)
1*	0.1305 (b_1)
12	−0.5652 (a_1)
11	−0.6586 (b_2)
10	−0.6666 (a_2)
9	−0.7256 (b_1)
8	−0.7568 (a_1)
7	−0.7650 (b_2)
6	−0.8314 (a_1)
5	−0.6586 (b_2)
4	−1.6922 (a_1)
3	−7.7604 (a_1)
2	−26.3583 (b_2)
1	−26.3584 (a_1)
Electronic energy	−285.725562
Nuclear energy	61.974189
Total energy	−223.751373

The first virtual orbital is a π-type orbital and is concentrated largely on the boron p_z orbitals.

Electron Distribution.—The gross atomic and bond overlap populations obtained from the (7, 3, 3) basis set calculation are given in Table II. These figures show that boron possesses a large positive charge (1.049) while the fluorines share the negative charge leaving the hydrogen neutrally charged. It is rather surprising that the hydrogen should retain its electronic charge although adjacent to a large positive charge. The flow of electrons from boron to fluorine on bonding consists of a large movement of 0.594 σ electron from the boron to each fluorine coupled with a small back-donation of 0.12 π electron from each fluorine. As expected boron is strongly bonded to the fluorines and the hydrogen. The overlap population of the latter bond is smaller than those for the terminal B–H bond in diborane[15] (0.880) and for those in BH_3[16] (0.804). Both the fluorine–hydrogen and the fluorine–fluorine bonds are antibonding with the former having the larger antibonding character. This might be a reason why the ∠FBF angle is less than 120.° Also included in Table II is the calculated dipole moment of HBF_2 which is in satisfactory agreement with the experimental value of 0.971 D.[9]

TABLE II

ELECTRON DENSITIES, BOND POPULATIONS, AND DIPOLE MOMENT OF HBF_2

Electron densities			Bond populations		
Hydrogen		1.101	H–B		0.706
Boron	s	2.714	B–F	σ	0.434
	p_x	0.347		π	0.129
	p_y	0.650		Total	0.563
	p_z	0.240	H–F		−0.083
	Total	3.951	F–F		−0.043
Fluorine	s	3.981			
	p_x	1.752	Dipole moment, 1.35 D		
	p_y	1.861			
	p_z	1.880			
	Total	9.474			

Structural Investigations.—The structure of HBF_2 was examined by a series of calculations in which one parameter was altered while keeping the other parameters at the experimental value used previously. The (5, 2, 2) basis set was used throughout these calculations.

Potential energy curves of HBF_2 were constructed as a function of the ∠FBF angle and B–F and B–H bond lengths. By fitting parabolas to these curves the following equilibrium values for the parameters were obtained: ∠FBF = 117.1° (exptl, 118.3°), B–H = 1.204 Å (exptl, 1.189 Å), and B–F = 1.307 Å (exptl, 1.311 Å). Excellent agreement is obtained between the calculated and experimental parameters.

In the previous calculations the planarity of HBF_2 was assumed. As a check that this postulate was valid, calculations were performed in which the out-of-plane angle was altered by increments of 10.° It

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was found that the planar structure is indeed the stable configuration.

Reorganization and π-Localization Energies.—Planar boron compounds are well known for their donor–acceptor properties.[17] The energy required to transform the planar molecule into a pyramidal configuration appropriate for complex formation is known as the reorganization energy.[18] The energy is regarded as the main factor determining the complex-forming powers of the acceptor. There have been several empirical[18] and semiempirical[19–21] calculations of this energy but so far only one nonempirical[22] determination of this quantity which was for BH_3 has been reported. As the number of *ab initio* calculations of this energy for different boron molecules is likely to be very small because of the limitations of the available computers, a nonempirical determination of the reorganization energy of HBF_2 would be of interest.

The total energy and orbital energies of pyramidal HBF_2 calculated using a (7, 3, 3) basis set are presented in Table III. The B–F bond length and ∠FBF angle used in the calculation were the same as those reported in the structure of $BF_3 \cdot NH_3$[23] and the B–H structural parameters were taken from a microwave study on $BH_3 \cdot CO$.[24] From the results in Table III it can be seen that the pyramidal form of HBF_2 is less stable than the planar configuration by 24.4 kcal/mol. This increase in energy is caused by a greater increase in the electronic energy than the accompanying decrease in the nuclear energy when HBF_2 is inverted.

