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Articles

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Microwave Spectrum, Boron Skeletal Structure, and Dipole Moment of 5-Fluoro-2,4-dicarbaheptaborane(7) ($C_2B_5H_6F$)

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The microwave spectra of five isotopic species of 5-fluoro-2,4-dicarbaheptaborane(7), $C_2B_5H_6F$, have been observed and assigned between 8.0 and 40.0 GHz. The boron skeletal structure has been determined by using the Kraitchman substitution method, giving the following structural parameters: $r(B_1–B_7) = 2.343 \pm 0.002$ Å, $r(B_1–B_3) = 1.825 \pm 0.003$ Å, $r(B_1–B_5) = 1.813 \pm 0.003$ Å, $r(B_1–B_6) = 1.844 \pm 0.005$ Å, $r(B_3–B_5) = 2.667 \pm 0.012$ Å, $r(B_3–B_6) = 2.700 \pm 0.013$ Å, and $r(B_5–B_6) = 1.56 \pm 0.03$ Å. From the moments of inertia and center of mass conditions, along with estimates of the carbon and hydrogen atom coordinates, $r(B–F) = 1.33 \pm 0.03$ Å was calculated. This short bond length indicates double-bond character for the B–F bond. The framework of this molecule is slightly enlarged compared to that of the parent unfluorinated compound, $C_2B_5H_7$, and it appears that the fluorine atom does back-bond to the cage to relieve some of the electron deficiency in the cage.

Introduction

It has been suggested that the substitution of fluorine atoms for terminal hydrogens in carboranes[1-4] might donate additional electron density to the cage and reduce the electron deficiency. The mechanism suggested for this is the back-bonding of electrons from the fluorine filled p orbitals to the cage. Fluorine is the only halogen capable of providing sufficient back-bonding, since the outer p orbitals in the larger halogens are too far from the cage to effectively overlap with it. There are some indications that with multiple fluorine substitutions, sufficient electron density is provided that the molecule can revert to a classical structure and that it does not need a cage structure to satisfy its bonding requirements. For example, Timms[5] has shown by reacting boron monofluoride with acetylene that 1,4-difluoro-1,4-diboracyclohexadiene, $(CH)_4(BF)_2$, is formed. This is the classical analogue to tetracarbahexaborane(6), $C_4B_2H_6$. However, since the fluorocarborane was prepared by a completely different route, it is possible that the cage form of this compound also exists.

Though bromo- and chlorocarboranes have been made, very few fluorocarboranes have been synthesized.[6] Recently, Ng and Onak have found a synthetic route for producing fluorocarboranes by substituting fluorine for other halogens by frontside attack.[7] They have succeeded in isolating 5-fluoro-2,4-dicarbaheptaborane(7).

A comparison of the molecular structure of this compound with the parent might provide an opportunity to test this hypothesis of back-donation. If the fluorine does provide additional electron density to the cage, the molecular structure around the fluorinated boron might have bond distances larger than those of the parent compound, whose molecular structure has already been determined. Ideally it would be interesting to determine the molecular structures of a whole set of progressively more highly fluorinated carboranes to determine if there is a gradual change in bond lengths and bond angles consistent with this hypothesis.

The microwave spectra of five isotopic species of 5-fluoro-2,4-dicarbaheptaborane(7), $C_2B_5H_6F$, listed in Table I, have been observed and assigned. The boron skeletal structure, along with approximate locations of the fluorine, carbon, and hydrogen atoms, are shown in Figure 1, which includes the numbering of atoms and principal-axis orientations in the normal species of 5-fluoro-2,4-dicarbaheptaborane(7).

Table I. Isotopic Species Found in Natural Abundance[a] in a Sample of 5-Fluoro-2,4-dicarbaheptaborane(7) ($C_2B_5H_6F$)

no.	species	rel isotopic abundance	no.	species	rel isotopic abundance
1	normal	0.3249	4	B_5	0.0801
2	B_1	0.1602	5	B_3	0.0801
3	B_6	0.0801			

[a] The relative abundance in each sample is statistically estimated and is based on a pure sample. The natural isotopic abundances are 0.9889 for ^{12}C, 0.0111 for ^{13}C, 0.1978 for ^{10}B, and 0.8022 for ^{11}B. The designations used are all ^{11}B and ^{12}C for the normal species, while the rest represent ^{10}B substitution at the specified atoms. Nineteen other isotopic species, including singly, doubly, triply, and quadruply ^{10}B-substituted species, along with singly ^{13}C-substituted species, account for an additional 25% in the sample.

Since yields were too low to synthesize a ^{13}C-enriched sample, the carbon atoms could not be well located. Thus, only the B–B interatomic distances could be determined by the Kraitchman method. Unfortunately, large uncertainties resulted for the B_5 and B_6 coordinates since these atoms lie very close to a principal axis. Estimates of the B–C and B–F bonds were made by fitting the structure of the molecule to center of mass coordinates, moments of inertia, and reproducing the principal-axis coordinates of the boron atoms.

