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Vibrational Spectra and Structure of Perfluorovinyldifluoroborane and Perfluorovinyldichloroborane

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Received March 3, 1977 AIC70168I

The infrared spectra of gaseous (3000–30 cm^{-1}) and solid (3000–200 cm^{-1}) perfluorovinyldifluoroborane and perfluorovinyldichloroborane have been recorded along with the Raman spectra (3000–30 cm^{-1}) of all three physical states. The vibrational data have been interpreted in detail and are consistent with a planar geometry for both compounds. The question of π delocalization through the C–B bond is discussed.

Introduction

In tricoordinate boranes, the empty p orbital on the boron atom is potentially available for favorable interaction with suitable π-donor substituents. Vinyl groups, for instance, might be expected to act as efficient π donors and a number of studies involving vinylboranes have appeared in the literature.

Recently vinyldifluoroborane has been studied by infrared, Raman, microwave,[1,2] and nuclear magnetic resonance[3] spectroscopy. The molecule has been found to exist in a single, planar form. The planarity of the molecule was attributed to a π overlap,[1] and the ^{13}C chemical shifts of a series of vinyl boranes were found to be consistent with this interpretation.[3] However, a detailed structural analysis failed to provide direct evidence (in the form of a shortening of the B—C bond and a lengthening of the C=C bond) for delocalization.[2]

Trivinylborane has also been studied with regard to possible π overlap. Two vibrational studies have been reported,[4,5] and it has been found that the molecule exists as a mixture of two conformations in the fluid phases but in a single, planar form in the solid state.[4] An electron diffraction[6] study has verified a planar BC$_3$ skeleton while the orientations of the vinyl groups are not satisfactorily determined. The lengthening of the C=C bond relative to ethylene[6] and increased B—C vibrational frequencies relative to trialkylboranes[5] have been interpreted as proof of π overlap in the B—C bond.

In order to extend these studies to molecules having electronegative substituents on the vinyl groups, we have undertaken the study of perfluorovinylborane compounds. The infrared spectra of perfluorovinyldifluoroborane and perfluorovinyldichloroborane (henceforth referred to as V$_f$BF$_2$ and V$_f$BCl$_2$, respectively) have been reported previously[7] over a limited frequency range.

Experimental Section

All preparative work was carried out in a conventional high-vacuum system employing greaseless stopcocks. Bis(perfluorovinyl)dimethyltin was prepared according to the published procedure[8] from (CH$_3$)$_2$SnCl$_2$ (Alfa), Mg powder (Alfa), and BrC$_2$F$_3$ (PCR). Perfluorovinyldichloroborane was prepared[9] by the reaction of (CH$_3$)$_2$Sn(C$_2$F$_3$)$_2$ and purified BCl$_3$ (Matheson). Perfluorovinyldifluoroborane was prepared[9] by the fluorination of V$_f$BCl$_2$ using *freshly* sublimed SbF$_3$. Fluorination of 5.7 mmol of V$_f$BCl$_2$ at −78 °C for 2 h afforded 5.2 mmol of V$_f$BF$_2$ (91%) and very little BF$_3$. Final purification of both products was achieved by means of a cold-column vacuum fractionation.[10] Purity was checked by vapor pressure measurements and ^{19}F NMR and mass spectral measurements. We report herein detailed vibrational assignments for these molecules based on the infrared and Raman spectra of the fluid and solid phases.

Raman spectra were recorded on a Cary Model 82 spectrophotometer equipped with either a Coherent Radiation Laboratories Model 53A or a Spectra Physics Model 171 argon ion laser. The 5145-Å line was used for excitation, and the power at the sample was varied between 0.5 and 2 W depending upon the physical state being examined. The spectra of the vapors were recorded using standard Cary gas cells and multipass optics. The Raman spectra of crystalline samples were obtained in either of two cells. One is a variable-temperature cell of the Miller-Harney design[11] in which a Pyrex capillary is cooled with vaporized liquid nitrogen. The other consists of a liquid nitrogen cold finger with a brass block onto which samples are deposited. Raman spectra of V$_f$BF$_2$ and V$_f$BCl$_2$ are shown in Figures 1 and 2.

