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Microwave, Infrared, Raman, and NMR Spectra, Structure, Dipole Moment, and Barrier to Internal Rotation of Cyclopropyldifluoroborane

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Abstract: The microwave spectra of c-$C_3H_5{}^{10}BF_2$ and c-$C_3H_5{}^{11}BF_2$ have been recorded from 26.5 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 five excited states of the $^{11}BF_2$ torsion. The rotational constants for the ground vibrational state are as follows: for c-$C_3H_5{}^{11}BF_2$, A = 6929.79 ± 1.03, B = 2467.69 ± 0.01, and C = 2119.84 ± 0.01 MHz; for c-$C_3H_5{}^{10}BF_2$, A = 6931.80 ± 0.95, B = 2474.00 ± 0.01, and C = 2124.43 ± 0.01 MHz. From a diagnostic least-squares adjustment to fit the six rotational constants, the following structural parameters were obtained: $r(B-F) = 1.328 \pm 0.004$ Å, $r(B-C) = 1.589 \pm 0.004$ Å, $r(C_2-C_3) = 1.496 \pm 0.003$ Å, $\angle FBF = 115.9 \pm 0.9°$, $\angle C_2C_1B = 115.0 \pm 0.8°$, $\angle(\text{tilt}) = 2.9 \pm 1.8°$. These parameters are compared to the corresponding ones in some other organoboranes. The total dipole moment was determined to be 2.18 ± 0.06 D with components $\mu_a = 2.17 \pm 0.5$ D and $\mu_b = 0.18 \pm 0.14$ D. The infrared (3500–40 cm^{-1}) and Raman spectra (3500–0 cm^{-1}) have been recorded for both the gas and solid. Additionally, the Raman spectrum of the liquid was recorded and qualitative depolarization values were obtained. All of the normal modes have been assigned. The BF_2 internal torsional mode was observed at 70 cm^{-1} in both the infrared and Raman spectra of the gas, and a twofold periodic barrier of 4.23 kcal/mol was calculated. These data are consistent with the relative intensity measurements in the microwave spectrum. This barrier value is compared to other BF_2 barriers in other organoboranes and to the similar quantity in some isoelectronic organonitro compounds. Carbon-13 NMR studies of c-$C_3H_5BF_2$ demonstrate that the C_β chemical shift is deshielded by approximately 7.6 ppm with respect to cyclopropane, implying substantial mesomeric interaction between the ring and the BF_2 substituent. Multinuclear NMR studies (^1H, ^{11}B, ^{13}C, ^{19}F, ^{31}P) of the 1:1 adduct of c-$C_3H_5BF_2$ with $P(CH_3)_3$ demonstrate that complexation through the empty boron p orbital effectively eliminates the mesomeric interaction which is observed in the parent Lewis acid.

Introduction

For several years in our laboratories, we have been interested in the structure and bonding of organoboranes. Of particular interest have been those compounds in which an electron-rich organic moiety is bonded to an electron-deficient trigonal boron atom. Nuclear magnetic resonance, microwave, infrared, and Raman spectroscopic studies have been extremely valuable in elucidating the conformational properties and bonding in vinylboranes, phenylboranes, and boron-substituted heterocycles.

When one considers the bent-bond valence bond description of the carbon–carbon double bond and the strained cyclopropane ring, it becomes evident that there is a close analogy between the two systems. Our studies of vinylboranes have shown that delocalization of the π-electron density occurs and that the molecules adopt the stabilized planar geometry. Currently, there is considerable interest in the conjugating ability of the cyclopropyl system with respect to the extraannular substituents. The bonding in cyclopropane as described by Walsh[1] and revised by Hoffman[2] predicts specific substituent effects and conformations depending upon whether the substituent is a mesomeric acceptor or donor. The symmetrical conformation of substituted cyclopropane (Figure 1a) allows the ring to behave as a mesomeric acceptor while the bisected conformation (Figure 1b) should be the more stable geometry for an electron-deficient substituent which can accept π-electron density from the ring.

The synthesis of several cyclopropylboranes was reported by Cowley and Furtsch.[3] NMR chemical shift data (^{11}B, ^{19}F) gave some indication of a π-type interaction, but low-temperature studies did not demonstrate that a preferred geometry was adopted. No structural studies of these compounds have been reported nor have infrared and Raman studies been used to identify conformers. We have undertaken such studies on the cyclopropyldifluoroborane molecule, and the results are reported herein. Since we have previously used ^{13}C NMR to study π-delocalization in vinylboranes, we report here the ^{13}C results for c-$C_3H_5BF_2$ and compare them to the parent molecule, cyclopropane, as well as to vinyldifluoroborane.[4] We have also prepared the 1:1 adduct of c-$C_3H_5BF_2$ with $P(CH_3)_3$ and have used multinuclear magnetic

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† Taken in part from the theses of Z. Szafran and S. A. Johnston which will be submitted to the Department of Chemistry in partial fulfillment of their Ph.D. degrees.

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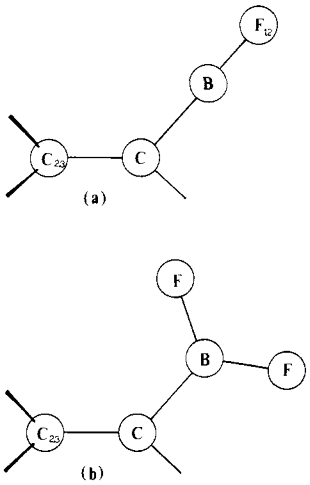

Figure 1. Possible conformations of cyclopropyldifluoroborane: (a) symmetrical; (b) bisected.

resonance experiments to study the effect of the elimination of the mesomeric interaction in cyclopropyldifluoroborane.

Experimental Section

Tin(IV) chloride (Allied), cyclopropyl bromide (Columbia Organic Chemicals), boron trichloride (Stauffer), and antimony trifluoride (Ozark Mahoning) were obtained commercially. The tin(IV) chloride and cyclopropyl bromide were used without further purification. The boron trichloride was checked as to vapor pressure and fractionated if necessary, and the antimony trifluoride was sublimed before use. Trimethylphosphine was obtained commercially (Strem Chemical Co.) and purified by trap-to-trap fractionation. Standard high-vacuum techniques were employed on an all-glass vacuum system equipped with greaseless stopcocks[5] in all cases except in the preparation of cyclopropyltin [(c-$C_3H_5)_4Sn$], which was prepared under an inert atmosphere by using known literature methods.[6]

In a typical reaction, cyclopropyltin (5.9 mmol) was syringed into a stopcock tube, which was then attached to the vacuum system, and freeze–thaw degassed. BCl_3 (11.8 mmol) was then condensed into the stopcock tube at −196 °C. The tube was isolated from the vacuum system and allowed to warm to room temperature. Reaction was evidenced by formation of a precipitate and a solution color change from clear to red brown. Volatiles were removed and fractionated on a low-temperature fractionation column. Cyclopropyldichloroborane (c-$C_3H_5BCl_2$) was obtained in 85% yield (10 mmol).

