discussions on several parts of this study as well as Mlle. C. Chappuis and Mme. C. Mimouni for their technical assistence.

Registry No. $[(Et)_4N]_2MnBr_4$, 2536-14-3; $[(Et)_4N]_2MnCl_4$, 6667-73-8; $[(Et)_4N]_2Mn(NCO)_4$, 14127-43-6; $[(Me)_4N]_2CoBr_4$, 22033-49-4; $[(Et)_4N]_2CoBr_4$, 2041-04-5; $[(Me)_4N]_2CoCl_4$, 16594-85-7; $[(Et)_4N]_2CoCl_4$, 6667-75-0; $[(Me)_4N]_2Co(NCO)_4$, 29950-55-8; $[(Et)_4N]_2Co(NCO)_4$, 14283-72-8; $[(Me)_4N]_2Co(NCS)_4$, 14052-14-3; $[(Et)_4N]_2Co(NCS)_4$, 14518-17-3; $[(Bu)_4N]_2Co(NCS)_4$, 23467-62-1; $[(Me)_4N]_2Co(NCSe)_4$, 29950-53-6; $[(Me)_4N]_4Co(NCSe)_6$, 10171-20-7; $[(Et)_4N]_2NiBr_4$, 35063-90-2; $[(Et)_4N]_2NiCl_4$, 5964-71-6; $[(Me)_4N]_2Ni(NCS)_4$, 42615-06-5; $[(Me)_4N]_4Ni(NCS)_6$, 14054-70-7; $[(Et)_4N]_4Ni(NCS)_6$, 14096-03-8; $[(Et)_4N]_4Ni(NCSe)_6$, 10478-60-1; $[(Me)_4N]_2CuBr_4$, 15692-22-5; $[(Me)_4N]_2CuCl_4$, 15692-26-9; $[(Et)_4N]_2CuCl_4$, 13927-32-7; $[(Me)_4N]_2ZnBr_4$, 2041-07-8; $[(Et)_4N]_2ZnBr_4$, 2041-06-7; $[(Me)_4N]_2ZnCl_4$, 14240-97-2; $[(Et)_4N]_2ZnCl_4$, 5964-74-9; $[(Me)_4N]_2Zn(NCO)_4$, 29950-56-9; $[(Et)_4N]_2Zn(NCO)_4$, 14283-74-0; $[(Me)_4N]_2Zn(NCS)_4$, 14187-47-4; $[(Et)_4N]_2Zn(NCS)_4$, 34287-49-5; $[(Me)_4N]_2Zn(NCSe)_4$, 29950-54-7; $[(Et)_4N]_2Zn(NCSe)_4$, 29950-54-7; $[(Et)_4N]_2CuBr_4$, 13927-35-0.

Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208

Microwave, Infrared and Raman Spectra, Structure, Dipole Moment and Barrier to Internal Rotation of Vinyldifluoroborane[1]

J. R. DURIG,* R. O. CARTER, and J. D. ODOM

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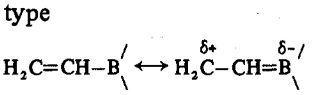
The microwave spectra of $CH_2CH^{10}BF_2$ and $CH_2CH^{11}BF_2$ have been recorded from 12.4 to 40.0 GHz. Both A- and B-type transitions were observed and Q- and R-branch assignments have been made for the ground state. Satellite lines resulting from the excited states of the BF_2 torsion and two skeletal deformation modes were also identified and assigned. From the near-zero value of the inertial defect, $\Delta = I_C - (I_A + I_B) = 0.032$ amu Å², it is concluded that the molecule is planar. The total dipole moment was determined to be 1.74 ± 0.04 D, with components $\mu_a = 1.69 \pm 0.04$ D and $\mu_b = 0.37 \pm 0.02$ D. The infrared (200–4000 cm^{-1}) and Raman spectra (0–3500 cm^{-1}) have been recorded for both the gas and the solid. A complete vibrational assignment is proposed. The internal torsional mode was observed at 103 cm^{-1} in the Raman spectrum of the gas and a twofold periodic barrier of 4.17 kcal/mol was calculated. These data were consistent with the relative intensity measurements in the microwave spectrum. The B–C bond distance appears reasonable relative to the values reported for this distance in other organoboranes.

Introduction

The compound vinyldifluoroborane was first prepared and characterized by Brinckman and Stone[2] in 1960. Since that time, this particular compound has received very little attention although vinylboranes in general have been widely investigated. Interest in this general class of compounds has centered on the question of boron–carbon π bonding since the boron atom has a low-lying vacant p_π orbital which could accept electron density from delocalization of the π system of the vinyl group. Mesomeric interactions of the type



$$H_2C{=}CH{-}B\Big< \longleftrightarrow H_2\overset{\delta+}{C}{-}CH{=}\overset{\delta-}{B}\Big<$$

could make a substantial contribution to the bonding in vinylboranes. Studies of the acceptor ability of vinylboranes,[3] ^{19}F nmr studies of vinylfluoroboranes,[3] a study of the absorption frequencies of the C=C stretching band in α,β-unsaturated organoboron compounds,[4] as well as a consideration of the position and intensities of the C=C stretching absorption in the infrared spectra[4] of $H_2C{=}CHBCl_2$ and $Me_3N{\cdot}BCl_2(CH{=}CH_2)$ have been used as chemical and spectroscopic evidence for the occurrence of π character in the boron–carbon bonds of these compounds. In addition, B–C π bonding has been invoked as a possible explanation for the relative stability towards disproportionation of vinylalkylboron compounds,[5] as well as the absence of reaction between trivinylboron and oxygen at room temperature.[5]

