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Microwave, Infrared, and Raman Spectra, Conformation, Dipole Moment, and Vibrational Assignment of Ethyldifluoroborane

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Abstract: The microwave spectra of $\text{CH}_3\text{CH}_2^{10}\text{BF}_2$ and $\text{CH}_3\text{CH}_2^{11}\text{BF}_2$ have been recorded from 26.0 to 40.0 GHz. A-type transitions were observed and R-branch assignments have been made for the ground vibrational state for both ^{10}B and ^{11}B and four excited states of the $^{11}\text{BF}_2$ torsion. B-Type transitions were also assigned for the ground and first excited state of the $^{11}\text{BF}_2$ torsion. From the small value of $I_a + I_b - I_c = 6.318\text{ amu \AA}^2$, it is concluded that the major conformation of ethyldifluoroborane has all heavy atoms coplanar and that this quantity arises mainly from the four out-of-plane hydrogens of the ethyl moiety. The total dipole moment was determined to be $1.69 \pm 0.02\text{ D}$, with components $\mu_a = 1.15 \pm 0.02\text{ D}$ and $\mu_b = 0.75 \pm 0.02\text{ D}$. The infrared ($20\text{--}3500\text{ cm}^{-1}$) and Raman spectra ($0\text{--}3500\text{ cm}^{-1}$) have been recorded for both the gas and solid. Additionally, the Raman spectrum of the liquid was recorded and qualitative depolarization values obtained. The BF_2 internal torsional mode was observed at 44 cm^{-1} in the infrared spectrum of the gas and a twofold periodic barrier of 1.17 kcal/mol was calculated. These data are consistent with the relative intensity measurements in the microwave spectrum. The structural results are compared with previous ab initio calculations for ethylborane in which the most stable conformation is a staggered structure. The barrier to internal rotation of the BF_2 moiety is also compared to that of the isoelectronic molecule nitroethane which exhibits free rotation of the nitro group. The B-C bond distance of 1.572 \AA appears reasonable relative to the values reported for this distance in other organoboranes.

Introduction

In general there has been very little structural information reported for organoboron compounds, particularly gas-phase determinations.¹ Recently we have initiated a program to investigate the spectra and structure of organoboranes.²⁻⁸ A structural study of the vinylidifluoroborane molecule^{3,8} included the microwave spectra of 15 isotopic species as well as the complete assignment of the infrared and Raman spectra. The molecule was planar and had a twofold barrier to internal rotation of 4.17 kcal/mol . As a continuation of these studies,

we have investigated the infrared, Raman, and microwave spectra of ethyldifluoroborane, $\text{C}_2\text{H}_5\text{BF}_2$.

Dill et al.⁹ recently reported a theoretical study of the energies and conformations of a series of XCH_2Y molecules which included ethylborane, $\text{CH}_3\text{CH}_2\text{BH}_2$. Ab initio molecular orbital theory predicts⁹ the conformation of this hypothetical molecule to have the BH_2 group staggered with respect to the methyl moiety (i.e., the methyl group bisects the HBH angle) with a B-C rotational barrier of 0.2 kcal/mol . We felt that a determination of the conformation and barrier to in-

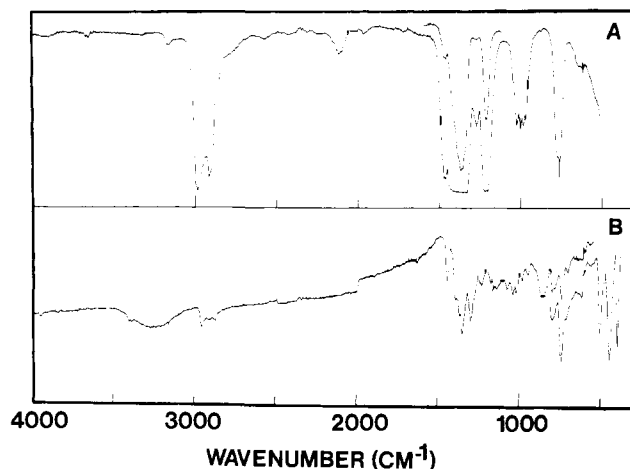


Figure 1. Infrared spectrum of ethyldifluoroborane: (A) gas, (B) solid. Abscissa in arbitrary units of absorption.

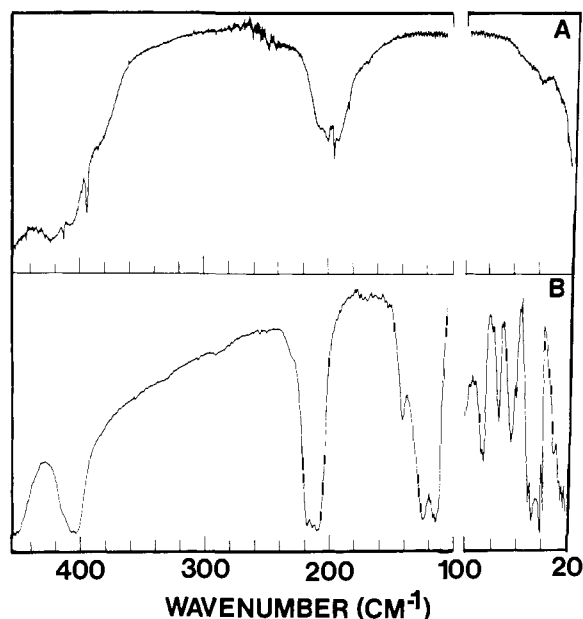


Figure 2. Far-infrared spectrum of ethyldifluoroborane: (A) gas, (B) solid. Abscissa in arbitrary units of absorption.

ternal rotation of $\text{CH}_3\text{CH}_2\text{BF}_2$ would provide an interesting experimental comparison with the above calculations and would also provide useful information for our investigations of the bonding and structures of organoborane molecules. The results of our vibrational and rotational studies are reported herein.