In the preparation of cyclopropyldifluoroborane, c-$C_3H_5BCl_2$ was condensed onto freshly sublimed antimony trifluoride. The system was warmed to room temperature and allowed to stand for a period of 15 min. Volatiles were fractionated on a low-temperature distillation column, resulting in >90% yield of c-$C_3H_5BF_2$. The purity of the cyclopropyl compounds was checked by comparison to published data[3] of ^{11}B and ^{19}F NMR and infrared spectra.

The 1:1 adduct (c-$C_3H_5)F_2B{\cdot}P(CH_3)_3$ was prepared by the reaction of equimolar amounts of the Lewis acid and base. The $P(CH_3)_3$ was condensed onto c-$C_3H_5BF_2$ in an evacuated stopcock tube at boiling liquid-nitrogen temperature. The tube was then isolated from the vacuum system and then warmed slowly to room temperature. The adduct is a white, crystalline solid with a melting point of approximately 34 °C. Integration of the 90.0-MHz ^1H NMR spectrum of this adduct exhibited the expected 9:4:1 area ratios of the resonances of the methyl hydrogens:C_β hydrogens:C_α hydrogen.

^{13}C (20.0-MHz; 25.2-MHz) NMR spectra were obtained on Varian Associates CFT-20 and XL-100-15 spectrometers. ^1H (90.0-MHz) NMR spectra were obtained on a Perkin-Elmer R-32 spectrometer. ^{11}B (32.1-MHz), ^{19}F (94.1-MHz), and ^{31}P (40.5-MHz) NMR spectra were obtained on a Varian Associates XL-100-15 spectrometer. NMR spectra of c-$C_3H_5BF_2$ were obtained in a 5-mm o.d. NMR tube as ca. a 50% (v/v) solution in $CDCl_3$ which also provided the deuterium lock signal and served as an internal reference for the ^{13}C spectra. NMR spectra of (c-$C_3H_5)F_2B{\cdot}P(CH_3)_3$ were obtained in a 5-mm o.d. NMR tube as ca. a 10% solution in $CDCl_3$ which also provided the deuterium lock signal. Chemical shifts were measured in relation to external Me_4Si (^1H, ^{13}C), $BF_3O(C_2H_5)_2$ (^{11}B), F_3CCOOH (^{19}F) and 85% ortho-H_3PO_4 (^{31}P). A negative sign denotes increased shielding. Chemical shifts are accurate to ±0.5 ppm.

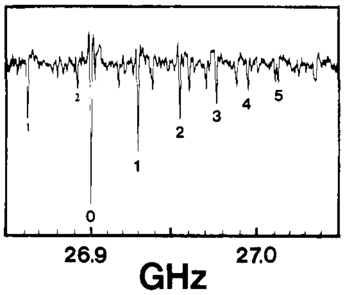

Figure 2. Rotational transitions for the 6_{06}–5_{05} transition in the $v = 0$, 1, 2, 3, 4, and 5 excited states of the torsional mode and the $v = 1$ and 2 excited states of the BF_2 wagging motion.

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 Stark cell at Dry Ice temperature. Frequency measurements are estimated to be accurate to ±0.1 MHz. Due to decomposition of the sample in the cell, resampling was necessary at 1-h intervals.

The mid-infrared spectra from 3500–400 cm^{-1} were recorded on a Perkin-Elmer Model 621 spectrophotometer. A 10-cm cell with cesium iodide windows was used to obtain the spectrum of the gaseous phase. The spectrum of the solid was obtained at 20 K by using a Spectrim spectrometric sample conditioner controlled by a Lake Shore Electronics, Inc., cryogenic temperature indicator/controller. The sample was deposited on a cesium iodide plate and annealed until no further change in the spectrum was observed.

The far-infrared spectra were recorded on a Digilab FTS-15B interferometer using a 6.25-μm beamsplitter (450–100 cm^{-1}) and a 12.5-μm beamsplitter (220–40 cm^{-1}). The gas cell was equipped with polyethylene windows. Interferograms were obtained after 5000 scans each of the sample and empty cell and were transformed by using a boxcar apodization function. Theoretical resolution is 0.5 cm^{-1} for the gas-phase data. The data for the solid phase were obtained by using the cryostat described previously. The sample was deposited on a silicon substrate and annealed until no further change in the spectrum was observed. Interferograms were obtained after 500 scans of the sample and empty cell and were transformed by using a boxcar apodization function. Theoretical resolution is 2 cm^{-1} for the solid-phase data.

The Raman spectra were recorded on a Cary 82 spectrophotometer equipped with a Spectra-Physics Model 171 argon ion laser. The spectrum of the gas phase was recorded by using the standard Cary multipass accessory. The laser power was 1.5 W at the sample, using the 514.5-nm line. The spectrum of the liquid was obtained at −95 °C by using a Miller–Harney[7] type cell with a power of 1 W at the sample. The spectrum of the solid was obtained by using a low-temperature cell equipped with quartz windows. The sample holder consists of a solid brass plate held at an angle of 15° from the normal. The substrate was held at approximately 77 K, and the film was annealed until no change in the spectrum was observed. Spectra obtained by using the cryostat described above yielded no additional information. Raman frequencies are expected to be accurate to ±1 cm^{-1}.

Microwave Spectrum

Depending on the orientation of the BF_2 group relative to the cyclopropyl ring, there are two possible conformers for cyclopropyldifluoroborane. As can be seen from Figure 1, both a and b have a plane of symmetry. A structure extrapolated from the parameters in cyclopropyl chloride[8] and vinyldifluoroborane[4] was used to make a preliminary prediction of the rotational transitions for both conformers. On the basis of these 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 and one expects both a- and b-type transitions.

The microwave spectrum shows essentially R-branch transitions with a-type selection rules. The initial assignment was made on the basis of the rigid-rotor model and the qualitative Stark effect.