Theoretical studies have also addressed themselves to the question of π bonding. An approximate linear combination of atomic orbitals-molecular orbitals computation,[6] as well as self-consistent field calculations,[7] has been performed to investigate delocalization in these systems. These calculations predicted a considerable π-electron density contribution by the halogen atoms to the boron atom in halovinylboranes. By contrast the vinyl group was found to supply little π-electron density to the boron atom. More recently, the photoelectron spectrum of trivinylborane has been obtained[8] and the conclusion reached that there is only limited conjugation in the molecule.

Thus, the question of boron–carbon π bonding in vinylboranes is still in doubt. We have embarked on a program to investigate various vinylboranes from a vibrational, rotational, and nmr point of view in order to elucidate more fully appropriate parameters of these molecules. The determination of boron–carbon bond lengths, the barrier to internal rotation about the boron-carbon bond, and boron–carbon coupling constants should all present a clearer picture of the bonding in vinylboranes. In this paper we

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present a vibrational and rotational study of vinyldifluoroborane.

Experimental Section

The sample of vinyldifluoroborane was prepared by the reaction of boron trifluoride and tetravinyltin.[2] The reactants were contained in an evacuated glass bulb which was maintained at 60° for 24 hr. Preliminary purification was accomplished by pumping the reaction products through a cold trap maintained at −130° (n-C_5H_{12} slush bath). Final purification was achieved by passing the sample through a low-temperature, high-vacuum fractionation column[9] to remove any remaining boron trifluoride. Purity was checked by ir[2] and ^{11}B nmr.[4]

The samples were always held in glass containers equipped with greaseless Teflon stopcocks and stored in liquid nitrogen whenever possible. All transfers were made in either all-glass or glass and stainless steel manifolds equipped with greaseless stopcocks.

The microwave spectra were recorded with a Hewlett-Packard 8460A MRR microwave spectrometer, using a Stark modulation frequency of 33.33 kHz. Frequency measurements were made with the Stark cell at room temperature and cooled with Dry Ice. Scans to both high and low frequency were made to achieve frequency accuracy to ±0.02 MHz.

Infrared spectra were recorded from 200 to 4000 cm^{-1} using a Perkin-Elmer Model 621 spectrophotometer. Atmospheric water vapor was removed from the spectrophotometer housing by flushing with dry nitrogen. In the high-frequency region, the instrument was calibrated in the usual manner,[10] whereas the lower frequency region was calibrated with atmospheric water vapor and the assignments of Hall and Dowling.[11] The infrared frequencies are felt to be accurate to ±2 cm^{-1}. Cesium iodide plates were used as windows for the gas and cold cell as well as the substrate for the low-temperature experiment.

Raman spectra were recorded on a Cary 82 Raman spectrophotomer[12] equipped with a Coherent Radiation Model 53A argon ion laser. The Raman frequencies are known to ±2 cm^{-1}. The spectrum of the gas was recorded using a standard Cary multipass gas cell. The Raman spectra of liquid and solid vinyldifluoroborane were obtained using a Harney-Miller[13] type cell, cooled with the vapors of boiling liquid nitrogen. The 5145-Å laser line was used with an estimated power of 2 W at the sample.

Microwave Spectrum and Assignment

The microwave spectrum of vinyldifluoroborane, scanned from 12.4 to 40.0 GHz, possesses numerous groups of lines at irregular intervals. A portion of this spectrum is shown in Figure 1. This spectrum was tentatively assigned as the R branches of an A-type rotor in accordance with an assumed structure which was based on previously suggested structural parameters for propylene[14] and methyldifluoroborane.[15] This tentative assignment was confirmed by Stark studies on several lines. Each observed transition was found to have three relatively strong vibrational satellites associated with the ground state lines (see Figure 2). In addition, the ^{10}B isotope (~20% natural abundance) is expected to absorb at nearly the same frequency as the ^{11}B isotope, since the center of mass is very near the boron position in the assumed structure. The most intense line in each transitional series was measured and fitted with the rigid-rotor approximation. Using this fit two B-type Q-branch transitions were located and their frequencies measured. The 19 measured R- and Q-branch transitions were again fit to the rigid-rotor approximation *via* an iterative least-squares program which reproduced the observed frequencies to less than ±0.36 MHz (see Table I). The rotational constants were determined to be $A = 9632.65$ MHz, $B = 3836.03$ MHz, and $C = 2743.00$ MHz. (See Table II.)

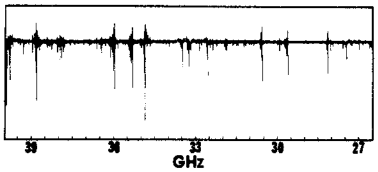

Figure 1. Microwave survey spectrum of vinyldifluoroborane from 26.5 to 40.0 GHz recorded at 10 MHz/sec and a sample pressure of 70 μ. The waveguide was cooled with Dry Ice.