Experimental Section

All manipulations were carried out in an oxygen-free drybox or in a standard vacuum line equipped with greaseless stopcocks. Boron trichloride (Matheson) and antimony trifluoride (Ozark-Mahoning) were obtained commercially and triethylaluminum was kindly donated by Ethyl Corp. Ethyldichloroborane was prepared by the dropwise addition of $\text{Al}(\text{C}_2\text{H}_5)_3$ to a chlorobenzene solution of boron trichloride as described previously by Nöth and Storch.¹⁰ The addition of 0.287 mol of $\text{Al}(\text{C}_2\text{H}_5)_3$ to 0.929 mol of BCl_3 resulted in the preparation of 0.381 mol of $\text{Cl}_2\text{BC}_2\text{H}_5$ (42.2 g, 44.2%). Ethyldifluoroborane was prepared by the fluorination of ethyldichloroborane. In a typical reaction 15.8 mmol of $\text{Cl}_2\text{BC}_2\text{H}_5$ was condensed into a bulb containing an excess of SbF_3 which had been sublimed twice. After 1.5 h, all volatile materials were fractionated on a low-temperature vacuum fractionation column.¹¹ A trace of BF_3 and 15.31 mmol of $\text{F}_2\text{BC}_2\text{H}_5$ (97%) were obtained. Purity of the $\text{F}_2\text{BC}_2\text{H}_5$ was checked by mass spectrometry and ^{11}B NMR ($\delta_{11\text{B}}$ 28.7 ppm deshielded from $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, $J_{\text{BF}} = 82.0$ Hz; lit. δ 28.6 ppm¹² $J_{\text{BF}} = 82$ Hz¹²). ^{19}F NMR

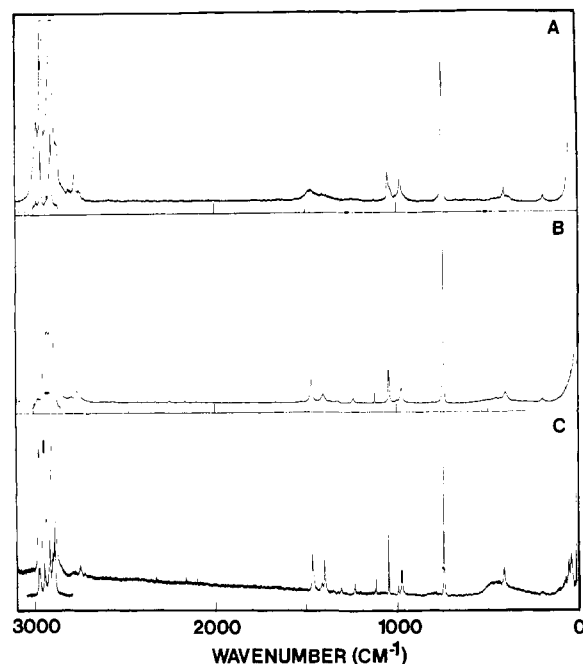


Figure 3. Raman spectrum of ethyldifluoroborane: (A) gas, (B) liquid, (C) solid. Abscissa in arbitrary units of scattering intensity.

spectra were obtained on a Varian Associates XL-100-15 spectrometer operating at 94.1 MHz in the FT mode. Low-temperature spectra were obtained on a 20% (v/v) solution using a 50/50 mixture of isopentane and toluene as a solvent. Temperature measurements were obtained using a thermocouple inserted into the probe.

The microwave spectrum and measurements were taken with a Hewlett-Packard 8460A MRR spectrometer, using a Stark modulation frequency of 33.33 kHz. Spectra were recorded with the waveguide at ambient temperatures. Frequency measurements are estimated to be accurate to ± 0.1 MHz.

A Perkin-Elmer Model 621 infrared spectrophotometer was used for recording the mid-infrared spectra ($3500\text{--}400$ cm^{-1}) and a Digilab FTS-15B interferometer was used for recording far-infrared spectra ($450\text{--}20$ cm^{-1}). Both instruments were purged with dry nitrogen gas. The instruments were calibrated with standard gases¹³ in the high-frequency region and atmospheric water vapor¹⁴ in the lower frequency region. The infrared frequencies are accurate to ± 2 cm^{-1} . Typical spectra are shown in Figures 1 and 2. Cesium iodide plates were used as windows for the gas and cold cells as well as the substrate for the low-temperature solid experiment with the Perkin-Elmer Model 621. Polyethylene plates were used as windows for the gas and cold cells, and a wedged silicon window was used for the solid firm support plate at low temperature in the far-infrared studies.