The cage structure of this molecule is slightly enlarged compared to that of the parent compound, since all B–B bonds, except $B_5–B_6$, show an increase in length over the parent. Also, the B–F bond length indicates double bonding for this moiety. Thus, it appears that a single fluorine does relieve some of the electron deficiency and has a significant effect on the structure.

Experimental Section

A 0.03-mmol sample of 5-fluoro-2,4-dicarbaheptaborane(7), 0.12 mole fraction in completely deuterated benzene, was provided by F. Gomez and T. Onak and was shown to be pure by ^{11}B NMR spectroscopy. An initial survey spectrum recorded between 18.0 and 26.5 GHz was acquired by introducing 0.020 Torr of the gas phase above the liquid sample solution at room temperature into a gold-plated waveguide. The Stark cell was cooled to dry-ice temperature, –78 °C, to simplify the spectrum by reducing the intensity of vibrationally excited states of $C_2B_5H_6F$. The poor quality of this first spectrum precluded any attempt at analysis. Although $C_2B_5H_6F$ has a vapor pressure higher than that of perdeuterated benzene at room temperature, the actual gas-phase concentration of $C_2B_5H_6F$ was low, due to the small $C_2B_5H_6F$ concentration in

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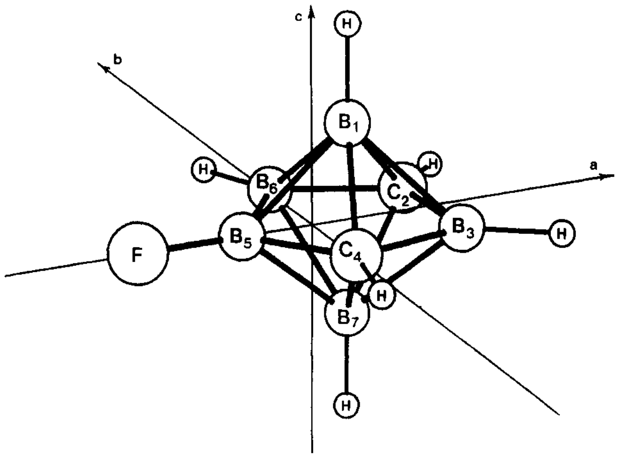

Figure 1. Molecular structure of $C_2B_5H_6F$. Principal-axis orientations are shown for the normal species.

the mixture. Thus, the waveguide contained mostly C_6D_6, which, of course, has no dipole moment and no microwave spectrum, and acted simply as a line-broadening agent for the weak spectrum recorded.

A Clausius–Clapeyron calculation showed that, assuming ideal behavior, the partial pressure of $C_2B_5H_6F$ would be 0.035 Torr at dry-ice temperature, while the partial pressure of C_6D_6 would be about 0.005 Torr. Upon cooling of the sample tube in a dry ice/acetone bath, the total vapor pressure of this mixture was measured by a thermocouple gauge as 0.035 Torr, which supported the calculations. Thus, the sample was distilled from the sample tube at −78 °C into the absorption cell. Fortunately, this pressure was adequate to attempt spectral work. Again, the spectrum was recorded between 18.0 and 26.5 GHz, at three different values of the applied ac Stark field, 200, 400, and 1000 V/cm. The resulting spectrum was extremely dense, well-resolved, and greatly improved over the initial survey spectrum. Many very intense lines were recorded, and some had pronounced, clearly resolvable Stark lobes, which ultimately led to their identification and a complete analysis of this rotational spectrum.

Though $C_2B_5H_6F$ and carboranes in general are much more stable than boron hydrides with respect to oxidation, hydrolysis, or thermal decomposition, the $C_2B_5H_6F$ sample was kept in liquid nitrogen when not in use, primarily to prevent dissolving of the stopcock grease in the Pyrex sample tube. No problems due to impurities or decomposition products were encountered.

The rotational spectra in the 18.0-26.5-GHz region were recorded with a Hewlett-Packard 8460A MRR spectrometer, and the spectra in the 26.5–40.0-GHz region with a Hewlett-Packard KII-8400B spectrometer, both stark-modulated at 33 kHz. Gold-plated waveguides were used. Spectra in the 8.0–18.0-GHz region were observed with a homebuilt instrument with a 3-m copper Stark cell. Sample pressures varied between 0.01 and 0.04 Torr.

Spectra and Assignment

Structural parameters from the microwave[8] study of the parent compound 2,4-dicarbaheptaborane(7), $C_2B_5H_7$, were used to estimate rotational constants for the five most abundant isotopic species of 5-fluoro-2,4-dicarbaheptaborane(7), listed in Table I. An approximate value of 1.50 Å was initially used for the B–F bond length. These values were entered into an MNDO program,[9] and all bond lengths and bond angles were optimized by constraining the equatorial atoms (C_2, B_3, C_4, B_5, B_6, along with the attached hydrogens and fluorine) to lie in a plane. The output geometry from this calculation gave a value of 1.32 Å for the B–F bond length, as well as a value of 2.41 D for the total dipole moment.