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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 2). Listed in Table I are the rotational transitions of c-$C_3H_5{}^{11}BF_2$ in both the ground and excited vibrational states. Since the measured excited-state lines in Table I 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. However an approximation of 72 ± 15 cm^{-1} can be given for the BF_2 torsional mode from the relative intensities of the excited-state lines with respect to the corresponding ground-state line.

For each rotational transition, frequencies have been measured up to the fifth BF_2 torsional state. The deviation of observed frequencies from those calculated using the rigid-rotor model (Tables I and II) probably arises from the centrifugal distortion. Ground-state transitions due to the ^{10}B isotopic species have also been assigned and are listed in Table III. No splitting due to the internal rotations of the BF_2 group or the boron quadrupole interaction was observed.

From Tables I and III, it is seen that the measured rotational transitions for the ^{10}B species fall within 100 MHz of the corresponding transitions in the ^{11}B species. This indicates that the boron atom is very close to the center of mass in cyclopropyldifluoroborane.

A second series of lines can also be seen in Figure 2. These lines are associated with the next to the lowest vibrational frequency. These satellites are assigned as the excited states of the BF_2 wag. Listed in Table IV are the rotational transitions of these excited states of cyclopropyldifluoroborane along with their rotational constants.

Dipole Moment

Stark effect measurements have been made on the $M = 1$, 2, and 3 components of the $5_{14} \leftarrow 4_{13}$ transition and the $M = 1$ component of the $6_{25} \leftarrow 5_{24}$ transition of c-$C_3H_5{}^{11}BF_2$ in its ground vibrational state. Electrical fields were calibrated from the measured Stark effects of the $2 \leftarrow 1$ transition and the $3 \leftarrow 2$ transition of the OCS molecule and its dipole moment of 0.71521 D.[9] Analysis of the data has been carried out by the method of Golden and Wilson,[10] and the results are listed in Table V. For the "symmetrical" conformer (Figure 1a), μ_b should be zero, and for the "bisected" conformer (Figure 1b), $\mu_c = 0$. The values for the rotational constants indicate that the "bisected" conformer is present, and this is supported by the vibrational study. The resultant dipole moment (2.18 D) is larger than that of ethyldifluoroborane (1.69 D),[11] vinyldifluoroborane (1.74),[4] and methyldifluoroborane (1.67 D).[12] It is however considerably smaller than that of nitrocyclopropane (3.78 D).[13]

Structure

One of the goals of this study was to determine the conformation and structure of cyclopropyldifluoroborane. The two most likely conformers, the symmetrical conformation and the bisected conformation, are shown in Figure 1. Both the ^{11}B and ^{10}B isotopic species have approximately the same value of $I_a + I_b - I_c$ in the ground state, 39.323 and 39.295 amu Å^2, respectively, indicating that the boron atom lies in the plane of symmetry. Therefore we only need to consider the two conformers shown in Figure 1.

It is possible to distinguish between the two proposed conformations by using the values for the inertial defects. The structural parameters for the cyclopropyl ring have been accurately determined for cyclopropyl chloride.[8] The distances and angles found for the cyclopropyl ring by Schwendeman et al.[8] for cyclopropyl

Table I. Rotational Transitions (MHz) of c-$C_3H_5{}^{11}BF_2$ in $v = 0$, 1, 2, 3, 4, and 5 Vibrational States

transition	$v = 0$		$v = 1$		$v = 2$		$v = 3$		$v = 4$		$v = 5$	
	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)	ν(obsd)	$\Delta\nu$(obsd − calcd)
$6_{06}-5_{05}$	26 959.30	[a]	26 928.56	0.19	26 953.72	0.12	26 975.67	0.21	26 994.82	0.16	27 011.34	0.01
$6_{15}-5_{14}$	28 392.70	0.20	28 413.89	0.13	28 431.73	0.21	28 446.35	0.11	28 458.16	−0.17	28 467.34	0.20
$6_{25}-5_{24}$	27 437.34	−0.01	27 463.53	0.01	27 486.23	0.18	27 505.58	−0.04				
$6_{24}-5_{23}$	28 061.96	0.04	28 085.49	0.11			28 121.80	0.11	28 135.16	0.13		
$7_{07}-6_{06}$	31 175.48	0.05	31 209.75	0.08	31 240.13	−0.03	31 266.70	0.09	31 290.04	0.01		
$7_{17}-6_{16}$	30 678.98	0.22	30 715.98	0.05	30 749.10	0.22	30 778.30	0.04	30 804.01	0.26	30 826.58	0.06
$7_{16}-6_{15}$	33 029.34	0.01	33 054.44	−0.08	33 075.69	−0.03	33 093.18	−0.08	33 108.19	0.33	33 118.60	−0.11
$7_{26}-6_{25}$	31 961.27	−0.14	31 991.95	−0.20	32 018.64	−0.04	32 041.60	−0.11	32 060.92	−0.28	32 077.24	−0.14
$7_{25}-6_{24}$	32 896.13	−0.13	32 922.81	−0.06	32 944.48	−0.22	32 963.61	−0.07	32 978.34	−0.15		
$8_{08}-7_{07}$	35 408.58	−0.18	35 448.84	−0.15	35 484.64	−0.29	35 516.07	−0.17	35 543.79	−0.25		

[a] Not used in fit.

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(12) R. E. Naylor, Jr., and E. B. Wilson, *J. Chem. Phys.*, **26**, 1057 (1957).

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Table II. Rotational Constants (MHz) and Moments of Inertia (amu Å^2)[a] of c-$C_3H_5{}^{11}BF_2$ in the $\upsilon = 0, 1, 2, 3, 4,$ and 5 States

	$\upsilon = 0$	$\upsilon = 1$	$\upsilon = 2$	$\upsilon = 3$	$\upsilon = 4$	$\upsilon = 5$
A	6929.79 ± 1.03	6904.65 ± 0.89	6883.47 ± 1.40	6857.92 ± 0.85	6839.77 ± 1.61	6820.23 ± 2.70
B	2467.69 ± 0.01	2468.96 ± 0.01	2469.93 ± 0.02	2470.67 ± 0.01	2471.19 ± 0.02	2471.40 ± 0.02
C	2119.84 ± 0.01	2122.86 ± 0.01	2125.57 ± 0.02	2128.04 ± 0.01	2130.19 ± 0.02	2132.17 ± 0.02
κ	−0.85534	−0.85522	−0.85523	−0.85510	−0.85516	−0.85525
I_a	72.930	73.196	73.421	73.695	73.890	74.102
I_b	204.803	204.700	204.618	204.556	204.513	204.496
I_c	238.410	238.071	237.767	237.491	237.252	237.031
$I_a + I_b - I_c$	39.323	39.825	40.272	40.760	41.151	41.567

[a] Conversion factor 505 391 MHz amu Å^2.