Raman spectra were recorded on a Cary 82 Raman spectrometer equipped with a Spectra Physics Model 171 or a Coherent Radiation Model 53A argon ion laser utilizing the 5145-Å line as the excitation source. Spectra of the gas phase were obtained using the Cary multipass cell at a sample pressure of approximately 65 Torr. The spectra of the liquid phase were recorded with the sample in a sealed glass capillary and at reduced temperatures using the method of Miller and Harney.¹⁵ The same type cell cooled with the vapor of boiling liquid nitrogen was used to record the Raman spectrum of the solid phase. Typical spectra are shown in Figure 3.

Microwave Spectrum

Depending on the orientation of the BF_2 group relative to the ethyl group along the BC bond, there are four possible conformers for ethyldifluoroborane. As can be seen from Figure 4, both (a) and (c) have staggered configurations while (b) and (d) have partially eclipsed configurations. A structure combined from those of propane¹⁶ and vinyl difluoroborane⁸ was used to make a preliminary prediction of the rotational transitions for conformers (a) and (b). Both (a) and (b) structures have planes of symmetry formed by the CCB atoms.

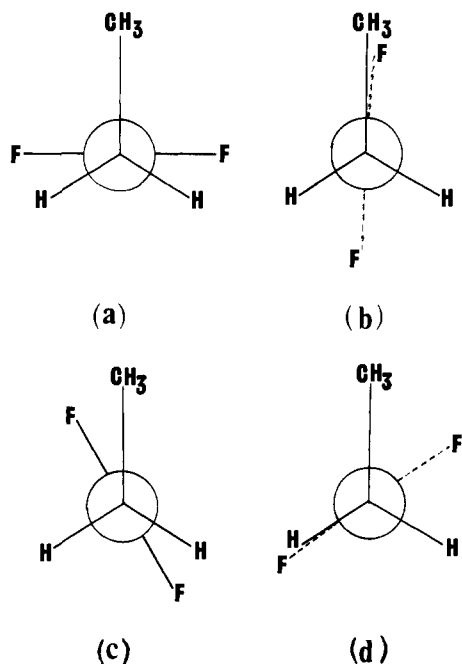


Figure 4. Different Newman projections of ethyldifluoroborane along the B-C bond.

Based on the assumed molecular structural parameters, conformer (a) has the b axis perpendicular to the plane of symmetry and one may expect both a- and c-type transitions. For conformer (b), the c axis is perpendicular to the plane of symmetry formed by all the heavy atoms in the molecule, and one expects both a- and b-type transitions.

The microwave spectrum shows essentially R-branch transitions with a-type selection rules. Initial assignment was made on the basis of the rigid rotor model and the qualitative Stark effect. In addition to the ground-state lines, a series of satellites was observed for each transition. Their similarities in Stark effect with the corresponding ground-state line indicate that the satellites arise from excited vibrational states (see Figure 5). Listed in Table I are the rotational transitions of $\text{CH}_3\text{CH}_2^{11}\text{BF}_2$ in both the ground and excited vibrational states. Since the measured excited-state lines belong to the most intense series of satellites and since the BF_2 torsion is expected to have the lowest vibrational frequency, these satellites are assigned as the excited states of the BF_2 torsion. No splitting was observed for any of these excited-state lines. Due to the possible interference from other lines and varying background absorption, relative intensity measurements did not give reasonably consistent results for different rotational transitions. However, a frequency range from 20 to 60 cm^{-1} can be given for the BF_2 torsional mode from the satellite lines.

For each rotational transition, frequencies have been measured up to the fourth BF_2 torsional state. The deviation of observed frequencies from those calculated using the rigid rotor model (see Tables I and II) probably arises from the centrifugal distortion. It is very interesting to note that the value of $I_a + I_b - I_c$ (6.318 amu \AA^2) arises mainly from the four out-of-plane hydrogens in the ethyl group.¹⁷ For this reason it is concluded that the major conformation of ethyldifluoroborane in the gas phase has all heavy atoms coplanar. Ground-state transitions due to the ^{10}B isotopic species have also been assigned and are listed in Table III. Additionally, B-type transitions for the ground and first excited state of the $^{11}\text{BF}_2$ torsion have been assigned. From Tables II and III, it should be noted that both the ^{11}B and ^{10}B isotopic species have identical values of $I_a + I_b - I_c$ in the ground state.

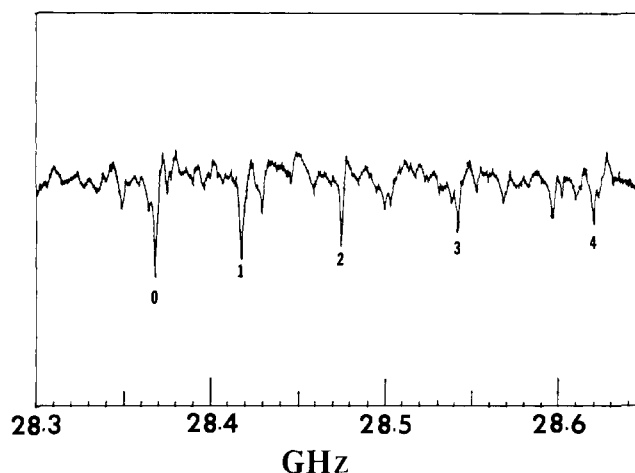


Figure 5. Rotational transitions for the $5_{05} \leftarrow 4_{04}$ transition in the $v = 0, 1, 2, 3$ and 4 states.