Since the B–F bond length in a similar fluorocarborane has not been reported in the literature, and values varied among the compounds BF,[10] BF_3,[11] BHF_2,[12] and NH_4BF_4[13] (1.26, 1.30, 1.31, and 1.43 Å, respectively), a range of possible rotational constants was calculated by varying the B–F bond length between 1.30 and 1.50 Å. All of these calculations for the normal species (all ^{11}B and ^{12}C) showed that the heavy fluorine atom was located practically on the *a* axis and in the *ab* plane. Rotational constants for this model predicted $C_2B_5H_6F$ to be a near-prolate rotor with asymmetry parameters varying from −0.81 to −0.85 for assumed values of *r*(B–F) varying from 1.30 to 1.50 Å, respectively. As seen in Table II, calculations gave nearly identical values of the *A* rotational constant, while the *B* and *C* constants varied as the B–F bond length was changed. Since the fluorine atom is placed nearly on the *a* axis for all assumed geometries, increases in the B–F bond length give rise only to increases in the moments of inertia I_b and I_c, or, equivalently, to decrease in the *B* and *C* rotational constants.

Table II. Initial Estimates of Rotational Constants of Normal $C_2B_5H_6F$, Assuming Various Values for the B–F Bond Length[a]

	B–F, Å					
param	1.30	1.32	1.35	1.40	1.50	final
A, MHz	4735.15	4735.12	4735.09	4735.93	4734.93	4705.69
B, MHz	2327.99	2309.83	2282.88	2153.17	2153.17	2292.06
C, MHz	2079.44	2064.93	2043.36	1936.79	1938.79	2062.33
κ	−0.8128	−0.8166	−0.8220	−0.8454	−0.8467	−0.8262
B + *C*, MHz	4407.43	4374.76	4326.24	4089.96	4091.96	4354.39

[a] Note that the final experimental rotational constants agree closely with initial estimates for a B–F bond length of 1.32 Å.

These estimates indicated that $C_2B_5H_6F$ had a very dense spectrum due to the small values of $B + C$ of 4.4 GHz. The predicted spectrum consisted of strong *a*-type, low-*J*, R-branch transitions and less intense *b*-type, high-*J*, Q-branch transitions. A study of the spectra in the range 19–23 GHz led to the assignment of four strong a-type, $J = 5 \leftarrow 4$ lines of the normal species, $5_{05} \leftarrow 4_{04}$, $5_{24} \leftarrow 4_{23}$, $5_{23} \leftarrow 4_{22}$, and $5_{14} \leftarrow 4_{13}$, at 21 479.02, 21 737.28, 22 029.94, and 22 270.68 MHz, respectively. The Stark effects for these transitions were strong and well-resolved. Refined rotational constants allowed the other five members of this set of nine lines to be located. Subsequently all eleven $J = 6 \leftarrow 5$ lines were located within 1 MHz of their predicted positions, in the range 25–27 GHz.

Using the refined rotational constants of the normal species and approximate atomic coordinates of the B_1 atom, we estimated a rotational spectrum for the B_1 species. Strong *a*-type, $J = 5 \leftarrow 4$, B_1-candidate lines, in expected absorption regions, were subjected to Stark field excursions from 100 to 2000 V/cm. All $J = 5 \leftarrow 4$ as well as $J = 6 \leftarrow 5$, *a*-type, B_1-species lines were found near their predicted locations and assigned on the basis of the similarity of their Stark patterns to those of the normal species lines, as well as least-squares fits to a rigid asymmetric rotor. These lines were reduced in intensity from the normal species lines by about a factor of 2, as expected from statistical calculations shown in Table I.

The identity of the remaining three observed species (B_6, B_5, B_3) was determined in an analogous way, again guided by estimated rotational spectra and Stark effects. These three species had relative intensities roughly equal to each other and about one-fourth that of the normal species in accord with values in Table I. The *a*-type, $J = 3 \leftarrow 2$, $4 \leftarrow 3$, $5 \leftarrow 4$, and $6 \leftarrow 5$ transition frequencies for all five observed isotopic species of $C_2B_5H_6F$ are listed in Table III.

The origin of a large number of unassigned lines, which produced a very dense background spectrum, was attributed to either sample impurities, or high-*J*, *b*-type transitions. MNDO calculations, which were found to accurately predict some of the essential features of the $C_2B_5H_6F$ species, gave values of $\mu_b = 1.18$ D. After the Stark effect measurements, shown below, determined that $\mu_b = 0.74$ D, a search was initiated for *b*-type transitions. Due to low intensities, few *b*-type, low-*J* lines were assigned even for the most abundant normal species. However, many higher *J* lines, listed in Table IV, were observed and assigned for both the normal and B_1 species. These lines were assigned on the basis