Table III. Transitions, Rotational Constants (MHz), and Moments of Inertia (amu Å^2)[a] of c-$C_3H_5{}^{10}BF_2$ in the Ground State

transition	ν(obsd)	$\Delta\nu$(obsd − calcd)
6_{06}-5_{05}	26959.30	−0.03
6_{15}-5_{14}	28461.19	0.07
6_{25}-5_{24}	27501.90	0.01
7_{07}-6_{06}	31243.23	−0.04
7_{17}-6_{16}	30747.10	0.06
7_{26}-6_{25}	32036.07	−0.12

$A = 6931.80 \pm 0.95$ $I_a = 72.909$
$B = 2474.00 \pm 0.01$ $I_b = 204.281$
$C = 2124.43 \pm 0.01$ $I_c = 237.895$
$\kappa = -0.854\ 56$ $I_a + I_b - I_c = 39.295$

[a] Conversion factor 505 391 MHz amu Å^2.

Table IV. Transitions, Rotational Constants (MHz), and Moments of Inertia (amu Å^2) of c-$C_3H_5{}^{11}BF_2$ in the $\upsilon = 1$ and 2 Vibrational States of the BF_2 Wag

	$\upsilon = 1$		$\upsilon = 2$	
transition	ν(obsd)	$\Delta\nu$(obsd − calcd)	ν(obsd)	$\Delta\nu$(obsd − calcd)
6_{06}-5_{05}			26 891.79	0.24
6_{15}-5_{14}	28 357.41	0.15	28 376.66	0.20
6_{24}-5_{23}	28 026.30	0.06	28 047.71	0.09
7_{07}-6_{06}	31 120.19	0.11		
7_{17}-6_{16}	30 632.65	0.08	30 672.81	0.08
7_{16}-6_{15}	32 987.93	−0.05	33 011.00	−0.11
7_{26}-6_{25}	31 917.71	−0.20	31 948.51	−0.23
7_{25}-6_{24}	32 854.93	−0.04	32 878.70	−0.06
8_{08}-7_{07}	35 356.39	−0.08	35 399.5	−0.11

	$\upsilon = 1$	$\upsilon = 2$
A	6934.61 ± 0.85	6904.68 ± 1.22
B	2464.97 ± 0.01	2465.83 ± 0.02
C	2116.39 ± 0.01	2119.79 ± 0.02
κ	−0.85529	−0.85533
I_a	72.880	73.195
I_b	205.030	204.958
I_c	238.799	238.416
$I_a + I_b - I_c$	39.111	39.737

Table V. Stark Coefficients (MHz cm^2 V^{-2}) and Dipole Moments (D) of c-$C_3H_5{}^{11}BF_2$

		$10^6\Delta\upsilon/E^2$	
transition	$\lvert M \rvert$	obsd	calcd
$5_{14} \leftarrow 4_{13}$	1	−1.18	−1.22
$5_{14} \leftarrow 4_{13}$	2	−2.41	−2.34
$5_{14} \leftarrow 4_{13}$	3	−4.17	−4.20
$6_{25} \leftarrow 5_{24}$	1	−6.06	−6.06

$\lvert\mu_a\rvert = 2.17 \pm 0.05$ D $\lvert\mu_c\rvert = 0.0$ (assumed)
$\lvert\mu_b\rvert = 0.18 \pm 0.14$ D $\lvert\mu_t\rvert = 2.18 \pm 0.06$ D

Table VI. Diagnostic Least-Squares Adjustment of the Structural Parameters in c-$C_3H_5BF_2$

parameter	starting value[a]	estd uncertainty	adjustd value
$r(C_1–C_2)$, Å	1.514	0.010[b]	1.514 ± 0.008
$r(C_1–C_3)$, Å	1.514	0.010[b]	1.514 ± 0.008
$r(C_2–C_3)$,[c] Å	1.486	±0.02	1.496 ± 0.003
r(B–C), Å	1.572	±0.02	1.589 ± 0.004
r(B–F),[d] Å	1.331	±0.01	1.328 ± 0.004
$r(C–H_{cis})$, Å	1.086	fixed	
$r(C–H_{trans})$, Å	1.082	fixed	
$r(C–H_{sec})$, Å	1.079	fixed	
$\angle C_2C_1C_3$,[c] deg	60	1.0	59.2 ± 0.2
∠CCH(cis), deg	116.2	fixed	
∠CCH(trans), deg	116.2	fixed	
∠CCH(sec), deg	116.1	fixed	
$\angle BC_1C_2$, deg	114.6	±1.0	115.0 ± 0.8
∠F-B-F, deg	116.0	±1.0	115.9 ± 0.9
∠(tilt), deg	0.0	±10.0	2.9 ± 1.8

	^{11}B		^{10}B	
rotational const	obsd	obsd − calcd	obsd	obsd − calcd
A	6929.79 ± 1.03	−1.25	6931.80 ± 0.95	+1.27
B	2467.69 ± 0.01	−0.03	2474.00 ± 0.01	−0.01
C	2119.84 ± 0.01	−0.02	2124.43 ± 0.01	−0.01

[a] Taken from ref 4 and 8, r(B–C) is taken from ref 11. [b] These two parameters were varied equally to preserve the symmetry. [c] Note that these two parameters are not independent. [d] The B-F distances were varied equally.

chloride and the distances and angles found for the BF_2 group by Durig et al.[4] for vinyldifluoroborane can be combined to give an assumed structure for c-$C_3H_5BF_2$. For the symmetrical conformation, where the b principal axis is perpendicular to the symmetry plane, the value for the inertial defect $\Delta_b = I_a - I_b + I_c = 133.94$ amu Å^2 and $\Delta_c = I_a + I_b - I_c = 29.38$ amu Å^2. For the bisected conformation where the c principal axis is perpendicular to the plane of symmetry the value for the inertial defect $\Delta_b = 107.12$ amu Å^2 and $\Delta_c = 40.12$ amu Å^2. The experimental values are 106.54 amu Å^2 for Δ_b and 39.32 amu Å^2 for Δ_c which are closer to the values obtained for the bisected conformer. From these values, it is concluded that the bisected conformation is the preferred conformer with the BF_2 group lying in the plane of symmetry. The Raman depolarization data support this conclusion since both the symmetric and asymmetric BF_2 stretches are clearly polarized (see next section).