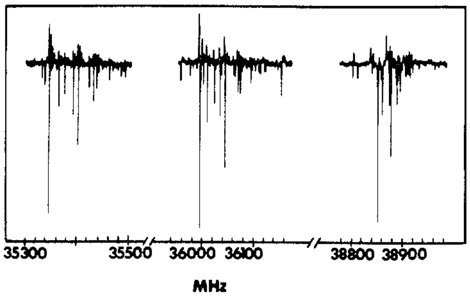

Figure 2. Microwave spectra of selected rotational transitions showing the relative intensity of the vibrationally excited satellites. These spectra were recorded at room temperature, 70 μ sample pressure, and a sweep speed of 1 MHz/sec.

The spectrum of the ^{10}B isotope was calculated from the assumed structure and assigned on the basis of the predicted differences between the lines for the ^{10}B and ^{11}B isotopes. These lines were confirmed by comparing the assigned ^{10}B line intensities with those for the ^{11}B lines, as well as comparing the relative intensities at ambient and Dry Ice temperature. There were cases where the ^{10}B intensities were stronger than expected; however, these lines could always be accounted for by the coincidence of the ^{10}B line and an excited vibrational state of the ^{11}B species. Nine R-branch lines of the ^{10}B isotope, which were not overlapped by transitions of the ^{11}B-containing molecule, were fit to the rigid-rotor model. This fit reproduced the observed frequencies to within ±0.44 MHz and gave the following rotational constants: $A = 9632.8$ MHz, $B = 3840.47$ MHz, and $C = 2745.22$ MHz. (See Table II.)

Five R-branch transitions for the three most intense vibrationally excited states of the ^{11}B species were measured and also fit to the rigid-rotor approximation (see Table II). All attempts to locate ^{13}C species proved futile as they could not be distinguished from the multitude of B-type lines which occurred throughout the spectral region investigated.

The assignment of the three vibrationally excited states, in-plane and out-of-plane motions, were made on the basis of the observed inertial defects for these three series of lines. Two of the lines, labeled $\nu_{18} = 1$ and $\nu_{17} = 1$, are assigned to out-of-plane modes of a'' symmetry, since they were found to have relatively large negative inertial defects. The third vibrationally excited state has been assigned to a mode of a' symmetry, since the inertial defect found for this state was more nearly equal to zero. It should be pointed out that the inertial defect has been used only as a qualitative tool, since highly accurate rotational constants could not be obtained. Only $J = 5 \leftarrow 4$ and $J = 6 \leftarrow 5$ transitions were used in determining the

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Table I. Rotational Transition Frequencies (MHz) of Vinyldifluorobrane

	$CH_2CH^{11}BF_2$								$CH_2CH^{10}BF_2$, ground state	
	Ground state		$\nu_{18} = 1$		$\nu_{17} = 1$		$\nu_{13} = 1$			
Transition	Obsd	Obsd – calcd	Obsd	Obsd – calcd	Obsd	Obsd – calcd	Obsd	Obsd – calcd	Obsd	Obsd – calcd
$2_{02} \leftarrow 1_{01}$	13,017.74	0.20								
$2_{11} \leftarrow 1_{01}$	14,251.22	0.17								
$3_{13} \leftarrow 2_{12}$	18,014.80	0.09								
$3_{21} \leftarrow 2_{20}$	20,284.06	−0.15								
$3_{12} \leftarrow 2_{11}$	21,282.35	−0.02								
$4_{14} \leftarrow 3_{13}$	23,880.09	0.06								
$4_{04} \leftarrow 3_{03}$	25,032.01	0.02								
$4_{22} \leftarrow 3_{21}$	27,489.62	−0.21							27,521.42	0.12
$4_{13} \leftarrow 3_{12}$	28,184.50	0.02							28,214.20	0.15
$5_{15} \leftarrow 4_{14}$	29,654.94	0.13							29,680.60	0.11
$5_{05} \leftarrow 4_{04}$	30,592.10	0.22	30,627.49	0.11	30,620.20	0.06	30,602.50	0.19	30,616.60	0.04
$5_{24} \leftarrow 4_{23}$	32,583.12	−0.22	32,603.06	0.13	32,601.00	0.13	32,590.40	0.19	32,614.80	0.44
$5_{33} \leftarrow 4_{32}$	33,269.45	−0.25							33,304.62	−0.28
$5_{32} \leftarrow 4_{31}$	33,500.49	−0.22							33,537.31	0.33
$6_{16} \leftarrow 5_{15}$	35,345.34	0.05	35,401.88	0.02	35,392.00	0.00	35,364.00	0.03	35,375.33	0.04
$6_{06} \leftarrow 5_{05}$	36,001.52	0.13	36,050.38	−0.07	36,040.50	−0.03	36,016.00	−0.14	36,029.75	−0.07
$6_{25} \leftarrow 5_{24}$	38,848.43	−0.36	38,874.43	−0.12	38,871.20	−0.12	38,857.50	−0.02		
$7_{26} \leftarrow 7_{17}$	35,174.41	0.25								
$7_{35} \leftarrow 7_{26}$	35,609.25	−0.19								

Table II. Rotational Constants and Moments of Inertia of Vinyldifluoroborane in the Ground and Excited Vibrational States[a]