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Table III. Measured *a*-Type Transition Frequencies[a] of the Isotopic Species of 5-Fluoro-2,4-dicarbaheptaborane(7)

	normal		B_1		B_6		B_5		B_3	
transn	ν_{obs}	Δ	ν_{obs}	Δ	ν_{obs}	Δ	ν_{obs}	Δ	ν_{obs}	Δ
$3_{13} \leftarrow 2_{12}$	12709.31	0.18	12741.53	0.26						
$3_{03} \leftarrow 2_{02}$	13001.21	0.08								
$3_{12} \leftarrow 2_{11}$	13397.71	0.06								
$4_{14} \leftarrow 3_{13}$	16928.98	0.14	16970.05	0.24	17027.42	0.32	16988.29	0.13	17145.26	0.13
$4_{04} \leftarrow 3_{03}$	17265.53	0.08	17323.18	0.15	17351.43	0.23	17326.21	0.11	17480.26	0.22
$4_{23} \leftarrow 3_{22}$	17405.51	0.11	17478.37	0.20	17470.11	0.18	17468.36	−0.07	17618.57	0.15
$4_{22} \leftarrow 3_{21}$	17557.69	0.19	17647.02	0.21	17598.72	−0.19	17623.29	0.12	17768.34	0.16
$4_{13} \leftarrow 3_{12}$	17843.73	0.04	17944.01	0.13	17880.54	0.13	17909.67	−0.03	18053.95	−0.02
$5_{15} \leftarrow 4_{14}$	21135.89	−0.01	21184.63	0.02	21262.41	−0.02	21209.74	−0.03	21406.71	−0.04
$5_{05} \leftarrow 4_{04}$	21479.09	0.01	21540.87	0.02	21600.35	0.01	21553.36	−0.07	21749.49	0.03
$5_{24} \leftarrow 4_{23}$	21737.28	0.03	21826.04	0.03	21820.95	−0.01	21815.75	0.02	22003.85	0.02
$5_{42} \leftarrow 4_{41}$	21806.75	0.06	21903.23	0.05	21879.53	−0.03	21886.47	0.06	22072.21	0.04
$5_{41} \leftarrow 4_{40}$	21806.75	−0.13	21903.36	−0.05	21879.53	−0.16	21886.47	−0.13	22072.21	−0.14
$5_{33} \leftarrow 4_{32}$	21819.08	0.05	21916.70	0.11	21890.54	0.06	21898.95	0.05	22084.38	0.01
$5_{32} \leftarrow 4_{31}$	21832.87	−0.03	21932.63	−0.03	21901.12	0.03	21913.11	−0.05	22097.79	−0.10
$5_{23} \leftarrow 4_{22}$	22029.94	−0.01	22149.58	0.05	22070.71	−0.03	22113.23	−0.02	22292.07	−0.12
$5_{14} \leftarrow 4_{13}$	22270.68	0.00	22391.94	0.06	22322.29	0.03	22352.53	−0.03	22534.07	−0.02
$6_{16} \leftarrow 5_{15}$	25329.53	−0.01	25384.69	0.03	25485.92	0.00	25417.67	−0.01	25654.95	−0.07
$6_{06} \leftarrow 5_{05}$	25644.47	−0.02	25707.16	−0.03	25805.28	−0.01	25731.96	−0.02	25970.41	−0.03
$6_{25} \leftarrow 5_{24}$	26056.24	−0.02	26159.64	0.01	26161.01	−0.10	26149.99	0.05	26376.50	−0.10
$6_{52} \leftarrow 5_{51}$	26165.35	−0.17	26820.93	−0.11	26253.13	−0.21	26261.23	0.09	26483.99	−0.14
$6_{51} \leftarrow 5_{50}$	26165.35	−0.18	26820.93	−0.11	26253.13	−0.22	26261.23	0.08	26483.99	−0.15
$6_{43} \leftarrow 5_{42}$	26179.79	0.55	26296.39	0.14	26265.36	0.39	26275.11	0.31	26497.90	0.26
$6_{42} \leftarrow 5_{41}$	26179.79	−0.30	26297.03	−0.24	26265.36	−0.20	26275.11	−0.52	26497.90	−0.55
$6_{34} \leftarrow 5_{33}$	26194.84	0.00	26312.89	0.05	26279.39	−0.01	26290.75	−0.06	26513.02	−0.11
$6_{33} \leftarrow 5_{32}$	26231.33	−0.06	26355.09	−0.04	26307.35	−0.07	26328.27	−0.10	26548.61	−0.16
$6_{24} \leftarrow 5_{23}$	26537.29	0.00	26688.98	0.05	26575.51	−0.04	26638.34	−0.02	26850.88	−0.07
$6_{15} \leftarrow 5_{14}$	26671.36	−0.01	26810.40	0.03	26742.38	−0.04	26768.59	0.02	26988.38	−0.02

[a] Lines reported to 0.01 MHz have been measured to better than ±0.05 MHz. $\Delta = \nu_{obs} - \nu_{calc}$.