Infrared spectra were recorded from 4000 to 40 cm^{-1} using a Perkin-Elmer Model 621 grating spectrophotometer and a Digilab FTS-15B interferometer.[12] Atmospheric water vapor was removed from the spectrometer housings by flushing with dry nitrogen. The instruments were calibrated using standard gases[13] and solutions[14] in the high-frequency region, whereas the lower frequency region was calibrated with water vapor.[15] Cesium iodide plates and polyethylene were used as window material in the mid- and far-infrared regions, respectively. All frequency measurements are accurate to within 2 cm^{-1}. Typical infrared spectra are shown in Figures 3–5.

Vibrational Assignments

The symmetry of a molecule of the type F$_2$CCFBX$_2$ depends upon the orientation of the BX$_2$ group with respect to the remainder of the molecule. If the dihedral angle associated with the C–B bond is 0°, the molecule is planar with C_s symmetry. For a dihedral angle of 90° the symmetry is still C_s while any intermediate angle corresponds to C_1 symmetry. On the basis of results involving other molecules with BX$_2$ groups,[1,16] we expect the dihedral angle to be either 0 or 90°. For the planar structure the vibrational motions span the irreducible representations 13 A′ + 5 A″, while for the nonplanar, twisted structure the vibrations can be described as 12 A′ + 6 A″. The difference in the vibrational spectra of these two possible configurations are expected to be slight, the most significant difference being that the BX$_2$ antisymmetric stretch would be an A′ mode for the planar form and an A″ mode for the twisted species. The only other difference is that the BX$_2$ wag is A′ and the BX$_2$ rock is A″ for a dihedral angle of 0°, while this is reversed if the dihedral angle is 90°. For any intermediate angle, all vibrations are of A symmetry.

Perfluorovinyldifluoroborane. Because vinyldifluoroborane[1] is planar, we expected perfluorodifluoroborane to be planar also and have formulated the following vibrational assignment on this basis. It should also be mentioned that there is some resemblance of V$_f$BF$_2$ to B$_2$F$_4$ and it has been found to possess a planar conformation as well.[17] The Raman spectra of the fluid phases should consist of polarized lines for A′ vibrations and depolarized lines for the A″ motions. In the principal axis system of the molecule, the A axis is approximately parallel to the nonbonded B---C line, and the B axis is the other axis in the molecular plane. The P–R separations for A-type and B-type infrared bands have been calculated to be 12 and 8 cm^{-1}, respectively, and the A′ vibrations are expected to exhibit A, B, or A/B hybrid bands. Out-of-plane, A″, modes should give rise to C-type band contours in the infrared spectra of the gas. The observed vibrational frequencies and the following assignments are given in Table I.

In assigning the vibrations associated with the perfluorovinyl group it is worthwhile to examine molecules of the form

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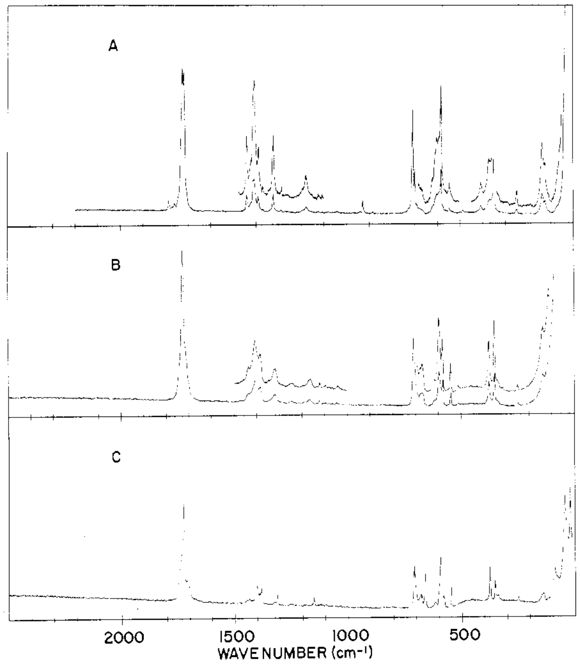

Figure 1. Raman spectra of perfluorovinyldifluoroborane: (A) gas phase, 300 Torr; (B) liquid, −20 °C; (C) crystalline solid.