Penn and Boggs[14] have shown that analysis of the planar moments of substituted cyclopropyl derivatives studied by microwave spectroscopy indicates a shortening of the C_2–C_3 bond opposite an unsaturated substituent compared with the corresponding bond length opposite a saturated substituent. Penn and Boggs[14] have shown by using eq 1, which assumes the H and C coordinates

$$r(\text{Å}) = 1.515 + 4.29 \times 10^{-2}[P_{zz} - 20.34] \qquad (1)$$

change by the same amount, and the moments of cyclopropyl chloride as a reference that the bond length, r, is related to the planar moment, P_{zz}. Using this equation one obtains a value of 1.486 Å for the C_2–C_3 bond distance in c-$C_3H_5BF_2$. Utilizing this value for the C_2–C_3 bond length, we obtained the structural parameters by allowing them to vary, using the method of diagnostic least squares as described by Curl.[15] The initial values with the estimated uncertainties of the remaining parameters were taken from cyclopropyl chloride[8] and vinyldifluoroborane[4] for the

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(14) R. E. Penn and J. E. Boggs, *Chem. Commun.*, 666 (1972).
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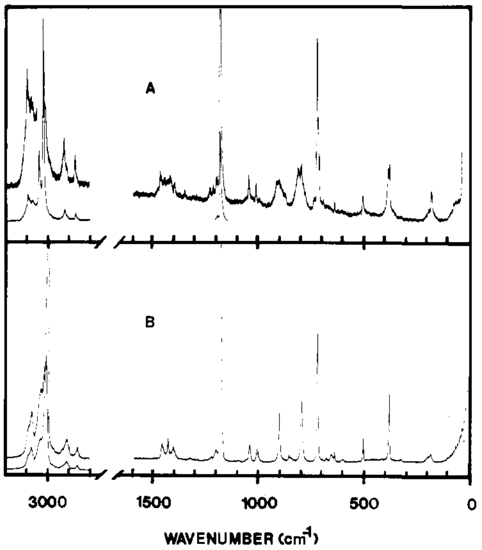

Figure 3. Raman spectra of gaseous (A) and liquid (B) cyclopropyldifluoroborane.

parameter involving the ring and BF_2 moiety, respectively. The refined parameters and their relative uncertainties are given in Table VI and the calculated rotational constants agree well with the experimental values.

Vibrational Assignment

The normal vibrations of the bisected conformer (Figure 1b) span the irreducible representations 16 A′ + 11 A″. Both symmetry species are Raman and infrared active. Motions which preserve the plane of symmetry (A′) give rise to polarized Raman bands and are expected to have A, B, or A/B hybrid infrared gas-phase contours. Depolarized Raman bands correspond to motions which destroy the plane of symmetry (A″) which should have C-type infrared gas-phase contours. Assignment of the spectra was made by using the Raman depolarization data, infrared gas-phase band contours, and group frequency correlations (see Table VII).

There are three motions associated with the carbon atoms in the cyclopropyl ring. The ring-breathing mode appears as the strongest band in the Raman spectrum (see Figure 3) at 1189 cm^{-1}. The two ring deformations are assigned to the only two bands of reasonable intensity within the characteristic region.[16] The depolarized band at 910 cm^{-1} is assigned to the A″ ring deformation, and the polarized band at 806 cm^{-1} is assigned to the A′ ring deformation.

The antisymmetric CH_2 stretch (A″) appears as a depolarized Raman band at 3096 cm^{-1}. The other antisymmetric CH_2 stretch (A′) appears as a weak band in the Raman spectrum of the gas at 3050 cm^{-1}. The symmetric CH_2 stretches occur at 3080 cm^{-1} for the A″ mode and at 3030 cm^{-1} for the A′ mode. The C–H stretch on the carbon which is attached to the boron atom is assigned to the polarized shoulder at 3102 cm^{-1}.

The assignment of the bands associated with the BF_2 moiety was fairly straightforward. The BF_2 asymmetric stretch for the ^{11}B isotope occurs at 1466 cm^{-1} and that for the ^{10}B isotope at 1488 cm^{-1} in the infrared spectrum of the solid (see Figure 4). The symmetric BF_2 stretch is assigned to a B-type band centered at 1355 cm^{-1}. The A-type band at 514 cm^{-1} is assigned to the BF_2 scissors. The BF_2 rock occurs at 386 cm^{-1}, and the BF_2 wag occurs at 206 cm^{-1}. These bands fall well within the regions suggested from the corresponding modes in vinyldifluoroborane[4] and ethyldifluoroborane.[11] The two ring-boron bends occur at 330 cm^{-1} for the A″ motion and at 210 cm^{-1} for the A′ motion. The B–C stretch is assigned to the polarized Raman band at 731 cm^{-1}.

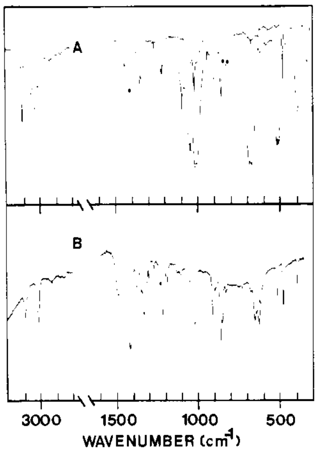

Figure 4. Infrared spectra of gaseous (A) and solid (B) cyclopropyldifluoroborane.

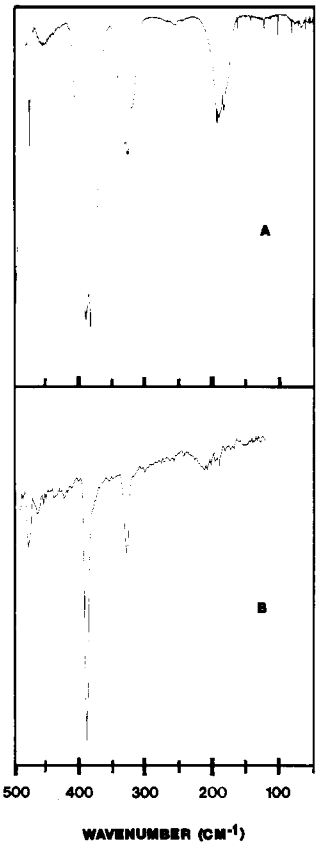

Figure 5. Far-infrared spectra of gaseous (A) and solid (B) cyclopropyldifluoroborane.