Dipole Moment

Stark effect measurements have been made on the $|M| = 0, 1,$ and 2 components of the $4_{04} \leftarrow 3_{03}$ transition and the $M = 0$ component of the $4_{23} \leftarrow 3_{22}$ transition of $\text{CH}_3\text{CH}_2^{11}\text{BF}_2$ in its ground vibrational state. Electric fields were calibrated from the measured Stark effect of the $2 \leftarrow 1$ transition of the OCS molecule and its dipole moment of 0.715 21 D .¹⁸ Analysis of the data has been carried out by the method of Golden and Wilson¹⁹ and the results are listed in Table IV. The resultant dipole moment (1.69 D) is slightly smaller than that of vinyl-difluoroborane (1.74 D)³ as one might expect and is comparable to that for methyldifluoroborane (1.67 D).²⁰

Vibrational Assignment

It is clear from the microwave study that ethyldifluoroborane has a coplanar heavy atom conformation with C_s point group symmetry. All 24 fundamental vibrations are expected to be both infrared and Raman active with the following irreducible representations: $15A' + 9A''$. From group theory, one expects 15 normal modes from the motions of the hydrogen atoms ($8A' + 7A''$) and 9 normal modes from the vibrations of the heavy atoms in the symmetry plane ($7A' + 2A''$). The fundamentals belonging to the A' species should give rise to polarized Raman lines whereas depolarized lines are expected from the modes of A'' species. The smallest and intermediate moments of inertia lie in the symmetry plane; therefore, the normal modes which give dipole moment changes in the symmetry plane (A' species) will have type-A or type-B or hybrid A-B band contours. The type-C contour arises when the dipole moment change is perpendicular to the symmetry plane and all A'' modes give rise to this band type with its distinct and strong Q branch. Based on the experimental moments of inertia of $\text{CH}_3\text{CH}_2^{11}\text{BF}_2$, the separation between the maxima of P and R branches is calculated to be 19 and 14 cm^{-1} for the type A and type B bands, respectively. Most of our fundamental assignments are based on the depolarization values, the gas-phase band contours, and group frequency correlations.

The assignment of the fundamental vibrations is given in Table V. No extensive discussion of these fundamental motions will be given. As mentioned in the microwave section, the principal axes perpendicular to the symmetry plane are different in conformers (a) and (b) (see Figure 4). It is therefore possible to obtain some information about the molecular conformation from the contours of the observed out-of-plane motions. For the C-H motions, we have assigned both type-C infrared bands at 1003 and 765 cm^{-1} to the CH_3 out-of-plane rocking and the CH_2 rocking modes, respectively (see Figure 1).

Table I. Rotational Transitions (MHz) of $\text{CH}_3\text{CH}_2^{11}\text{BF}_2$ in $\nu = 0, 1, 2, 3,$ and 4 Vibrational States

Transitions	$\nu = 0$		$\nu = 1$		$\nu = 2$		$\nu = 3$		$\nu = 4$	
	ν_{obsd}	$\Delta\nu$ (obsd - calcd)	ν_{obsd}	$\Delta\nu$ (obsd - calcd)	ν_{obsd}	$\Delta\nu$ (obsd - calcd)	ν_{obsd}	$\Delta\nu$ (obsd - calcd)	ν_{obsd}	$\Delta\nu$ (obsd - calcd)
5 ₀₅ -4 ₀₄	28 369.29	0.17	28 418.80	0.07	28 476.25	0.12	28 543.04	0.13	28 621.02	0.16
5 ₁₅ -4 ₁₄	27 485.93	0.15	27 543.77	0.06	27 610.08	0.07	27 686.41	0.09	27 774.61	0.04
5 ₁₄ -4 ₁₃	31 767.28	0.01	31 767.85	0.03	31 776.98	0.12	31 795.01	0.15	31 822.68	0.16
5 ₂₄ -4 ₂₃	29 845.93	-0.12	29 871.24	-0.11	29 905.32	0.04	29 948.70	-0.05	30 002.97	-0.04
5 ₂₃ -4 ₂₂	31 540.49	-0.20	31 537.86	-0.05	31 544.69	-0.01	31 561.28	0.00	31 588.19	0.00
6 ₀₆ -5 ₀₅	33 464.62	0.06	33 531.93	-0.11	33 608.81	-0.04	33 696.97	-0.04	33 798.82	-0.07
6 ₁₆ -5 ₁₅	32 802.03	0.06	32 874.28	-0.11	32 956.67	-0.09	33 051.05	-0.08	33 159.86	-0.02
6 ₁₅ -5 ₁₄	37 740.58	-0.22	37 748.32	-0.20	37 765.97	-0.12	37 794.13	-0.12	37 833.93	-0.12
6 ₂₄ -5 ₂₃	38 237.08	-0.47	38 229.34	-0.33						
6 ₃₃ -5 ₃₂	36 824.42	-0.70	36 836.35	-0.60						
3 ₂₁ -3 ₁₂	15 529.00	0.13								
4 ₂₂ -4 ₁₃	14 830.40	0.09	14 693.20	0.22						
5 ₁₄ -5 ₀₅	14 830.40	0.16	14 644.96	0.08						
5 ₂₃ -5 ₁₄	14 603.46	-0.32	14 462.81	-0.27						