	$CH_2CH^{11}BF_2$				$CH_2CH^{10}BF_2$
	$\nu = 0$	$\nu_{18} = 1$	$\nu_{17} = 1$	$\nu_{13} = 1$	$\nu = 0$
A	9632.65 ± 0.05	9568.6 ± 1.0	9573.3 ± 1.0	9603.6 ± 1.8	9632.8 ± 0.8
B	3836.03 ± 0.01	3832.88 ± 0.04	3833.80 ± 0.03	3835.09 ± 0.06	3840.47 ± 0.03
C	2743.00 ± 0.01	2749.59 ± 0.03	2748.44 ± 0.02	2745.23 ± 0.05	2745.22 ± 0.02
κ	−0.682783	−0.68227	−0.68194	−0.68219	−0.68196
I_A	52.4650 ± 0.0003	52.816 ± 0.005	52.790 ± 0.005	52.624 ± 0.009	52.464 ± 0.004
I_B	131.745 ± 0.0005	131.853 ± 0.002	131.821 ± 0.002	131.777 ± 0.002	131.592 ± 0.001
I_C	184.242 ± 0.0005	183.801 ± 0.002	183.878 ± 0.002	184.093 ± 0.002	184.093 ± 0.001
Δ	+0.032	− 0.868	−0.733	−0.308	+0.037

[a] Rotational constants are in megahertz and moments of inertia are in atomic mass units times angstroms squared and obtained with the conversion factor 505,377 MHz amu Å^2. The errors in the moments of inertia are those implied by the error in the corresponding rotational constants.

rotational constants for the three excited states because at lower J values the vibrationally excited rotational lines coalesced to a degree where identification and accurate measurement of individual lines became impossible. Further discussion of the assignment of these vibrational states is presented in the vibrational assignment section.

Structure

A complete structural analysis is not possible from the data obtained. There is, however, some information which can be obtained from the two boron isotopes studied. There are two possible conformations which should be considered for vinyldifluoroborane, as a result of the rotation of the BF_2 group about the B–C bond. In one conformation, the molecule is completely planar, whereas in the other conformation the plane of the BF_2 group is perpendicular (90°) to the plane of the vinyl group. There is no reason to expect some intermediate angle for the BF_2 group. In the case of the planar structure an inertial defect [*i.e.*, $\Delta = I_C - (I_A + I_B)$] of nearly zero is predicted for the vibrational ground state. In fact, a small but slightly positive number is expected.[16] As can be seen in Table II, the inertial defect, Δ, for the ground vibrational state is indeed a positive number and very nearly zero. Thus, one can conclude that the vinyldifluoroborane molecule is planar, *i.e.*, the plane of the BF_2 group is coplanar with that of the vinyl group.

Although bond distances and angles cannot be calculated from the rotational constants for the two isotopes these data can be used to suggest an approximate structure if the vinyl structure is assumed and the other parameters are fit to the measured moments of inertia by an iterative least-squares computer program. Since the structure was always taken as planar in the least-squares fit, only two of the three moments are independent so that refinement is limited to four moments for the two species. The vinyl group structure was assumed to be the same as that found in propylene,[14] and the fluorines were assumed to be symmetric about the axis of the B–C bond. By changing the ∠CCB from 119 to 123° on successive runs, r_{B-F}, r_{B-C}, and ∠BF_2 were adjusted to fit the measured moments of inertia. r_{B-F} and ∠BF_2 were found to be 1.336 ± 0.002 Å and 114.5 ± 0.3° although r_{B-C} varied more widely. Then by varying the r_{B-F} and ∠BF_2 over the limits found above the r_{B-C} was found to be 1.536 ± 0.020 Å and ∠CCB to be 120.2 ± 2.0°.

We feel the values themselves are better than the error limits indicate, since the moments of inertia of the structure with values as listed reproduced the observed I_B and I_C to ±0.002 amu Å^2 and gave I_A to ±0.004 amu Å^2 of that expected when taking the inertial defect into account (even though I_A was not included in the fit).

Dipole Moment

Quantitative Stark effect measurements were made on the $|M| = 4$, $|M| = 3$, and $|M| = 2$ components of the $J = 5_{05} \leftarrow 4_{04}$ transition for the ^{11}B isotope of vinyldifluoroborane in the ground vibrational state. The effective field in the Stark cell was determined from measurements

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Table III. Stark Coefficients (MHz cm^2/V^2) and Dipole Moment of Vinyldifluoroborane As Measured for the $5_{05} \leftarrow 4_{04}$ Transition

$\lvert M \rvert$	Obsd	Calcd
4	0.880 ± 0.05	0.8800
3	0.619 ± 0.05	0.6186
2	0.432 ± 0.03	0.4318

$\lvert\mu_a\rvert = 1.69 \pm 0.04$ D, $\lvert\mu_b\rvert = 0.37 \pm 0.02$ D, $\lvert\mu_{\text{total}}\rvert = 1.74 \pm 0.04$ D

of the Stark effect of the $J = 3 \leftarrow 2$ transitions of OCS and its dipole moment of 0.71521 D.[17] The observed and calculated results are listed in Table III. The μ_C component is zero since the molecule has been shown to be planar and the dipole moment must lie entirely in the A-B plane. The total dipole moment of 1.74 D is between that of ethynyldifluoroborane, 1.876 ± 0.01 D,[18] and that of methyldifluoroborane, 1.67 ± 0.02 D.[19]

Vibrational Assignment

From the microwave study of vinyldifluoroborane it has been shown that all atoms must lie on a plane of symmetry so that the molecule has C_s symmetry, with 18 degrees of vibrational freedom. The normal modes are divided into 13 of a$'$ symmetry and 5 of a$''$ symmetry. Both symmetry species are allowed in the infrared and Raman spectra, and polarized Raman bands are expected for normal modes of a$'$ symmetry. Also, in-plane motions (a$'$) are expected to have A, B, or AB hybrid infrared gas-phase contours, whereas the out-of-plane (a$''$) modes should have C contours with strong, sharp Q branches. In addition to the band contours from the infrared spectrum and depolarization ratios from the Raman effect, group characteristic frequencies were also used in making the assignment. All of the observed infrared and Raman frequencies are listed in Table IV. and the assignments are given in Table V.