The BF_2 torsion is assigned to a very weak band in the far-infrared region at approximately 69 cm^{-1}. This is very close to the frequency predicted from the microwave data (72 ± 15 cm^{-1}). Two weak, broad, featureless bands at 460 and 250 cm^{-1} in the far-infrared spectrum of the gas (see Figure 5) are assigned to combinations of the BF_2 torsion with the BF_2 rock and BF_2 wag, respectively. Using 69 cm^{-1} as the torsional frequency, one obtains V_2 = 1485 cm^{-1} = 4.23 kcal/mol for the first potential coefficient in the potential function $V(\alpha) = (V_2/2)(1 - \cos 2\alpha) + (V_4/2)(1 - \cos 4\alpha)$, governing the internal rotation of the BF_2 group (V_4 was assumed to be zero). The reduced internal rotation constant about the top axis, F, was calculated by using the structural parameters in Table VI and has a value of 0.821 cm^{-1}.

The remaining motions to be assigned are those associated with the CH_2 groups on the ring. The CH_2 deformations occur at 1438 cm^{-1} for the A″ mode and at 1414 cm^{-1} for the A′ mode. The CH_2 twists occur at 1104 and 1049 cm^{-1} for the A″ and A′ modes, respectively. The A′ CH_2 rock is assigned to a band appearing

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[16] C. J. Wurrey and A. B. Nease in "Vibrational Spectra and Structure", Vol. VII, J. R. Durig, Ed., Elsevier, New York, 1978, Chapter 1.

Table VII. Observed Infrared and Raman Frequencies (cm^{-1}) of c-$C_3H_5BF_2$[a]

infrared		Raman				
gas	solid	gas	liquid	solid	assignt	
		3102 p, m			ν_1	CH stretch
3102 m	3091 m	3096 dp, w	3098 dp, sh	3098 m	ν_{17}	CH_2 antisymmetric stretch
		3080 ?, m	3086 dp, m	3088 s	ν_{18}	CH_2 symmetric stretch
3048 m		3050 p, s	3042 p, sh	3042 s	ν_2	CH_2 antisymmetric stretch
3024 s	3011 s	3030 p, vs	3018 p, vs	3019 vs	ν_3	CH_2 symmetric stretch
3005 sh						
	2942 w					
		2928 p, m	2918 p, w	2920 w, br		
	2870 w	2874 p, m	2868 p, w			
	1488 sh					$^{10}BF_2$ asymmetric stretch
	1477 sh					
1461 sh	1466 sh	1470 p, w	1468 p, m	1463 m	ν_4	$^{11}BF_2$ asymmetric stretch
1433 sh	1438 sh	1450 dp, w, br	1438 dp, m	1439 m	ν_{19}	CH_2 deformation
1427 sh	1423 sh	1427 p, w				
1419 s	1402 vs	1405 p, w	1414 p, m	1414 m, br	ν_5	CH_2 deformation
	1371 m					
	1345 sh					$^{10}BF_2$ symmetric stretch
1360 R 1350 P } B, s	1329 s	1357 p, w			ν_6	$^{11}BF_2$ symmetric stretch
1300 vw	1297 w					
1272 w	1268 w					
	1232 m	1230 p, w	1225 p, w			
1228 R 1222 Q } A, s 1214 P	1214 s	1220 p, w	1213 p, w	1206 vw	ν_7	C–H in-plane bend
1185 vw	1186 m	1189 p, s	1188 p, vs	1187 vs	ν_8	ring breathing
1107 vw	1104 w				ν_{20}	CH_2 twist
1068 sh	1068 w				ν_{21}	CH_2 wag
1060 R 1053 Q } A, m 1046 P	1049 m	1057 p, m	1051 p, m	1050 m	ν_9	CH_2 twist
1026 R 1018 Q } A/B, m 1010 R	1020 s	1020 p, m	1016 p, m	1016 m	ν_{10}	CH_2 wag
911 m	908 s	915 dp, m, br	910 dp, m	908 s	ν_{22}	ring deformation
865 Q, C, m	862 s		865 dp, w	863 m	ν_{23}	CH_2 rock
832 A/B, m	829 w				ν_{11}	CH_2 rock
		821 p, m				
		804 p, m	806 p, m	804 s	ν_{12}	ring deformation
		727 p, m	731 p, m	730 s	ν_{13}	B–C stretch
			687 p, w	682 w		
677 C, w	651 s		655 dp, w	658 m	ν_{24}	C–H out-of-plane bend
		646 ?, w	640 p, w	648 w		$2\nu_{25}$
	627 s					
			611 p, w			
521 R 514 Q } A, w 507 P	516 s	513 p, m	513 p, m	513 m	ν_{14}	BF_2 scissors
479 C w	477 w					BF_3 impurity
460 vw, br						BF_2 rock + BF_2 torsion ($\nu_{15} + \nu_{27}$)
393 R 386 Q } A, w 381 P	390 s	392 p, m, 385 p, m	391 p, m	389 m	ν_{15}	BF_2 rock
335 R 330 Q } A, w 325 P	330 m				ν_{25}	ring-boron bend
250 vw						BF_2 wag + BF_2 torsion ($\nu_{26} + \nu_{27}$)
193 Q, w			206 dp, w	217 w	ν_{26}	BF_2 wag
186 Q, w	210 br, w	186 p, m	191 p, w	200 w	ν_{16}	ring-boron bend
181 sh, sh						
69 vvw		70 dp, m			ν_{27}	BF_2 torsion
				83 w		
				77 m		
				65 w		lattice modes
				51 m		
				29 m		

[a] Abbreviations used: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; p, polarized; dp, depolarized. A, B, A/B, and C refer to vapor-phase band contours.

only in the infrared spectra at 829 cm^{-1}, and the A″ CH_2 rock is assigned to the C-type band at 865 cm^{-1}. The A′ CH_2 wag occurs at 1016 cm^{-1}, and the A″ wag is assigned to a band which appears only in the infrared spectra at 1068 cm^{-1}. The C–H in-plane bend appears as a strong A-type band at 1222 cm^{-1}. The C–H out-of-plane bend appears as a C-type band at 677 cm^{-1}.