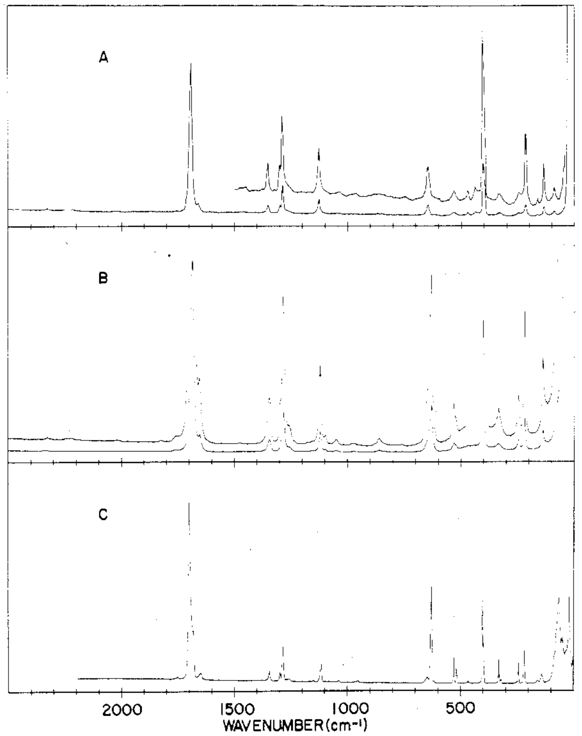

Figure 2. Raman spectra of perfluorovinyldichloroborane: (A) gas phase, 300 Torr; (B) liquid, 25 °C; (C) crystalline solid.

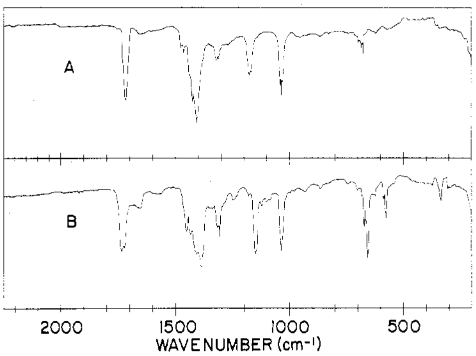

Figure 3. Infrared spectra of perfluorovinyldifluoroborane: (A) gas phase, 1 Torr; (B) crystalline solid.

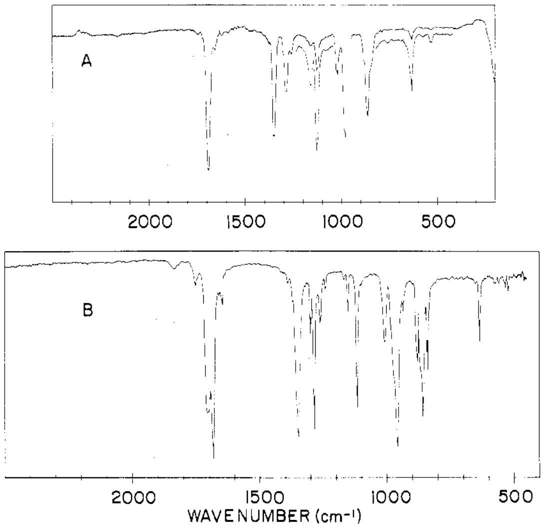

Figure 4. Infrared spectra of perfluorovinyldichloroborane: (A) gas phase, 2 Torr; (B) crystalline solid.