Table IV. Measured *b*-Type Transition Frequencies[a] in Normal and B_1 Species of 5-Fluoro-2,4-dicarbaheptaborane(7)

	normal		B_1	
transn	ν_{obs}	Δ	ν_{obs}	Δ
$4_{1,4} \leftarrow 3_{0,3}$	18836.14	0.10		
$6_{1,6} \leftarrow 5_{0,5}$	26556.97	−0.02		
$6_{0,6} \leftarrow 5_{1,5}$	24417.01	−0.03		
$10_{5,6} \leftarrow 10_{4,7}$	22567.76	0.33		
$10_{5,5} \leftarrow 10_{4,6}$	22502.13	0.39		
$11_{5,7} \leftarrow 11_{4,8}$	22511.29	0.19	22957.07	0.29
$11_{5,6} \leftarrow 11_{4,7}$	22374.58	0.28	22795.46	0.24
$12_{5,8} \leftarrow 12_{4,9}$	22452.40	−0.17	22896.33	0.21
$12_{5,7} \leftarrow 12_{4,8}$	22188.92	0.13	22580.54	0.26
$13_{5,9} \leftarrow 13_{4,10}$	22399.57	−0.02	22844.16	0.06
$13_{4,10} \leftarrow 13_{3,11}$	18172.84	0.04	18632.71	0.13
$13_{5,8} \leftarrow 13_{4,9}$	21924.08	0.00	22277.16	−0.05
$14_{5,10} \leftarrow 14_{4,11}$	22362.87	−0.14	22813.38	−0.06
$14_{5,9} \leftarrow 14_{4,10}$	21556.33	−0.19	21857.41	−0.09
$14_{4,11} \leftarrow 14_{3,12}$	18513.94	−0.07	19021.83	−0.03
$15_{3,13} \leftarrow 15_{2,14}$	18774.82	−0.09	19564.96	−0.13
$15_{5,10} \leftarrow 15_{4,11}$	21064.22	−0.31	21299.53	−0.29
$16_{5,12} \leftarrow 16_{4,13}$	22395.83	−0.43	22881.16	−0.33

[a] Lines reported to 0.01 MHz have been measured to better than ±0.05 MHz. $\Delta = \nu_{obs} - \nu_{calc}$.

of their Stark effects and proximity to estimated transition frequencies. A comparison of two separate regions, one where a *b*-type normal species line was expected, and the other where the analogous transition should occur for the B_1 species, proved to be a useful technique in selecting candidate *b*-type lines for each of these two species. Many such pairs of lines (one for normal, one for the B_1 species) were found for Q-branch, high-*J* transitions between $J = 10$ and $J = 31$.

Ground vibrational state rotational constants were obtained by using least-squares fitting to a rigid asymmetric rotor, incorporating all measured *a*- and *b*-type transitions for the normal and B_1 species but only *a*-type lines for the less abundant B_6, B_5, and B_3 species. Although centrifugal distortion effects were not included in the fit, good fits resulted to $J = 15$, with only a few megahertz deviations at $J = 31$, for both the normal and B_1 species. This is an indication of how well the rigid rotor model describes this molecule, which is expected to have few low-frequency normal modes becasue of its rigid cage structure. Also, high-*J* states of $C_2B_5H_6F$ actually have small total rotational energy, which is principally responsible for centrifugal distortion effects. The absence of observed *b*-type transitions led to slightly larger uncertainties in the *A* rotational constants of the B_6, B_5, and B_3 species. Final rotational constants, moments of inertia, and asymmetry parameters for all isotopic species observed are listed in Table V.

Dipole Moment

Stark effect measurements were obtained on the two *a*-type $J = 5 \leftarrow 4$ transitions, $5_{05} \leftarrow 4_{04}$ at 21 479.09 MHz and $5_{23} \leftarrow$

Table V. Rotational Constants, Moments of Inertia, and Asymmetry Parameters of the Isotopic Species of 5-Fluoro-2,4-dicarbaheptaborane(7)[a]

param	normal	B_1	B_6	B_5	B_3
A, MHz	4705.408 (6)	4766.621 (6)	4787.89 (28)	4706.03 (26)	4739.18 (28)
B, MHz	2292.057 (4)	2308.794 (4)	2292.068 (4)	2300.812 (4)	2317.883 (4)
C, MHz	2062.336 (4)	2064.130 (4)	2077.980 (4)	2069.399 (4)	2089.706 (4)
κ	−0.82617	−0.81893	−0.84200	−0.82446	−0.82776
I_a	107.40388 (14)	106.02460 (13)	105.5536 (62)	107.3897 (59)	106.6385 (63)
I_b	220.49148 (38)	218.89309 (38)	220.49043 (39)	219.65248 (38)	218.03476 (38)
I_c	245.05175 (47)	244.83877 (47)	243.20689 (47)	244.21538 (48)	241.84218 (47)

[a] Errors quoted are standard deviations from least-squares fits. Masses are 104.091 882 2 amu for the normal and 103.095 515 7 amu for the singly ^{10}B-substituted species. Conversion factor of 505 379.05 amu·Å²·MHz was used. Units for moments of inertia are amu·Å². $\kappa = (2B - A - C)/(A - C)$.