NMR Spectra

The 20.0-MHz proton-decoupled ^{13}C NMR spectrum of c-$C_3H_5BF_2$ consists of a sharp singlet 4.7 ppm deshielded from

Table VIII. Chemical Shifts[a] in c-$C_3H_5BF_2$ and (c-C_3H_5)$F_2B{\cdot}P(CH_3)_3$

nucleus	c-$C_3H_5BF_2$	(c-C_3H_5)$F_2B{\cdot}P(CH_3)_3$
^1H	−0.04 (α) +0.74 (β)	−0.69 (α) −0.02 (β)
^{11}B	+28.48	+8.13
^{13}C	+4.7 (β)	+0.01 (β)
^{19}F	−15.66	−78.02
^{31}P		−35.25

[a] Chemical shifts are in parts per million. A negative sign denotes increased shielding.

Me_4Si. From previous ^{13}C NMR studies in our laboratory on alkylboranes,[17] vinylboranes,[18] phenylboranes,[19] and boron-substituted aromatic heterocycles,[19] the signal is assigned to the resonance of the two unsubstituted C_β atoms. Thus, at ambient probe temperature, due to coupling and relaxation effects, the resonance of the substituted carbon atom, C_α, is not observed. A low-temperature (−67 °C) proton-decoupled ^{13}C spectrum was obtained in order to ascertain if thermal decoupling of the boron nucleus would result in observation of the C_α resonance. A broad resonance appeared directly under the C_β resonance which can tentatively be assigned to the C_α resonance. A triple-resonance experiment (^{13}C observe (25 MHz) and ^1H and ^{11}B decoupled) on c-$C_3H_5BCl_2$ demonstrated that C_α and C_β have approximately the same chemical shifts, although only one signal is observed in that compound at ambient temperature.

It is interesting to note that long-range carbon–fluorine spin–spin coupling is not observed in c-$C_3H_5BF_2$ even though $^3J_{C-F}$ = 8.5 Hz has been observed in vinyldifluoroborane,[18] $C_2H_3BF_2$. Also of interest in this molecule is a comparison of the C_β chemical shift to the corresponding shift in the parent cyclopropane molecule. It has been demonstrated[18] in vinylboranes that the C_β chemical shift is a sensitive indicator with regard to mesomeric interactions of the vinyl moiety with the empty boron pπ orbital. The chemical shift of C_β is deshielded by 7.6 ppm in c-$C_3H_5BF_2$ relative to c-C_3H_6[20] which would indicate some mesomeric interaction and would lend support to the microwave and vibrational data which show the bisected structure to be the most stable conformer. However it should be pointed out that the resonance of C_β in vinyldifluoroborane is 22.2 ppm deshielded from the ^{13}C resonance of ethylene.[18] It would be a mistake to attempt to compare the two C_β chemical shifts and conclude that delocalization is less in the cyclopropyl compound. In fact, since the cyclopropyl moiety presumably has less π-electron density to mesomerically donate, if the barrier to rotation about the boron–carbon bond is any indication of the mesomeric ability of the organic group, the cyclopropyl system may be more effective as a mesomeric donor. The barriers to rotation about the B–C bond in the two molecules are essentially identical ($C_2H_3BF_2$, 4.17 kcal/mol;[21] c-$C_3H_5BF_2$, 4.23 kcal/mol). The almost identical values of the C_α and C_β chemical shifts in cyclopropyldifluoroborane may also have some bearing on this point, but more data will be required before we can begin to understand the carbon chemical shifts in these systems.

The fact that a large deshielding observed for the β-carbons can be attributed to mesomeric effects is supported by the ^{13}C chemical shift data of the trimethylphosphine complex of c-$C_3H_5BF_2$. Adduct formation is viewed as only changing the hybridization of boron so that it no longer contains an available pπ orbital. As such, we would expect the ^{13}C C_β resonance in the adduct to be shielded from that of c-$C_3H_5BF_2$, and this is found to be true. Table VIII summarizes the chemical shifts for both c-$C_3H_5BF_2$ and the $P(CH_3)_3$ adduct. The ^{13}C C_β resonance in (c-C_3H_5)$F_2B{\cdot}P(CH_3)_3$ is found to be shielded by 4.7 ppm from c-$C_3H_5BF_2$. Similarly, the α- and β-hydrogens in the adduct are shielded from those of c-$C_3H_5BF_2$ by 0.65 and 0.75 ppm, respectively, in the ^1H NMR spectrum.

The ^{11}B spectrum shows the boron resonance of the adduct to be shielded by 20.5 ppm from the ^{11}B resonance in c-$C_3H_5BF_2$. The ^{19}F spectrum shows the fluorine resonance of the adduct to be shielded by 62.4 ppm, indicating loss of fluorine pπ–pπ back-bonding in the tetrahedral complex, as expected. Finally, the ^{31}P spectrum shows the phosphorous resonance to be deshielded by 26.8 ppm in the adduct relative to the ^{31}P resonance in $P(CH_3)_3$, indicating electron density donation from phosphorous to boron.

In summary, the ^{11}B, ^{19}F, and ^{31}P proton-decoupled spectra demonstrate the expected changes in chemical shift upon complexation. The multiplicities of these spectra, however, are not the expected ones. Each is a singlet, as opposed to the expected doublet of triplets, quartet, and quartet, respectively. An approximate spin–lattice relaxation time (T_1) determination by the standard inversion recovery sequence of the ^{11}B T_1 indicates that the value in c-$C_3H_5BF_2$ is almost twice the corresponding value in the adduct. Thus, the absence of observed spin–spin coupling to the boron nucleus must be tentatively attributed to variations in the electric field gradient and boron relaxation time (T_1) in the adduct.

Discussion

The peculiarities of electronic structure of cyclopropanes have been extensively treated theoretically[1,2] and in all cases the hybridization condition of the ring carbons is more similar to that in olefins than in saturated systems. In fact in a treatment[2b] concerning the relative conjugating ability of cyclopropane, the potential energy for rotation about the single bond was computed for some organocarboxaldehyde molecules where the organo group was cyclopropyl, vinyl, phenyl, isopropyl, and cyclobutyl. Hoffmann[2b] demonstrated that the cyclopropyl, vinyl, and phenyl systems were very similar in that their potential energy curves were characterized by two potential minima corresponding to positions of maximum overlap of the π systems. In all theoretical studies the preferred conformation of a cyclopropyl moiety bonded to an unsaturated substituent has been the bisected conformation shown in Figure 1b. Experimental structural studies have verified theoretical predictions.[22]

In the group of cyclopropyl compounds exhibiting the bisected conformation, the atom of the substituent group attached to the ring has most often been a carbon atom. The substituent carbon atom is generally considered to be sp^2 hybridized since it is part of a conjugated π system or the carbonyl functional group. Nitrocyclopropane[13] was the first molecule reported which exhibited this conformational preference and did not contain a directly bonded carbon atom in the substituent. On the basis of its strength as an electron-withdrawing group, the nitro group could be considered to have an electron deficient p orbital on the nitrogen suited for conjugation with the cyclopropyl ring. In view of these results it is not surprising to find that cyclopropyldifluoroborane also exhibits the bisected conformation. This fact is clearly shown by the inertial defect calculations and the Raman depolarization data.