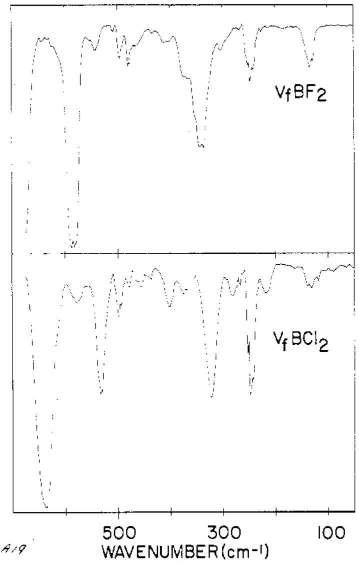

Figure 5. Far-infrared spectra of perfluorovinyldifluoroborane (700 Torr) and perfluorovinyldichloroborane (300 Torr).

F_2CCFX where X = H, D,[18] Cl,[19] and Br.[20] The C=C stretching mode in V_fBF_2 is readily assigned to the polarized Raman line at 1725 cm^{-1} in the spectrum of the gas. The region of the spectrum usually associated with the CF stretches is also a region where BF_2 stretches occur.[1] The C–F stretching modes have been assigned at 1410, 1390, and 1179 cm^{-1} for the most abundant isotopic species with a feature at 1441 cm^{-1} that corresponds to a ^{10}B species. The designations of these vibrations, as given in Table I, are primarily for convenience since these motions undoubtedly are heavily mixed with one another and with other vibrations. The $^{11}BF_2$ antisymmetric stretching mode is assigned in this region to a weak, polarized line at 1323 cm^{-1} in the Raman spectrum and the corresponding $^{10}BF_2$ motion is observed only in the solid phase. The BF_2 symmetric stretch and the C–B stretch are assigned to the strong, polarized Raman line at 709 cm^{-1} and the strong A-type band centered at 1040 cm^{-1} in the infrared, respectively. These motions are again expected to mix heavily, but the above designations are appropriate from a consid-

Table I. Observed Infrared and Raman Frequencies (cm^{-1}) for Perfluorovinyldifluoroborane, F_2CCFBF_2[a]

Infrared (solid)	Raman		Infrared (gas)	Raman (gas)	Assignment
	Solid	Liquid			
			1762 R 1758 Q } w 1752 P	1762 vw, p	$\nu_2 + \nu_{11} = 1759$ (A′)
1743 s 1729	1746 w, sh 1736 w, sh 1726 vs	1727 vs, p	1723 s, b	1725 vs, p	ν_1, C=C str
1458 m			1478 R 1473 Q } w 1468 P	1468 vw, dp	$\nu_2 + \nu_{18} = 1469$ (A″)
1441 m	1437 w, b	1439 w, sh, p	1444 R } m 1430 P	1441 w, p	ν_2, CF_2 antisym str (^{10}B)
1413 s	1403 m	1409 m, p	1420 R 1411 P	1410 m, p	ν_2, CF_2 antisym str (^{11}B)
1392 vs 1382 sh	1391 w 1383 m	1384 m, p	1385 sh	1390 w, p	ν_3, CF str
1323 sh	1324 w				ν_4, $^{10}BF_2$ antisym str
1311 m	1311 m	1321 w, p	1324 R } w 1316	1323 w, p	ν_4, $^{11}BF_2$ antisym str
			1262 Q vvw	1262 vvw, dp	$\nu_9 + \nu_{14} = 1266$ (A″)
1154 s 1146 sh	1150 m	1164 vw, b, p	1180 R } s 1172 P	1179 vw, p	ν_5, CF_2 sym str
1051 w, sh 1042 s 1031 m, sh	1053 1036 } vw	1044 vw, p	1045 R 1040 Q } s 1035 P	1040 vw, p	ν_6, B–C str
709 w	707 s	710 s, p	712 w, sh	709 s, p	ν_7, BF_2 sym str
			703 Q w		$\nu_9 + \nu_{17} = 708$ (A″)
		691 w, sh		700 m, p	$2 \times \nu_{11} = 702$ (A′)
690 w			691 Q w }		$\nu_{11} + \nu_{16} = 688$ (A″) or ν_{14}(^{10}B)
679 m	679 m	679 w, p			ν_8, CF_2 rock
672 w, sh				680 w, b	
663 s	662 s	671 w, dp	682 Q m }		ν_{14}, CF_2 wag
595 w, sh	593 s	598 m, dp		596 w	ν_{15}, BF_2 wag
582 m	579 w	582 w, p	588 R 583 Q } m 578 P	584 m, p	ν_9, BF_2 scissors
548 vw	547 m	547 w, p		548 vw, p	
			411 R } vw 403 P	407 vw, p	$\nu_{16} + \nu_{18} = 406$ (A′)
380 vw	377 s	378 m, p	374 R } vw 366 P	370 w, sh	ν_{10}, CF_2 scissors
354 sh	353 m	354 m, p	353 R 343 P	351 m, p	ν_{11}, BF_2 rock
342 m	339 w	337 vw, dp	335 Q m		ν_{16}, CF out-of-plane bend
	250 vw	251 vw, p	252 R 247 Q } w 242 P	248 vw, p	ν_{12}, CF in-plane bend
	147 m		134 w	138 m, p	ν_{13}, CCB bend
		141 w, dp			
	137 w		128 w	123 w, dp	ν_{17}, CF_2 twist
				69 vw	ν_{18}, BF_2 torsion
	99 91 47 37 21				Lattice modes