TABLE III

THE ORBITAL AND TOTAL ENERGIES (IN AU) OF THE PYRAMIDAL AND LOCALIZED CONFIGURATIONS OF HBF_2

	Pyramidal	Localized
2*	0.260 (a″)	0.237 (a_1)
1*	0.045 (a′)	−0.059 (b_1)
12	−0.553 (a′)	−0.565 (a_1)
11	−0.633 (a″)	−0.633 (b_2)
10	−0.645 (a″)	−0.669 (a_2)
9	−0.699 (a′)	−0.691 (b_1)
8	−0.733 (a″)	−0.744 (b_2)
7	−0.736 (a′)	−0.746 (a_1)
6	−0.818 (a′)	−0.815 (a_1)
5	−1.625 (a″)	−1.641 (b_2)
4	−1.664 (a′)	−1.675 (a_1)
3	−7.772 (a′)	−7.786 (a_1)
2	−26.341 (a″)	−26.322 (b_2)
1	−26.341 (a′)	−26.322 (a_1)
Electronic energy	−284.665312	−285.668511
Nuclear energy	60.952865	61.974189
Total energy	−223.712447	−223.694322

The occupied orbital energies of the pyramidal form of HBF_2 with one exception are less stable than those of the corresponding planar compound. This destabilization is most pronounced with π-type molecular orbitals. The exception is the third lowest occupied orbital which is largely composed of the boron 1s orbital. The electronic distribution of the pyramidal configuration presented in Table IV is very similar to that of the planar molecule.

TABLE IV

THE ELECTRON DENSITIES AND BOND POPULATIONS OF THE PYRAMIDAL AND LOCALIZED CONFIGURATIONS OF HBF_2

		Pyramidal	Localized
		Electron Densities	
Hydrogen		1.053	1.103
Boron	s	2.739	2.726
	p_x	0.336	0.383
	p_y	0.655	0.676
	p_z	0.235	0.0
	Total	3.965	3.785
Fluorine	s	3.986	3.982
	p_x	1.785	1.729
	p_y	1.885	1.845
	p_z	1.835	2.0
	Total	9.490	9.556
		Bond Populations	
	H–B	0.739	0.670
	B–F	0.524	0.463
	H–F	−0.076	−0.087
	F–F	−0.048	−0.042

The only previous nonempirical calculation of the reorganization energy was for BH_3 which amounted to 13.6 kcal/mol using a (7, 3, 3) basis set.[22] Hence HBF_2 requires 10.8 kcal/mol more than BH_3 to form a pyramidal configuration and this stems from the presence of boron–fluorine π bonds. Now it has been accepted that two factors are important in the reorganization process: (a) the energy of breaking of the π bonds and (b) the change in energy when the bonds are bent including the newly formed σ–π interaction energy. For BH_3 the first factor does not apply and hence the second process contributes solely to the reorganization energy. For HBF_2 both factors will contribute to the reorganization energy but it is only possible to calculate the first energy term. This has been determined as the difference between the delocalized molecule and a localized model in which the π electrons are held on the fluorines. Using a (7, 3, 3) basis set the π-bond (or π-localization) energy is calculated to 35.7 kcal/mol. This energy term is greater than the reorganization energy. Therefore, the second energy term stabilizes the system by an amount equal to $35.7 - 24.4 = 11.3$ kcal/mol. On inversion there will be an increase in stability due to σ–π interaction but a decrease due to the lengthening and bending of the bonds. If it can be assumed that the decrease in stability of HBF_2 due to the lengthening and bending of the bonds is the same as in BH_3 (*i.e.*, equal to the reorganization energy of BH_3 as there is no σ–π interaction in BH_3), then

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the increase in σ energy due to interaction of the π electrons is 11.3 + 13.6 = 24.9 kcal/mol. It can be concluded that the important terms in the reorganization process are the π-bond energy and the $\sigma-\pi$ interaction energy.