Table II. Rotational Constants (MHz) and Moments of Inertia ($\text{u } \text{Å}^2$)^a of $\text{CH}_3\text{CH}_2^{11}\text{BF}_2$ in the $\nu = 0, 1, 2, 3,$ and 4 States

ν	0	1	2	3	4	
<i>A</i>	8882.84 ± 0.09	8828.49 ± 0.09	8771.54 ± 0.78	8711.45 ± 0.87	<i>A</i>	8647.49 ± 0.86
<i>B</i>	3449.29 ± 0.03	3445.38 ± 0.03	3442.39 ± 0.02	3440.26 ± 0.02	<i>B</i>	3438.98 ± 0.02
<i>C</i>	2564.13 ± 0.03	2572.32 ± 0.03	2581.35 ± 0.02	2591.44 ± 0.02	<i>C</i>	2602.83 ± 0.02
<i>K</i>	-0.719 83	-0.717 29	-0.721 79	-0.722 59	<i>K</i>	-0.723 32
<i>I_a</i>	56.895	57.246	57.617	58.015	<i>I_a</i>	58.4447
<i>I_b</i>	146.520	146.687	146.814	146.905	<i>I_b</i>	146.960
<i>I_c</i>	197.100	196.473	195.786	195.023	<i>I_c</i>	194.170
<i>I_a + I_b - I_c</i>	6.315	7.459	8.645	9.896	<i>I_a + I_b - I_c</i>	11.234

^a Conversion factor: 505 391 MHz u Å².**Table III.** Transitions (MHz) and Rotational Constants of $\text{CH}_3\text{CH}_2^{10}\text{BF}_2$ in Ground State

Transition	ν_{obsd}	$\Delta\nu$ (obsd - calcd)
5 ₀₅ -4 ₀₄	28 397.67	0.15
5 ₁₅ -4 ₁₄	27 515.10	0.08
5 ₂₄ -4 ₂₃	29 881.27	0.04
5 ₂₃ -4 ₂₂	31 583.99	0.09
6 ₀₆ -5 ₀₅	33 497.20	-0.02
6 ₁₆ -5 ₁₅	32 836.27	-0.03
6 ₁₅ -5 ₁₄	37 784.82	0.03
6 ₂₅ -5 ₂₄	35 677.35	-0.24

A = 8881.86 ± 1.04 MHz *I_a* = 56.902 u Å²
B = 3454.00 ± 0.03 *I_b* = 146.320
C = 2566.70 ± 0.03 *I_c* = 196.903
K = -0.718 99 *I_a + I_b - I_c* = 6.319

Table IV. Stark Coefficients (MHz cm² V⁻²) and Dipole Moments (D) of $\text{CH}_3\text{CH}_2\text{BF}_2$

Transition	<i>M</i>	$\Delta V/E^2 \times 10^6$	
		Obsd	Calcd ^a
4 ₀₄ ← 3 ₀₃	0	-1.379	-1.377
4 ₀₄ ← 3 ₀₃	1	-0.639	-0.633
4 ₀₄ ← 3 ₀₃	2	1.598	1.599
4 ₂₃ ← 3 ₂₂	0	0.321	0.337

$|\mu_a| = 1.51 \pm 0.02$ D $|\mu_c| = 0.0$ (assumed)
 $|\mu_b| = 0.75 \pm 0.02$ D $|\mu_T| = 1.69 \pm 0.02$ D

first potential coefficient in the potential function, $V(\alpha) = (V_2/2)(1 - \cos 2\theta)$, governing the internal rotation of the BF_2 group.

A tentative assignment of the methyl torsional motion is made to the sharp line at 191 cm⁻¹ in the infrared spectrum of the gas phase. This assignment gives a barrier of 834 cm⁻¹ (or 2.38 kcal/mol) to internal rotation of the methyl group and predicts the 2 ← 1 torsional transition at 176 cm⁻¹. One may therefore assign the gas-phase infrared band at 178 cm⁻¹ as the 2 ← 1 methyl torsional transition.

In Table VI are summarized the assignments for the normal modes of ethyldifluoroborane. It should be noted that the descriptions of the motions are idealized and, with a molecule of this low symmetry, one expects extensive coupling between the C-H bending motions and the BF_2 motions. For the isoelectronic molecule, nitroethane, extensive coupling was found²¹ for all of the modes below 1400 cm⁻¹.