After determining the preferred conformation, we undertook a structural study of cyclopropyldifluoroborane. The length of the boron–carbon bond in tricoordinate boron compounds ranges from 1.513 Å in ethynyldifluoroborane[23] to 1.60 Å in methyldifluoroborane.[24] A trend which can be correlated with the hybridization of the carbon atom is observed in the boron–carbon bond length in the series of compounds: (C_2H)BF_2 (1.513 Å),[23] (C_2H_3)BF_2 (1.533 Å),[4] (C_6H_5)BF_2 (1.551 Å),[25] (C_2H_5)BF_2 (1.572

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Table IX. Barriers to Internal Rotation (kcal/mol) in Some Organoborane and the Corresponding Nitro Compounds

	BF_2	ref	NO_2	ref
CH_3XY_2	0.013	12	0.006	29
$CH_3CH_2XY_2$	1.17	11	*a*	
$C_6H_5XY_2$	3.17	25	3.0	28
c-$C_3H_5XY_2$	4.23	this work	4.6	27
$C_2H_3XY_2$	4.17	21	4.83	26

[a] Microwave spectroscopy[30] and matrix and gas-phase infrared spectra[12,31] have shown that the nitro group is undergoing free internal rotation.

Å),[11] and $(CH_3)BF_2$ (1.60 Å).[24] Cyclopropyldifluoroborane, (c-C_3H_5)BF_2 (1.589 Å), would have been expected to fit between phenyldifluoroborane and ethyldifluoroborane if this trend is due to lengthening of the bond as the hybridization of the carbon atom changes from sp to sp^3. However, the uncertainties in the bond length involved would allow for cyclopropyldifluoroborane to take its expected place in the series. The other structural parameters for the BF_2 moiety, r(B–F) = 1.328 ± 0.004 Å and ∠FBF = 115.9 ± 0.9°, are in agreement with those found in CH_3BF_2 (r(B–F) = 1.30 ± 0.02 Å, ∠FBF = 118°),[24] $(C_2H_3)BF_2$ (r(B–F) = 1.331 ± 0.002 Å, ∠FBF = 116.04 ± 0.41°),[4] and $(C_6H_5)BF_2$ (r(B–F) = 1.330 Å, ∠FBF = 116.0°).[25] A possible interaction between the fluorine atom and the eclipsed hydrogen atom results in a tilt of the BF_2 group toward the cyclopropyl ring. We are currently investigating the structure of cyclopropyldimethylborane to ascertain if the observed tilt of the borane moiety is due to a hydrogen–fluorine interaction. Using the method of Penn and Boggs,[14] we obtained a C_2–C_3 bond distance of 1.486 Å. After a diagnostic least-squares analysis was performed the length was determined to be 1.496 Å. This bond length is similar to those found in other compounds containing unsaturated substituents on the ring. The calculations[14] for the bond length in nitrocyclopropane (1.500 Å), *trans*-vinylcyclopropane (1.499 Å), and cyanocyclopropane (1.500 Å) indicate the shortening of this C_2–C_3 bond length.

Also of interest in this study is the barrier to internal rotation of the BF_2 group in cyclopropyldifluoroborane. The barrier has been found to be 4.23 kcal/mol. This is similar to the barrier (4.17 kcal/mol) found in vinyldifluoroborane[21] and slightly higher than the barrier of 3.17 kcal/mol in phenyldifluoroborane.[25] In the corresponding nitro compounds which are isoelectronic with BF_2 compounds, the same trend is visible. A comparison of the barriers of some organoborane compounds and the corresponding nitro compounds is given in Table IX. As shown in the table, nitroethylene (4.83 kcal/mol)[26] and nitrocyclopropane (4.6 kcal/mol)[27] have similar barriers which are higher than the barrier for nitrobenzene (3.0 kcal/mol).[28] It is also interesting to note that the barrier in c-$C_3H_5BF_2$ is so much higher than the barrier in ethyldifluoroborane (1.17 kcal/mol).[11] This large barrier difference clearly indicates a significant mesomeric interaction between the BF_2 moiety and the cyclopropyl ring.

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Millimeter Wave Spectrum of Glycine. A New Conformer

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Abstract: More sensitive observations on the vapor of glycine, the smallest amino acid, have been made in the millimeter region. This work has led to the identification of a second conformer in the gas phase. This conformer has the amino hydrogens hydrogen bonded to the carbonyl oxygen and the hydroxyl hydrogen in the normal cis configuration with respect to the carbonyl group. This new conformer is ≃490 (150) cm^{-1} *lower* in energy than the conformer originally reported. Its spectrum is weaker due to the smaller dipole moment ($\mu_a \simeq 1.00$ (15) D). The distortion fit of 37 transitions yield $A'' = 10341.76$ (17) MHz, $B'' = 3876.195$ (9) MHz, and $C'' = 2912.361$ (10) MHz for the ground state. The excellent agreement between experiment and theory is discussed.

Introduction

In our previous paper on the millimeter wave spectrum of glycine we reported the rotational spectrum of a particular conformer of glycine in the vapor phase (labeled conformer II here).[1] That conformer had a large molecular dipole moment which gave rise to the most intense spectrum of the various possible conformers of glycine in the gas phase. In that report we suggested the possibility that other conformers might be present in larger concentrations than conformer II, but due to smaller electric dipole moments, their rotational spectra might indeed be weaker than the spectrum of II.

Since glycine is the smallest amino acid, it is important to be able to ascertain if more than one conformer exists in the gas phase and, if so, to determine their structural conformations and relative energies. In addition, it is extremely important from an astronomical standpoint to know which conformer is the lowest in energy since in all likelihood the lowest energy conformer will be the most abundant form in cool interstellar dust clouds.

After our previous paper on glycine was published, we made a number of improvements in our spectrometer which have provided improved sensitivity. This paper describes the spectrometer

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