The three carbon-hydrogen stretching modes are found at 3090, 3032, and 2991 cm^{-1} with the lowest frequency mode assigned to the C-H motion and the highest one to the out-of-phase CH$_2$ stretch. The C=C stretch gives rise to an extremely strong Raman line at 1624 cm^{-1}. All other CH motions are expected to exhibit bands below 1500 cm^{-1}. The strong A-type band at 1422 cm^{-1} in the infrared spectrum is assigned to the CH$_2$ scissoring mode, ν_6. There are three C-H bending motions of a$''$ symmetry which should give rise to infrared bands with C-type contours. The three sharp Q branches seen in the infrared spectrum at 988, 750 and 729 cm^{-1} (see Figure 3) are assigned to the three out-of-plane CH modes. The 988-cm^{-1} band is assigned to the twisting mode since it is within the 995-985-cm^{-1} region found for the twist by Potts and Nyquist.[20] The 750-cm^{-1} band is assigned to the wagging mode, whereas the 729-cm^{-1} band is assigned to the =C-H out-of-plane bend. These two assignments could be reversed but they were assigned on the basis that the wagging mode is often without a counterpart in the Raman effect (see Figures 4 and 5), which is consistent with the 750-cm^{-1} band. The strong A-type infrared band at 1248 cm^{-1} and the medium infrared band at 1014 cm^{-1} are assigned to the =CH in-plane bend and =CH$_2$ rock, respectively.

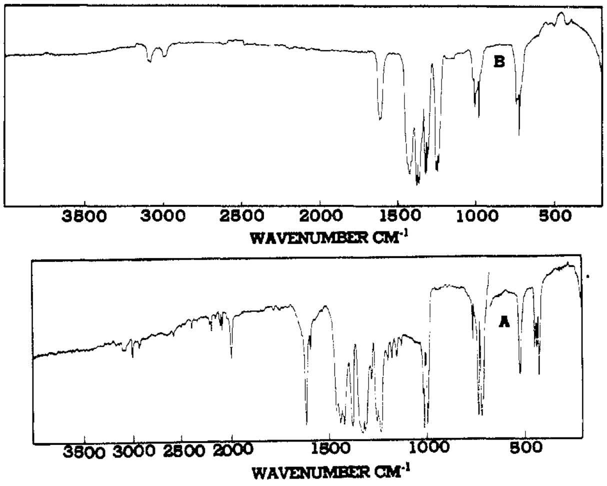

Figure 3. A. Mid-infrared spectrum of solid vinyldifluoroborane recorded at ~−140°. B. Mid-infrared spectrum of gaseous vinyldifluoroborane recorded with a sample pressure of ~10 mm in a 20-cm cell.

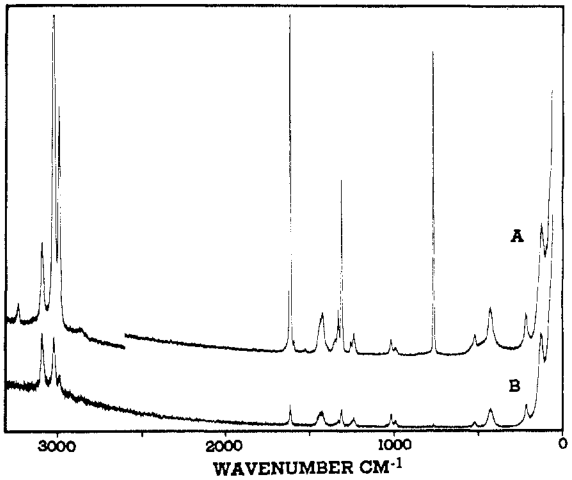

Figure 4. Raman spectra of liquid vinyldifluoroborane recorded at ~−20° and giving the relative intensities of the parallel (A) and perpendicular (B) polarizations.

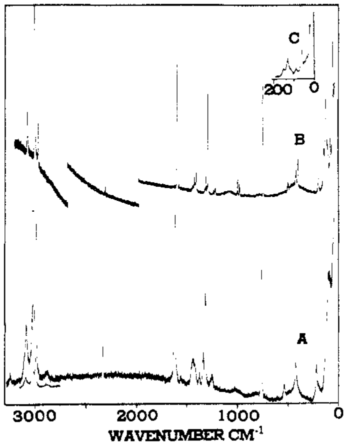

Figure 5. A. Raman spectrum of vinyldifluoroborane in the gas-phase recorded with a spectral slit width of 5 cm^{-1}. B. Raman spectrum of solid vinyldifluoroborane at ~−130° recorded with a spectral slit width of 2 cm^{-1}. C. An expansion of the low-frequency Raman spectrum of vinyldifluoroborane at ~−130° recorded at 2-cm^{-1} spectral slit width.