The large number of lattice modes indicates two and probably more molecules per primitive cell. There appears to be a one to one correspondence between the lattice modes observed in the Raman and infrared spectra which rules out the centrosymmetric primitive cells. The strong infrared band at 124

For the skeletal motions, the bands at 1388, 1347, 979, and 746 cm⁻¹ are assigned to the antisymmetric BF_2 , symmetric BF_2 , C-C, and C-B stretches, respectively. The polarized Raman line at 408 cm⁻¹ corresponds to the CBF_2 bending mode. On the basis of the vibrational assignment of vinylidifluoroborane,³ the remaining skeletal modes are expected to be at frequencies lower than ~250 cm⁻¹. Since there is only one gas-phase Raman band observed in this frequency region, this polarized Raman band (196 cm⁻¹) is assigned to the CCB bending motion. This vibration is observed at 195 and 209 cm⁻¹ in the infrared spectra of the gas and solid. The BF_2 wag may be assigned to the solid IR band at either 218 or 213 cm⁻¹. From microwave relative intensity measurements, one expects the frequency of the BF_2 torsion to be the lowest of all fundamental motions. Assignment is, therefore, made to the weak gas-phase infrared band at 44 cm⁻¹. With an *F* value of 1.25 cm⁻¹ calculated from the structure given in the microwave section, one obtains $V_2 = 410$ cm⁻¹ = 1.17 kcal/mol for the

Table V. Observed Infrared and Raman Frequencies (cm^{-1}) of $\text{CH}_3\text{CH}_2\text{BF}_2^a$

Infrared		Raman			Assignment
Gas	Solid	Gas	Liquid	Solid	
3166 vw					
2984 m		2983 m,p	2978 m,p	2978 s	$A' \nu_1$ antisymmetric CH_3 stretch
	2972 m		2970 m,p	2972 m	$A'' \nu_{16}$ antisymmetric CH_3 stretch
		2958 s,p	2950 s,p	2947 s	$A' \nu_2$ symmetric CH_3 stretch
	2920 w		2923 vw	2918 vs	$A'' \nu_{17}$ antisymmetric CH_2 stretch
				2901 s	
2908 m	2884	2902 s,p	2892 vs,p	2891 vs	A'_3 symmetric CH_2 stretch
		2871 w,p			Combination and overtones of CH_2 , CH_3 deformations and BF_2 stretches
		2805 vw,p			
		2772 m,p			
		2748 vw,p	2734 w,p	2750 w	
		2740 vw,p			
1471 m (B)	1461 m	1478 w,p		1467 m	$A' \nu_4$ CH_3 antisymmetric deformation
		1466 w,dp	1468 m,dp	1462 w	$A'' \nu_{18}$ CH_3 antisymmetric deformation
				1416 w	?
1403 s (B)	1406 s	1407 vw,p	1404 w,p	1401 m	$A' \nu_5$ CH_2 scissors
1380 vs (A,B)	1384 s	1388 vw,p		1389 w	$A' \nu_6$ BF_2 antisymmetric stretch
1347 s (B)	1364 s				$A' \nu_7$ BF_2 symmetric stretch
	1310 m		1323 w	1310 w	$A' \nu_8$ CH_3 symmetric deformation
1272 w	1263 w				?
1219 s	1248		1239 w,p	1239 w	$A' \nu_9$ CH_2 wag
1212 vs	1195 m				$A'' \nu_{19}$ CH_2 twist
	1178 m				?
			1123 w	1123 m	?
	1054 m	1047 m,p	1046 m,p	1050 m	$A' \nu_{10}$ CH_3 in-plane rock
		1032 w,p			?
1003 w (C)	1001 m		1001 w,dp	998 w	$A'' \nu_{20}$ CH_3 out-of-plane rock
979 w (B)	964 m	978 m,p	978 w,p	979 w	$A' \nu_{11}$ C-C stretch
	872 w				?
	813 w				?
781 w	797 w				?
765 m (C)	765 m				$A'' \nu_{21}$ CH_2 rock
		752 sh,p		751 w	$\text{C}-^{10}\text{B}$ stretch
	754 m	746 s,p	746 s,p	746 s	$A' \nu_{12}$ $\text{C}-^{11}\text{B}$ stretch
	718 w				?
	516 m				?
408 m (A)	409 s	408 m,p	405 w,p	414 m	$A' \nu_{13}$ BF_2 scissors
	218 s				$A' \nu_{14}$ CBF_2 bend
	213 s				
195 m	209 s	196 w,p	201 w,p	205 w	$A'' \nu_{22}$ BF_2 wag
191 m					$A' \nu_{15}$ C-C-B bend
178 w					$A'' \nu_{23}$ CH_3 torsion ($1 \leftarrow 0$)
					CH_3 torsion ($2 \leftarrow 1$)
	140 w				
	124 s ^b				
	89 m			88 vw	
	80 m			80 w	
	69 m			70 w	
	61 w			63 m	Lattice modes
	53 m			54 w	
	49 s			48 m	
	40 w			40 w	
	29 w			30 w	
	25 w			24 m	
44 w					$A'' \nu_{24}$ BF_2 torsion

^a Abbreviations used: m, medium; s, strong; w, weak, v, very; sh, shoulder; p, polarized; dp, depolarized; A, B, and C refer to the infrared band types in the gas phase. ^b The 124- cm^{-1} line may be the BF_2 torsion which has shifted with solidification.

cm^{-1} in the spectrum of the solid is probably the BF_2 torsion which has shifted from 44 cm^{-1} in the gas phase because of the added constraints of the solid state. This is typical behavior for torsional modes.

Discussion

In the present microwave study of ethyldifluoroborane, transitions due to molecules in the ground state as well as the lower vibrational states have been assigned and measured.