The orbital energies and electronic distribution of the localized state of HBF_2 are presented in Tables III and IV. The occupied molecular orbitals of the localized model of the molecule are less stable than the corresponding values of the delocalized molecule. This destabilization as expected is more pronounced with the π-type orbitals (a_2 and b_1). Conversely the first vacant orbital becomes stabilized and is now composed solely of the boron p_z orbital. The population analysis reveals that the localization of the π electrons produces an expected net flow of electrons to the fluorines although there is a small σ-electron flow to the boron.

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Molecular Beam Mass Spectra and Pyrolysis of Pentaborane(9), Tetraborane Carbonyl, and Pentaborane(11). Formation and Mass Spectrum of Tetraborane(8)[1-3]

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A mass spectrometer with an integral flow reactor was used to study the pyrolysis of $^{n}B_5H_9$, $^{10}B_4H_8CO$, and $^{10}B_5H_{11}$ at very low pressures and to measure their molecular beam mass spectra. (a) The room-temperature molecular beam mass spectrum of B_5H_9 agreed with the spectrum obtained with an instrument with a conventional ion source. A preliminary study of its pyrolysis revealed no evidence for the formation of any reactive intermediates or other volatile boron containing products. (b) The molecular beam mass spectrum of B_4H_8CO differs drastically from that produced by a "conventional" ion source instrument due to pyrolysis in the conventional inlet and ion source systems. The B_4H_8CO ion decomposition (fragmentation pattern) parallels the known chemistry of tetraborane carbonyl. In the pyrolysis, B_4H_8 is the initial decomposition product; no monoborane or triborane species could be observed. Small amounts of pentaboranes and possibily diborane were observed but no higher boranes. Appearance potentials were measured for all the major ions due to B_4H_8CO. The mass spectrum of tetraborane(8) is reported and confirms its classification as a "stable" borane. (c) The molecular beam mass spectrum of B_5H_{11} differed slightly from the conventional, but there were indications of contributions to the latter by pyrolysis products formed in the ion source. A study of the pyrolysis of B_5H_{11} has shown B_4H_8 and BH_3 to be decomposition products. No triborane species could be observed; diborane and pentaborane(9) were observed, but no higher boranes could be detected under these experimental conditions.

Introduction

There has been considerable discussion of the postulated existence of BH_3, B_3H_7 and/or B_3H_9, and B_4H_8 intermediates in the pyrolysis of diborane and in the decomposition of tetraborane(10).[4-7]

A commonly accepted mechanism is

$$B_2H_6 \longrightarrow 2BH_3 \qquad (1)$$

$$BH_3 + B_2H_6 \longrightarrow B_3H_9 \qquad (2)$$

$$B_3H_9 \longrightarrow B_3H_7 + H_2 \qquad (3)$$

$$B_3H_7 + B_2H_6 \longrightarrow B_4H_{10} + BH_3 \qquad (4)$$

$$B_4H_{10} \left\langle \begin{array}{ll} \nearrow B_3H_7 + BH_3 & (5) \\ \searrow B_4H_8 + H_2 & (6) \end{array} \right.$$

$$B_4H_8 + B_2H_6 \longrightarrow B_5H_{11} + BH_3 \qquad (7)$$

$$B_5H_{11} \longrightarrow B_4H_8 + BH_3 \qquad (8)$$

$$B_5H_{11} + BH_3 \longrightarrow \text{higher boranes} \qquad (9)$$

Pearson and Edwards[8] studied the kinetics of the thermal decomposition of tetraborane(10) alone and in the presence of diborane and hydrogen. They proposed that tetraborane(10) could decompose by two simultaneous first-order mechanisms as shown in eq 5 and 6, since each reaction was first order in tetraborane(10). Pentaborane(11) could be formed by reaction 7 and diborane formed by the reverse of reactions 2 and 3. However, Dupont and Schaeffer[9] discovered that the conversion of tetraborane(10) to pentaborane(11) proceeded more rapidly in the presence of diborane. They suggested tetraborane(10) would form pentaborane(11) *via* reactions 6 and 7, since any triborane(7)

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