[a] Abbreviations used are as follows: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad; p, polarized; dp, depolarized; P, Q, R, designation of rotational structure of infrared bands.

eration of the infrared band contours.

The remaining vibrations in the A′ symmetry block are bending motions. The CF_2 rock is assigned to the polarized Raman line at 679 cm^{-1} and the scissors to the weak, B-type infrared band centered at 370 cm^{-1} and a corresponding weak shoulder in the Raman spectrum. This order, $\nu_{\text{rock}} > \nu_{\text{scissors}}$, is contrary to the assignments made by Mann et al.[18-21] but is consistent with the assignments and normal-coordinate calculations for 1,1-difluoroallene and tetrafluoroallene.[22]

The BF_2 scissors and rock are assigned in the opposite order $\nu_{\text{scissors}} > \nu_{\text{rock}}$ on the basis of the assignments for B_2F_4,[17] XBF_2(X = Cl, Br),[23] and H_2CCHBF_2.[1,2] The scissors is assigned to the A-type infrared band centered at 583 cm^{-1} and a corresponding polarized Raman line at 584 cm^{-1}, while the rock gives rise to a Raman line at 351 cm^{-1} and a B-type infrared band. These assignments are consistent with the band types predicted from the assumed structure.

The remaining motions to be assigned are the C–F bend and CCB bend in the A′ block. The Raman spectra exhibit polarized lines at 248 and 138 cm^{-1} with corresponding bands in the infrared spectrum. We have assigned these to the C–F and CCB bending modes, respectively, although the mixing is expected to be considerable and the reverse assignment is perhaps just as valid.

The out-of-plane, A″, vibrations should occur at frequencies less than 750 cm^{-1} with the CF_2 twist and BF_2 torsion expected below 200 cm^{-1}. The wagging modes are assigned to the depolarized Raman lines at 671 and 598 cm^{-1} in the spectrum of the liquid. Additionally, there are C-type Q branches in the infrared spectra at 682 and 691 cm^{-1}. We have chosen the 682-cm^{-1} band (Raman 671 cm^{-1}) to describe the CF_2 wag primarily because this mode is not expected to shift significantly when the BX_2 group is changed.[18-20] As we shall see for the V_fBCl_2 molecule there is a line at 632 cm^{-1} while anything that might correspond to the 598 cm^{-1} line is absent. We conclude that the 598-cm^{-1} band in the spectrum of V_fBF_2 represents a BF_2 motion, the out-of-plane wag. The band at 691 cm^{-1} is either a combination band or the ^{10}B component of ν_{14}. The C–F out-of-plane bend is readily assigned to the C-type Q branch at 335 cm^{-1} in the infrared spectrum and to the depolarized Raman line at 337 cm^{-1}.