Their spectral pattern and relative intensities indicate that these satellites arise from a series of excited states of the same vibrational motion. When comparing the moments of inertia of the first excited state with those of the ground state, the inertial defect, Δ , in the expression $\frac{1}{2}(I_a + I_b - I_c) = I_\alpha - \Delta$, becomes more negative in the excited state. This change in Δ is characteristic for a molecule in an excited state of an out-of-plane vibration.¹⁷ If these satellites were due to molecules in the excited methyl torsional states, from their relative in-

Table VI. Summary of the Fundamental Vibrational Frequencies (cm^{-1}) of Ethyldifluoroborane^a

C_s species	Vibrational no.	Approximate description	cm^{-1}
A'	1	CH ₃ antisymmetric stretch	2984
	2	CH ₃ symmetric stretch	2958
	3	CH ₂ symmetric stretch	2902
	4	CH ₃ antisymmetric deformation	1478
	5	CH ₂ scissors	1407
	6	BF ₂ antisymmetric stretch	1388
	7	BF ₂ symmetric stretch	1347
	8	CH ₃ symmetric deformation	1323*
	9	CH ₂ wag	1219
	10	CH ₃ in-plane rock	1047
A''	11	C-C stretch	979
	12	C-B stretch	746
	13	BF ₂ scissors	456*
	14	CBF ₂ bend	408
	15	C-C-B bend	196
	16	CH ₃ antisymmetric stretch	2970*
	17	CH ₂ antisymmetric stretch	2923*
	18	CH ₃ antisymmetric deformation	1466
	19	CH ₂ twist	1212
	20	CH ₃ out-of-plane rock	1001
	21	CH ₂ rock	765
	22	CBF ₂ bend	215*
	23	CH ₃ torsion	191
	24	BF ₂ torsion	44

^a Values from the gas phase are recorded except for the frequencies indicated with an asterisk.

tensity one would have expected a very low barrier to internal rotation. If this were the case, splittings due to the internal rotation should have been observed.

The variations of the rotational constants with the excited states are plotted in Figure 6. The smooth curve indicates that the excited states of the BF₂ torsion are unlikely to lie close in energy to excited states of other vibrations. This statement is consistent with our vibrational assignment (see Table VI). Based on the vibrational assignment, there will be a better chance of interaction for the fifth BF₂ torsional state with the methyl torsion or CCB bending motion or both. Such an interaction would make it difficult to assign the rotational transitions in the fifth BF₂ torsional state and the first methyl torsional state.

One of the most interesting features in the present study is to find that the eclipsed configuration (conformer (b) in Figure 4) is the most stable rotational conformer of ethyldifluoroborane in the gas phase. Failure to observe other rotamers in the microwave spectrum indicates that if there is any other conformer present, its abundance will be less than approximately 15%.

Our limited isotopic information makes it difficult to obtain a detailed molecular structure of ethyldifluoroborane, on which our discussion of the molecular configuration may be based. However, we have assumed identical structures of ethyl and BF₂ groups in ethyldifluoroborane as those of propane¹⁶ and vinyl difluoroborane,⁸ respectively. Variations of the CB distance and CBF angle have been carried out in order to obtain a least-squares fit to the experimental rotational constant. The result gave $r(\text{CB}) = 1.572 \text{ \AA}$ and $\angle\text{CBF} = 122.2^\circ$.

Boron-carbon bond lengths in three-coordinate boron compounds range from 1.513 Å in ethylnyldifluoroborane²² to 1.60 Å in methyl difluoroborane.²³ A very smooth trend is observed in the boron-carbon bond length in the series of compounds (C₂H)BF₂ (1.513 Å), (C₂H₃)BF₂ (1.532 Å),⁸ and now (C₂H₅)BF₂ (1.572 Å) in which the boron-carbon bond

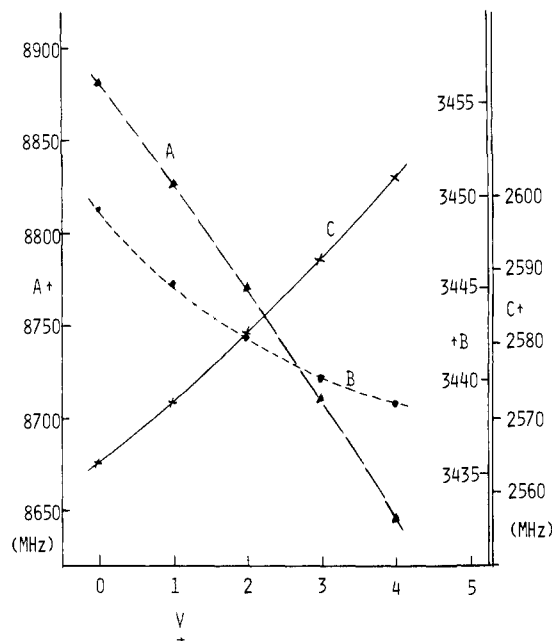


Figure 6. Variation of rotational constants with increasing quantum number of the BF₂ torsion.

lengthens as the hybridization of the carbon atom changes from sp to sp² to sp³. This behavior appears reasonable on the basis of decreasing s character in the B-C bond and thus the value of 1.572 Å which has been determined in this study is in accord with other reported values of this parameter.²⁴

As stated in the Introduction one of the driving forces for this investigation was a theoretical study⁹ in which the favored structure for ethylborane, C₂H₅BH₂, was found to be the staggered conformation (see Figure 4a). However, the barrier to rotation about the C-B bond was 0.2 kcal/mol and whether that small an energy difference in calculations of the type utilized is significant is questionable. For any theory to be viable, it must correctly predict experimental results. Unfortunately ethylborane cannot be isolated and studied experimentally and we were forced to study a compound in which the boron hydrogens have been substituted by fluorine.