Table VI. Stark Effect and Dipole Moment of Normal 5-Fluoro-2,4-dicarbaheptaborane(7)[a]

transn	M_J	$10^5\Delta\nu/E^2$	$10^6 A$	$10^6 B$
$5_{05} \leftarrow 4_{04}$	0	-0.1291 (04)	-0.2591	-0.01928
	1	-0.06067 (26)	-0.1953	0.06821
	2	0.1526 (09)	-0.003888	2.786
	3	0.5127 (11)	0.3152	6.294
$5_{23} \leftarrow 4_{22}$	1	-3.895 (13)	-8.709	-0.06549
	2	-15.75 (05)	-34.82	-0.2745
	3	-35.94 (17)	-78.33	-0.6229
	4	-65.82 (08)	-139.3	-1.111

$$\mu_a = 2.18 \pm 0.02 \text{ D}$$
$$\mu_b = 0.74 \pm 0.02 \text{ D}$$
$$\mu_{tot} = 2.30 \pm 0.03 \text{ D}$$

[a] Units for $\Delta\nu/E^2$ are MHz·$(V\text{·cm}^{-1})^{-2}$, while A and B are in units of MHz·$(V\text{·cm}^{-1})^{-2}$·D^{-2}. A and B are defined by the equation $\Delta\nu/E^2 = A\mu_a{}^2 + B\mu_b{}^2$.

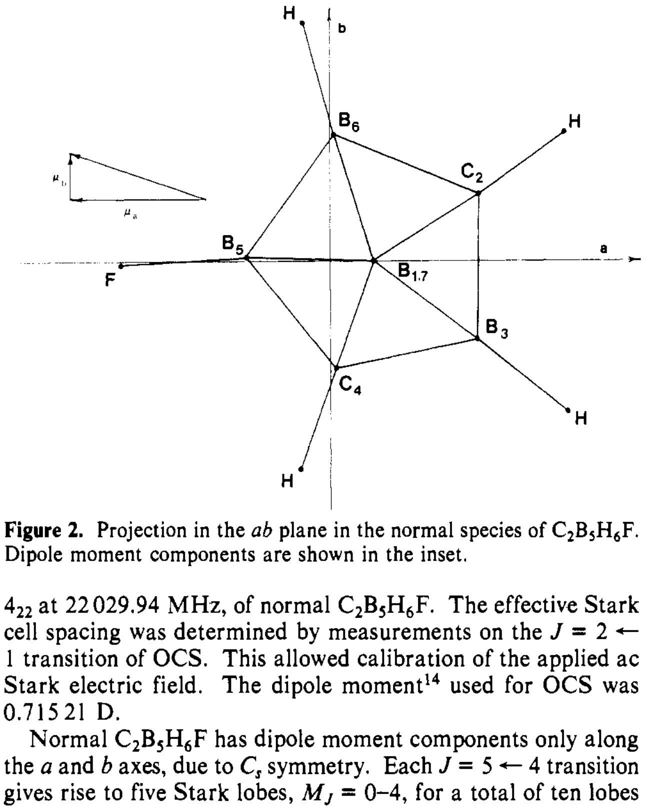

Figure 2. Projection in the ab plane in the normal species of $C_2B_5H_6F$. Dipole moment components are shown in the inset.

4_{22} at 22 029.94 MHz, of normal $C_2B_5H_6F$. The effective Stark cell spacing was determined by measurements on the $J = 2 \leftarrow 1$ transition of OCS. This allowed calibration of the applied ac Stark electric field. The dipole moment[14] used for OCS was 0.715 21 D.

Normal $C_2B_5H_6F$ has dipole moment components only along the a and b axes, due to C_s symmetry. Each $J = 5 \leftarrow 4$ transition gives rise to five Stark lobes, M_J = 0–4, for a total of ten lobes for the two studied transitions. However, the $M_J = 4$ lobe of the $5_{05} \leftarrow 4_{04}$ transition was very fast and broad, while the $M_J = 0$ lobe of the $5_{23} \leftarrow 4_{22}$ transition was very slow. Stark measurements were, therefore, completed on only eight of the ten lobes. The $5_{23} \leftarrow 4_{22}$ transition was found to be nearly independent of μ_b and gave a value of $\mu_a = 2.14 \pm 0.02$ D, while the $5_{05} \leftarrow 4_{04}$ transition led to values of $\mu_a = 2.24 \pm 0.01$ D, $\mu_b = 0.75 \pm 0.01$ D, and $\mu_{tot} = 2.36 \pm 0.01$ D. A least-squares program was used to find the best values of $\mu_a{}^2$ and $\mu_b{}^2$ as solutions to the eight simultaneous equations in the two unknowns. The Stark coefficients as well as least-squares slopes of $\Delta\nu$ vs E^2 curves for each of these eight lobes are given in Table VI.