The position of the CF_2 twist has been inferred from combination bands to be between 150 and 200 cm^{-1} for perfluorovinyl halides.[19-21] In the Raman spectrum of the gas we observe a depolarized line at 123 cm^{-1} while the infrared spectrum shows a weak feature at $\sim$128 cm^{-1}. We assign the CF_2 twisting mode to this frequency. The BF_2 torsion has been observed for vinyldifluoroborane at $\sim$100 cm^{-1}.[1] For a similar barrier height we predict the corresponding motion for V_fBF_2 at $\sim$50 cm^{-1}. In the Raman spectrum of the gas there is a very weak feature at 69 cm^{-1} which we tentatively assign to the BF_2 torsion.

Perfluorovinyldichloroborane. Because tetrachlorodiborane(4) exists in the twisted conformation in the fluid phases,[24] apparently because of steric interactions, we considered it a real possibility that V_fBCl_2 also had a dihedral angle of 90°. However, it is apparent that the spectra of V_fBCl_2 in the fluid and solid phases are identical. For B_2Cl_4, in which there is a conformational change on solidification, the spectral changes were related to activity *and* to band positions, especially in the low-frequency regions.[24] We find for V_fBCl_2 that the observed frequencies in the fluid and solid states are remarkably invariant. This indicates that V_fBCl_2 retains the same conformation in all physical states. The implication is that V_fBCl_2 exists in a planar form, by analogy with solid B_2Cl_4.[24] Additionally, one notes a striking similarity between the spectra of V_fBF_2 and V_fBCl_2. Major shifts in relative band positions are noticed for the BX_2 modes as would be expected for a more massive X atom.

Many of the vibrational assignments for V_fBCl_2 follow directly from the discussion of V_fBF_2. For the planar C_s symmetry, the selection rules and band types are the same as for V_fBF_2, with P–R separations of 10 and 6 cm^{-1} in A-type and B-type infrared bands, respectively. The observed vibrational frequencies and assignments for V_fBCl_2 are given in Table II, and a comparison of the fundamentals for both molecules is shown in Table III.

The C=C stretch is assigned to the very strong, polarized Raman line at 1694 cm^{-1}. That the BCl_2 group vibrations are mixing with many other vibrations can be seen in the shifts of the C=C and CF stretches. The CF_2 stretches are lower by 50–60 cm^{-1} in V_fBCl_2 than in V_fBF_2 with the antisymmetric and symmetric modes at 1353 and 1128 cm^{-1}, respectively. The CF stretch is assigned at 1290 cm^{-1} in the gas phase, which is 100 cm^{-1} lower than the corresponding mode in V_fBF_2. In the crystalline solid it is especially evident that the CF stretch is heavily coupled to the BCl_2 group. The CF stretch for the most abundant isotopic species appears at 1284 cm^{-1}. A ^{10}B component is observed at 1301 cm^{-1} and chlorine isotope splitting is apparent at 1264 and 1242 cm^{-1}.

The B–C stretch is assigned at 1023 cm^{-1} in the infrared spectrum. The BCl_2 antisymmetric and symmetric stretching modes are assigned to the very strong infrared bands at 981 and 864 cm^{-1}, respectively, in accordance with previous assignments for similar groups.[24,25] In the spectrum of the solid there is again evidence for boron and chlorine isotopes associated with the symmetric stretch.

The CF_2 rock and scissors are assigned at 532 and 329 cm^{-1}, respectively, for reasons similar to those cited in the assignments for V_fBF_2. For the more massive chlorine atoms the BX_2 bending modes shift to lower frequencies, giving rise to the polarized Raman signals at 404 and 163 cm^{-1} for the scissors and rock, respectively. The C–F in-plane bend and CCB bend are assigned at 217 and 135 cm^{-1}, but again these designations could probably be interchangeable.

In the A″ symmetry block, the CF motions can be assigned by analogy with the corresponding vibrations for V_fBF_2. The CF_2 wag appears as a depolarized Raman line at 632 cm^{-1}, the CF bend at 323 cm^{-1} in the infrared, and the CF_2 twist at 90 cm^{-1} in the Raman spectra. The BCl_2 wag must be associated with the depolarized Raman line at 245 cm^{-1}, but the BCl_2 torsion cannot be unequivocally assigned. The frequency of this vibration is expected to have a lower limit of 25 cm^{-1},[26] and if we assign the 1158-cm^{-1} band to $\nu_4 + \nu_{18}$, we infer a torsional frequency of at least 30 cm^{-1}.