The symmetric and antisymmetric BF$_2$ stretches are assigned to the infrared bands centered at 1316 (type A contour) and 1373 cm^{-1} (type B contour), respectively. Isotopic splitting of the ^{10}B and ^{11}B species is evident in both the

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Table IV. Infrared and Raman Spectra of Vinyldifluoroborane[a]

Infrared				Raman					
Gas $\bar{\nu}$, cm^{-1}	Band type[b]	Rel Intens	Solid $\bar{\nu}$, cm^{-1}	Gas $\overline{\Delta\nu}$, cm^{-1}	Liquid $\overline{\Delta\nu}$, cm^{-1}	Rel Intens	Depolarizn	Solid $\overline{\Delta\nu}$, cm^{-1}	Assignments
					8232	m	0.1		$2 \times \nu_4 = 3240$
3096 R	A	w							
3090 Q	A	w	3090	3189	3089	s	0.66	3095	ν_1
3082 P									
3032	?	vvw		3124	3021	vs	0.1	3023	ν_2
2998 R									
2991 Q	A	w	2991	2991	2990	s	0.1	2992	ν_3
2983 P									
1630 R									
1623 Q	A	m	1618	1624	1620	vs	0.10	1620	ν_4
1614 P									
				1600	1598	vw, sh	0.10	1594	
								1465	
1442	?	sh	1442	1442	1440	sh	0.38	1445	$2 \times \nu_{16} = 1442$
1428 R									
1422 Q	A	s	1422	1426	1426	m, b	0.30	1425	ν_5
1415 P									
1380 R									
1366 P	B	s	1380	1375	1350	w, sh, b	~0.60		ν_6
1344		sh	1344	1340	1332	m, sh	>0.1	1330	$\nu_7(^{10}B)$
				1327 sh					
1325 R									
1316 Q	A	s	1316	1318	1317	s	0.01	1306	$\nu_7(^{11}B)$
1308 P			1256	1266	1259	vw, sh	0.33	1259	$\nu_{10} + \nu_{11} = 1286$
1256 R									
1248 Q	A	s	1236	1253	1240	w	0.37	1238	ν_8
1240 P									
1024		sh	1021	1026	1020	w	dp	1017	
1014	?	m	1015					1001	ν_9
988	C	m	995		995	vw	dp	997	ν_{14}
768	?	w, sh	763	767	766	s	0.01	763	ν_{10}
750	C	w	736						ν_{15}
729	C	m	727		721	vw	?		ν_{16}
540	?	sh	522	538	520	m	0.35	519	ν_{11}
520 R									
511 Q	A	w							
505 P									
			448					439 sh	$2 \times \nu_{17}$?
			436					435	$2 \times \nu_{13} = 434$
434 R									
426 Q	A	w	424	427	427	s	0.39	421	ν_{12}
418 P									
				221	214	m	0.65	217	ν_{13}
				198 sh					ν_{17}
								160	Lattice
				103	125	m	dp	138	ν_{18}
								124	Lattice
								99	Lattice
								69	Lattice
								49	Lattice
								42	Lattice
								32	Lattice

[a] Abbreviations used: s, m, w, v, dp, sh, and b, denote strong, medium, weak, very, depolarized, shoulder, and broad, respectively. [b] A, B, and C refer to the infrared band envelope types, whereas ^{10}B and ^{11}B refer to the boron-10 and boron-11 isotopes.

infrared and Raman spectra for the symmetric mode only. The boron–carbon stretch is assigned to the strong Raman line at 766 cm^{-1}. It should be pointed out that these three stretching modes are believed to be coupled and that the lowest frequency mode is a symmetric stretch which is predominantly a boron–carbon motion. The assignment given is in good agreement with those given previously for the corresponding normal mode in similar molecules.[21,22]

There now remain five skeletal deformations unassigned, three of a′ symmetry and two of a″ symmetry. The torsional motion about the B–C bond is expected to be the lowest frequency mode. The Raman band with a shift frequency of 103 cm^{-1}, which is depolarized, is assigned to this mode. From the microwave intensities of vibrationally excited states, the lowest frequency mode is predicted to be at 106 ± 20 cm^{-1}. Furthermore, the inertial defect found for the most intense vibrationally excited state in the microwave spectrum was found to be indicative of an out-of-plane mode. A second low-frequency mode with an inertial defect characteristic of an out-of-plane motion was also measured in the microwave spectrum and has a frequency of 200 ± 20 cm^{-1}. This mode was observed to be of similar microwave intensity to a third satellite line which is believed to be associated with an in-plane motion having a frequency of 196 ± 20 cm^{-1} from microwave intensities. These two motions must be the in-plane BCC and the out-of-plane F_2BC bending modes. The in-plane bend is assigned to

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Table V. Summary of the Fundamental Vibrational Frequencies (cm^{-1}) of Vinyldifluoroborane