Experimental results are $\mu_a = 2.18 \pm 0.02$ D, $\mu_b = 0.74 \pm 0.02$ D, and $\mu_{tot} = 2.30 \pm 0.03$ D. These are to be compared to the MNDO calculations of $\mu_a = 2.10$ D, $\mu_b = 1.18$ D, and $\mu_{tot} = 2.41$ D. The quoted errors represent the standard deviations for the solutions of the eight simultaneous equations. Since the fluorine atom is the most electronegative atom in this molecule, a small negative charge is expected to reside there. The B_3 atom is the least electronegative atom in the parent $C_2B_5H_7$, so that the direction of the total dipole moment is selected as shown in the inset of Figure 2. This direction agrees with calculated MNDO results.

Table VII. Atomic Coordinates in the Principal-Axis System of Normal $C_2B_5H_6F$

atom	a, Å	b, Å	c, Å
B_3	1.5680 (03)	-0.8627 (36)	0.0000[a]
B_5	-0.9133 (05)	0.1156 (256)[b]	0.0000[a]
B_6	±0.0306 (132)	1.3562 (23)	0.0000[a]
B_1	0.4657 (11)	0.0000 (50)	1.1714 (04)
B_7	0.4657 (11)	0.0000 (50)	-1.1714 (04)

[a] Assumed to lie in ab plane. [b] Positive sign chosen to agree with fluorine atom fitting.

Molecular Structure

The Kraitchman substitution method[15] was used to calculate the principal-axis coordinates of the five boron atoms in normal $C_2B_5H_6F$ by using the rotational constants listed in Table V. Large uncertainties resulted for the c coordinates of the three boron atoms B_3, B_5, and B_6, which should be zero by symmetry. Also, problems arose in accurately locating the atoms B_5 and B_6 in the ab plane, since each atom lies very close to a principal axis. Since b-type transitions, which were necessary to reduce the uncertainties in the I_a moments of inertia, were not observed for the B_3, B_5, or B_6 species, the atomic coordinates for these three atoms were determined by assuming these atoms lied in the plane of symmetry and by using the standard Kraitchman equations for isotopic substitution in a plane.[16] The results are listed in Table VII.

Since fluorine has only one stable isotope (^{19}F), and a ^{13}C-enriched sample was unavailable, a fitting routine was developed to estimate carbon and fluorine atom positions. From the moments of inertia I_a and I_b, and the center of mass conditions for the a and b coordinates, the following equations can be derived:

$$m_C(a_{C_2}{}^2 + a_{C_4}{}^2) + m_F a_F{}^2 = k_1 \quad (\text{from } I_b) \tag{1}$$

$$m_C(a_{C_2} + a_{C_4}) + m_F a_F = k_2 \tag{2}$$

$$m_C(b_{C_2}{}^2 + b_{C_4}{}^2) + m_F b_F{}^2 = k_3 \quad (\text{from } I_a) \tag{3}$$

$$m_C(b_{C_2} + b_{C_4}) + m_F b_F = k_4 \tag{4}$$

All C–H bond lengths were assumed to be 1.09 Å, while the B–H bond lengths were set at 1.20 Å. All other atomic coordinates were incorporated into the constants k_i. The hydrogen atoms in the symmetry plane were assumed to bisect the external angles, while the apical hydrogens were placed on the line connecting atoms B_1 and B_7. As can be seen in the above equations, if a position of the fluorine atom is assumed, we are left with two independent sets of two equations, each with two unknowns, which can be solved to give positions of the atoms C_2 and C_4. This final set of coordinates depends, of course, on the assumptions made. The above fitting procedure was repeated for different values of the fluorine atom coordinates. This provided an array of values for the carbon coordinates. To select the optimum set, the three moments of inertia for each set were calculated and compared with the observed moments of inertia.

A set of coordinates was found to reproduce all three rotational constants within 10 MHz, principal-axis coordinates of all five boron atoms within 0.01 Å, and consistent distances for the bond lengths C_2–B_6, C_4–B_5 and C_2–B_3, C_4–B_3. The results of this procedure were sensitive to changes in the boron coordinates. It is interesting to note, however, that the B–F bond length did not vary appreciably when any of the boron atom positions was adjusted in the iterative program. The best value for the B–F distance was 1.33 ± 0.03 Å.

The above fitting procedure showed that, for consistency, the b coordinate for the B_5 atom could only be positive (+0.14 Å). Also, the fluorine b coordinate is negative, -0.10 ± 0.03 Å, since

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Table VIII. Comparison of Bond Lengths[a] in $C_2B_5H_6F$ and $C_2B_5H_7$

	bond length, Å		
bond	$C_2B_5H_6F$	$C_2B_5H_7$	Δ
B_1–B_7	2.343 (02) (2.410)	2.329 (05) (2.412)	0.014
B_1–B_3	1.825 (03) (1.894)	1.818 (05) (1.908)	0.007
B_1–B_5	1.813 (05) (1.882)	1.815 (05) (1.812)	–0.002
B_1–B_6	1.844 (05) (1.826)	1.815 (05) (1.812)	0.029
B_3–B_5	2.667 (12) (2.742)	2.648 (05) (2.675)	0.019
B_3–B_6	2.700 (13) (2.716)	2.648 (05) (2.675)	0.052
B_5–B_6	1.559 (31) (1.659)	1.651 (05) (1.672)	–0.092

[a] MNDO-calculated values are shown in parentheses below the experimental values.

its value was insensitive to any adjusted boron, carbon, or hydrogen coordinate, and no consistent fittings resulted for positive values. Furthermore, varying the assumed B–H bond lengths from 1.15 to 1.20 Å had negligible effects on the final fit.