The experimental structure of ethyldifluoroborane, C₂H₅BF₂, does not correspond to that calculated⁹ for ethylborane but instead exists in an eclipsed conformation (Figure 4b). In addition the barrier to rotation about the C-B bond is significantly larger (1.17 kcal/mol) than that calculated for the hydrogen compound. Although substitution of fluorine for hydrogen could certainly have profound effects on the electronic structure and hence on the most stable conformation of the molecule, there appears to be a contradiction between our results and the theory set forth for XCH₂Y molecules.⁹ In the theoretical treatment of these molecules it was stated that when X (a methyl group in this case) is a σ donor and when Y (the BF₂ group) is a π acceptor, the staggered conformation should be stabilized by π donation from the highly populated C-X bond into the Y acceptor orbital. However, it was also stated that, in addition to bond interaction effects, other interactions between X and Y, such as direct Coulomb attractive or repulsive energies and steric forces, should be considered. Although it can be argued that the methyl group is not a strong σ donor, it is clear that forces other than π interactions are dominating in C₂H₅BF₂.

Although the origin of the structure and the substantial barrier to rotation about the C-B bond are open to question, it appears that nonbonded fluorine-hydrogen steric interactions could account for some stability of the eclipsed structure. If one calculates the nonbonded distance between the fluorine

atoms and the methylene hydrogens using our experimental structure for $C_2H_5BF_2$, a value of 2.82 Å is obtained. Similarly, a calculation using the staggered conformation yields a nonbonded H-F distance of 2.65 Å. Although both distances are greater than the sum of the van der Waals radii (2.55 Å),²⁵ the eclipsed conformation clearly minimizes steric interactions. The closest nonbonded H-F distance between the fluorines and the methyl hydrogens (assuming a staggered C_2H_5 conformation) is 4.06 Å and thus steric forces between the BF_2 group and the methyl group are not a factor. It should be pointed out that these nonbonded distances are based on imprecise structural parameters; however, the same trend will be observed regardless of small changes in bond distances and angles in this molecule. With the same assumptions for the structural parameters, even smaller H-F distances would be expected for other possible conformations (Figures 4c and 1d). It should also be mentioned that a charge alternation effect²⁶ as induced by the fluorine atoms may also favor the eclipsing of the BF bond with the CC bond.

Interestingly, steric repulsive effects are cited⁹ in the $C_2H_5BH_2$ molecule as raising the methyl rotational barrier 0.65 kcal/mol in going from the more stable staggered form to the eclipsed form. The calculated rotational barrier about the C-C bond in $C_2H_5BH_2$ is 3.2 kcal/mol, which is very close to the calculated²⁷ ethane barrier (3.3 kcal/mol). The experimental value²⁸ of the rotational barrier in C_2H_6 is 2.9 kcal/mol and if our assignment of the gas-phase infrared band at 191 cm^{-1} is correct, a barrier to internal rotation of the methyl group of 2.38 kcal/mol is obtained. Thus, we see a substantial lowering of this value relative to ethane and again our experimental results are not in accord with the theoretical calculations on $C_2H_5BH_2$. There is a lack of data on the variation of C-C rotational barriers with substitution of various groups and the reason for this decrease is not clear. However, it can safely be assumed that the BF_2 group is an electron-withdrawing group which would lower the electron density in the carbon-carbon bond and thus reduce the barrier to rotation.

Another molecule which provides an interesting comparison with $C_2H_5BF_2$ in terms of conformation and rotational barrier is the isoelectronic nitroethane molecule, $C_2H_5NO_2$. Microwave spectroscopy²⁹ and matrix and gas-phase infrared spectra^{20,30} have shown that the nitro group is undergoing free internal rotation. Clearly these molecules, although isoelectronic, have very different electronic structures.

A low-temperature ^{19}F NMR study failed to show any indication of nonequivalent fluorine atoms which would signify that the internal rotation of the BF_2 group was slow with respect to the NMR time scale. This is not surprising in view of the low barrier which has been determined for this rotation. At ambient probe temperature the NMR spectrum consists of a single resonance which is a quartet ($J_{BF} = 82\text{ Hz}$). As the

temperature is lowered the coupling disappears and the line shape follows the pattern which is now well established for "thermal decoupling".³¹ At $-120\text{ }^\circ\text{C}$ the spectrum consists of a single, sharp line with no apparent spin coupling.

In conclusion, the structure determination of $C_2H_5BF_2$ and the barriers to internal rotation which have been obtained show no correspondence to theoretical calculations concerning the $C_2H_5BH_2$ molecule. It would appear that the disparity in results clearly dictate that a theoretical study on this molecule be carried out.

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