C_s species	Vibrational no.	Approx description	$\bar{\nu}$ gas	$\overline{\Delta\nu}$ liquid	$\bar{\nu}$ solid
A′	1	CH_2 antisym str	3090	3089	3096
	2	CH_2 sym str	3032	3021	3023
	3	CH str	2991	2990	2991
	4	C=C str	1623	1620	1618
	5	CH_2 scissors	1422	1426	1422
	6	BF_2 antisym str	1373		1380
	7	BF_2 sym str	1316	1317	1316
	8	CH in-plane bend	1248	1240	1236
	9	CH_2 rock	1014		1015
	10	B–C str	768	766	763
	11	BF_2 scissors	540	520	522
	12	CBF_2 bend	426	427	424
	13	BCC in-plane bend	221[a]	214	217
A″	14	CH_2 twist	988	995	995
	15	CH_2 wag	750		736
	16	CH out-of-plane	726	721	727
	17	CBF_2 bend	198[a]	214	217
	18	BF_2 torsion	103	125	138

[a] In the liquid and solid states, these two fundamentals seem to coalesce to one band.

a polarized Raman line with a shift frequency of 221 cm^{-1}. The F_2BC out-of-plane bend is assigned to the weak shoulder at 198 cm^{-1} as seen in the Raman spectrum of the gas. The two lines seem to coalesce in the liquid and solid Raman spectra which may account for the lowering of the scattering frequency on condensation. The other two in-plane bends are assigned to the two remaining polarized Raman bands (see Figure 5) at 538 and 427 cm^{-1}, with the higher frequency one attributed to the BF_2 scissoring mode and the lower frequency one to the CBF_2 in-plane bend. A series of bands was observed in the Raman spectrum of the solid phase at 160, 124, 99, 69, 49, 42, and 32 cm^{-1}. These bands were found to disappear completely just as the crystal melted; therefore, all are attributed to intermolecular fundamental vibrations. Such a large number of lattice vibrations indicates that there are at least two molecules per primitive cell and possibly more. Sufficient sample was not available for far-infrared studies, so the lattice modes could not be characterized further.

Barrier to Internal Rotation

The periodic barrier to internal rotation of the symmetric BF_2 group about the BC bond against the asymmetric frame was calculated according to the procedure given by Herschbach[23] by using Mathieu tables for high *s* values supplied by Fateley, Miller, and Witkowski.[24] The calculation assumes a cosine-shaped potential function of the form

$$V(\alpha) = {}^1/_2\,[V_2(1 + \cos 2\alpha) + V_4(1 + \cos 4\alpha) + \cdots]$$

where V_2 is the height of the twofold barrier and all higher terms were neglected. The torsional frequencies are related to the Mathieu eigenvalues by the expression

$$\omega_T = \Delta E_{v\sigma} = (n/2)^2 F \Delta b_{v\sigma}$$

where F is the reduced internal rotation constant about the top axis, $b_{v\sigma}$ are the eigenvalues of the Mathieu equation, v is the torsional quantum number, and σ is the index designating the sublevels. A value for the Mathieu equation eigenvalue can be computed from the reduced moment constant and the 0 → 1 torsional transition. From the calculated value of $\Delta b_{v\sigma}$ and high *s* value tables, a dimensionless parameter *s* is related to the twofold barrier height by $V_2 = Fs$. From the assigned torsional frequency of 103 cm^{-1} and a reduced moment of 1.863 cm^{-1}, a barrier of 1439 cm^{-1} or 4.17 kcal/mol was calculated. Possible frequency error of ±2 cm^{-1} leads to an error of ±0.2 kcal/mol.

Discussion

Vinyldifluoroborane has been shown to be planar from its near-zero inertial defect. The four independent rotational constants were used to obtain the structure of the BF_2 moiety and the boron–carbon distance assuming the vinyl structure to be unchanged from that of propylene.[14] This led to r_{B-C}, r_{B-F}, $\angle BF_2$, and $\angle CCB$ of 1.536 Å, 1.336 Å 114.5°, and 120.2°, respectively. The uncertainty in these parameters is difficult to assess, and the error limits given in the text are a result of the least-squares calculations and are probably not an accurate picture of parameter error. For example, the error in the $\angle BF_2$ is surely more than ±0.3° but conversely the error in the boron–carbon bond distance is probably less than ±0.02 Å. The r_{B-F} found is longer than that reported for ethynyldifluoroborane[18] (1.323 Å); similarly, the $\angle BF_2$ has been found to be 114.5°, which is considerably smaller than the corresponding angle in difluoroborane,[25] 118.3°, and ethynyldifluoroborane, 116.8°. The boron–carbon distance is longer than that of ethynyldifluoroborane (1.513 Å) but shorter than that for methyldifluoroborane[15] (1.60 Å). This trend in boron–carbon bond length is precisely what is expected when the hybridization of the carbon, bonded to a BF_2 group, changes from sp to sp^2 to sp^3. Thus, there is no reason to believe there is a bond shortening in the boron–carbon bond due to π overlap with the carbon–carbon double bond. However, the structural data are not yet complete especially in terms of the carbon–carbon distance which had to be assumed. In addition, there is no information at present to indicate what a normal sp^2 boron–sp^2 carbon bond distance should be. Finally, it is quite clear that the molecule is stabilized in the planar form and that this geometry would be favored by delocalization of charge from the double bond into the vacant p orbital of the boron. However, as yet there is no concrete evidence to argue either for or against π overlap in the boron–carbon bond.