Discussion

The planarity condition calculations shown in Table VII were used in calculating molecular structure parameters of $C_2B_5H_6F$, which are compared with those of the parent $C_2B_5H_7$ structure in Table VIII. It is seen that slight increases in bond lengths occur upon fluorination at the B_5 site. The B_1–B_7 distance is 0.013 Å larger in the fluoro derivative. Due to the larger than usual uncertainties in the locations of the B_5 and B_6 atoms, some structural comparisons are not as definitive as desired. Upon fluorination, the B_3–B_6 distance increases by 0.052 Å, while B_3–B_5 increases by 0.019 Å.

The estimated B–F bond length of 1.33 ± 0.03 Å is consistent with partial double-bond character. This can be compared with B–F bond lengths in several other molecules. Boron monofluoride, BF, is isoelectronic with CO and N_2 and with a short bond length of 1.26 Å is consistent with having a triple bond.[1,2] BF_3, with a 1.30-Å B–F bond length, has been described as having three sets of equivalent double bonds.[1,2] The B–F bond in $NH_4^+BF_4^-$ is a pure single bond, as expected by assuming four equivalent sp^3-hybridized orbitals on the boron, which agrees with the observed long 1.43-Å bond length.[13] By analogy, the B–F bond in $C_2B_5H_6F$ is thus viewed as having partial double-bond character.

Despite the problems associated with two boron atoms lying close to a principal axis, this molecule is slightly enlarged compared to the parent compound. This tends to support the hypothesis that back-donation by the fluorine atom causes the cage to expand. The only exception to this is the B_5–B_6 bond length, which appears contracted by 0.09 Å. This may be due to problems in locating the B_5 atom or may reflect an actual structural difference.

Interesting work remaining includes a comparison of structures of B_1- or B_3-substituted monofluoro compounds, along with successively further fluorinated species.

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Fluorination of Boron Chlorides and Boron Bromides by Reaction with Bis(trifluoromethyl)mercury, Trichlorofluoromethane, or Tribromofluoromethane: Synthesis of $BF_2B_5H_8$

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The interaction of BCl_3 with excess $CFCl_3$ has been examined by ^{11}B and ^{19}F NMR. Although small amounts of $BFCl_2$ and BF_2Cl, 9% each, are observed after 283 h at 65 °C, BF_3 is not a major product. At 130 °C, however, BF_3 is formed in 89% yield after 33 h. Boron trifluoride is isolated in 98 and 97% yields from the reactions of BCl_3 and BBr_3, respectively, with $CFBr_3$ at 130 °C. At ambient temperature, $Hg(CF_3)_2$ reacts with BCl_3 and BBr_3, generating BF_3 in 99 and 98% yields, respectively. The reaction of B_2Cl_4 with excess $CFCl_3$ was followed spectroscopically at 65, 90, and 130 °C, and the ^{19}F chemical shifts of the partially fluorinated diboron tetrahalides have been assigned. Diboron tetrafluoride was isolated from the reaction between B_2Cl_4 and $CFBr_3$ in 89% yield, from B_2Br_4 and $CFBr_3$ in 78% yield, and from B_2Cl_4 and $Hg(CF_3)_2$ in 89% yield. Within 45 min the reaction between 1-$BCl_2B_5H_8$ and $Hg(CF_3)_2$ produces the new compound 1-$BF_2B_5H_8$ in 96% yield. Tetraboron tetrachloride is by far the least reactive of the boron chlorides examined.

Introduction

Recently we have become interested in the preparation of the polynuclear boron fluorides, and as one early phase of this investigation we have elected to examine the possibility of developing fluorinating procedures that are viable alternatives to those currently employed. The classic reagent, of course, is antimony trifluoride, which was originally reported to transform B_2Cl_4 into B_2F_4 in 78% yield.[1] The disadvantage of the antimony fluoride reactions is that generally the reagent must be twice sublimed and then two separate applications of SbF_3 are required.[1]

Diboron tetrafluoride, the simplest of the polynuclear boron fluorides, has also been prepared by the action of SF_4 on B_2O_2, $B_2(OEt)_4$, and $B_2(OH)_4$, but in lesser yields, 50, 30, and 34%, respectively.[2] An alternative synthesis of B_2F_4 involves the interaction of TiF_4 with B_2Cl_4, a reaction that is stated to proceed readily.[3] Another preparative route to B_2F_4 is that developed by Timms, the high-temperature reduction of BF_3 with elemental boron.[4]

For the purposes at hand, however, the most interesting report in the literature is the one in which Schlesinger describes the reaction between allyl fluoride and B_2Cl_4, an apparently complex

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