The barrier of 4.17 kcal/mol restricting internal rotation in vinyldifluoroborane appears rather large compared to the threefold barriers of 1.98 and 1.56 kcal/mol found for propylene[26] and vinylsilane,[27] respectively. However, it should be pointed out that the threefold barriers of ~1.0 kcal/mol around O-H bonds[28] are found to increase to ~3.2 kcal/mol for molecules with twofold barriers.[24] Therefore, it is believed that the 4.17-kcal/mol barrier simply reflects the decrease in the foldness of the potential rather than any significant double-bond character in the B–C bond.

In an attempt to gain more insight into the factors which contribute to the stability of the planar conformation, we carried out an INDO calculation with the molecule in both the planar and twisted configuration. The planar configuration was found to be more stable, but the π-electron density in both the B–C and C=C bonds did not significantly

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differ between the two conformations. The calculated dipole had a value of 2.53 D which is considerably larger than the experimental value of 1.74 D. This discrepancy is somewhat larger than one would expect from such calculations. The calculations indicated that the dipole resulted mainly from the electron densities rather than from the polarizations. The distribution of the electronic charge was found for the planar form to be: $H_{1\beta}$, 1.00; $H_{2\beta}$, 1.01; H_{α}, 0.97; C_{α}, 4.16; C_{β}, 3.87; B, 2.44; F_1, F_2, 7.28. These data may indicate that the nonbonded interactions between the fluorine and hydrogen atoms play a significant role in the stabilization of the planar configuration. The calculated energy difference between the two forms was found to be 1.2 kcal/mol which agrees with the experimental value about as well as would be expected for these type of calculations.

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Contribution from the Chemistry Department,
University of South Dakota, Vermillion, South Dakota 57069

Hexamethylenetetramine-Borane Adducts

MARVIN D. RILEY[1] and NORMAN E. MILLER*

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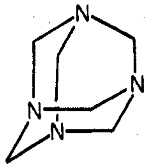
The four possible borane adducts of hexamethylenetetramine (hexamine) were prepared, three of which being hitherto unknown. Synthesis and purification procedures were worked out so that pure samples were available for chemical studies. Pyrolysis of the tetraadduct when controlled proceeded with rearrangement by hydride migration to form dimethylaminoborane derivatives. The adducts were not amenable to borane cation formation; those two cations eventually prepared, $(CH_2)_6N_4BH_2py^+$ and $(CH_2)_6N_4BH_2P(CH_3)_3^+$, were not very stable.

The four equivalent tertiary nitrogen sites in hexamine (hexamethylenetetramine) offer interesting possibilities for



multiple borane adducts. Moreover, adduct formation on vicinal base sites in this molecule might lead to charge build up and subsequent rearrangement.

A monoadduct, $(CH_2)_6N_4{\cdot}BH_3$, has previously been isolated in small yield (15%) from aqueous solutions of sodium borohydride and hexamine[2] or hexamine hydrochloride.[3] No other hexamine adducts have been reported, but bisborane adducts are known for ethylenediamine[4] and its *N*-methyl derivatives[5] as well as the analogous propanediamine bases[6] and *N,N*′-dimethylpiperazine (DMP).[7] These fully boranated adducts are air-stable, sublimable white solids in general. Some can be recrystallized from suitable solvents like acetonitrile.

Higher borane adducts of polyamines have been examined in neutron capture applications.[8] (^1H is the most effective element for moderating neutrons while ^{10}B has the highest capture cross section of the light elements.) The adducts prepared were: pentamethyldiethylenetriamine-trisborane, mp 185-186°; hexamethyltriethylenetetramine-bisborane, mp 118.5-119.5°; hexamethyltriethylenetetramine-tetrakisborane, mp 208-220°; pentamethyldi-*n*-propylenediamine-trisborane, mp 185-186.5°.

Only a few partially boranated polyamine bases are known, however. Tetramethylethylenediamine-borane ($TMEN{\cdot}BH_3$) is *not* stable above −1° and disproportionates to TMEN and $TMEN{\cdot}2BH_3$.[7] The analogous triethylenediamine (TEDA) monoborane adduct was precipitated from an equimolar mixture of TMEN and $TEDA{\cdot}2BH_3$ after heating to 70° and cooling. This monoadduct is sufficiently stable to be sublimed without purification.

Results and Discussion

Direct combination of hexamine and diborane at slightly greater than 2:1 mol ratio in benzene at 50° gives excellent yield (94%) of the monoadduct. This adduct is amazingly insoluble in all commonly available solvents. It was purified from traces of reactants and other adducts by long stirring in water.

The completely boranated adduct was sought initially in tetrahydrofuran solvent, but the product is analytically impure and very hazardous to handle, enflaming on prolonged contact with air (and one time in a capped vial). Similar experience was encountered with glyme (ethylene glycol dimethyl ether) and diethyl ether. Solvent incorporation, possibly by ether cleavage, seems to have occurred; consequently, a solvent free of oxygen was sought. Surprisingly, benzene was found to serve well, even though it is not commonly used in borane-adduct formation and it is not a good solvent for hexamine and the monoborane adduct. The monoadduct is first formed by addition of one-fourth the required borane and heating to 50° for 2 hr. (There is no reaction without heating.) The remaining diborane is added at room temperature and the result is an apparent solution of the tetraadduct, $(CH_2)_6N_4{\cdot}4BH_3$. All attempts to

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