Discussion

It seems quite apparent that both molecules, perfluorovinyldifluoroborane and perfluorovinyldichloroborane, are planar. The assignments for the crystalline solids are substantially the same as those for the fluid phases, and there are similarities between spectra of one molecule and those of the other. If conformational changes occur during the formation of the crystals, there should be marked changes in spectral features.[16] It is clear that there is a plane of symmetry since we observed depolarized Raman lines that coincide with the appropriate infrared band types. The spectra of the crystalline solids are consistent with more than one molecule per unit cell. The evidence for this lies in the fact that some of the peaks appear to be doubled with alternating intensities between the infrared and Raman spectra. This is not unlike the in-phase and out-of-phase behavior for the vibrations of a crystalline form with two molecules per primitive cell.

In discussing planar structures for V_fBX_2 molecules, it is worthwhile to consider the nonbonded distances that would be imposed upon the molecules. Assumed structures based on the structures of F_2CCFBr,[27] vinyldifluoroborane,[2] B_2F_4,[28] and B_2Cl_4[29] were determined. The van der Waals radii for H, F, and Cl are 1.2, 1.35, and 1.80 Å, respectively.[30] In vinyldifluoroborane the nonbonded H---F distances were determined to be greater than the sum of the van der Waals radii. For V_fBF_2 an average (B)F---F(C) distance is $\sim$2.7 Å, using the assumed structure, which is approximately the same as the minimum required by van der Waals radii. A planar structure for V_fBF_2 seems very reasonable. However, V_fBCl_2 is a slightly different case. The average (B)Cl---F(C) distance is $\sim$2.8 Å while the sum of the van der Waals radii is 3.15 Å. This steric problem could be alleviated if the BCl_2 angle were to close somewhat, but this would cause unfavorable Cl---Cl interactions. The fact that V_fBCl_2 is planar at all may be an indication of some π delocalization which stabilizes this form relative to a twisted conformation.

The C—B and C=C stretching frequencies have been suggested as possible indicators for the existence or lack of π delocalization.[7] The authors added, however, that these were not definitive measures. Indeed this sort of comparison would only be valid if these stretching motions constituted the normal modes of vibration. In vinyldifluoroborane it was found that these two motions were heavily mixed.[2] The C=C stretching frequencies for V_fBF_2 and V_fBCl_2 are lower than those for other perfluorovinyl compounds,[18-21] but it is apparent that considerable mixing of the normal modes is taking place. In Tables I and II, for instance, we note the effects of the ^{10}B and ^{11}B isotopic species on the vibrations of the CF_2 group. If mixing was negligible, the CF_2 modes would be charac-

Table II. Observed Infrared and Raman Frequencies (cm^{-1}) for Perfluorovinyldichloroborane, $F_2CCFBCl_2$[a]

Infrared (solid)	Raman		Infrared (gas)	Raman (gas)	Assignment
	Solid	Liquid			
1753 vw					
			1697 R		
1704 s	1703 vs	1687 vs, p	1693 Q vs	1694 vs, p	ν_1, C=C str
1682 vs	1686 m, sh		1689 P		
1648 vw	1651 w	1651 m, p			$\nu_4 + \nu_8 = 1660$
1355 sh			1355 R vs	1358 sh, p	ν_2, CF_2 antisym str (^{10}B)
1347 vs	1348 w	1347 m, p	1349 P	1353 m, p	ν_2, CF_2 antisym str (^{11}B)
1301 m	1301 w	1298 sh, p	1306 m	1301 m, p	ν_3, CF str (^{10}B)
			1293 R		
1284 s	1287 m	1283 s, p	1287 P vs	1290 s, p	ν_3, CF str (^{11}B)
1264 w	1261 vw	1262 w	1262 m		
1242 vw					
1156 sh					
1153 w			1161 m		$\nu_4 + \nu_{18}$?
	1122 sh				
1118 s	1118 m	1123 m, p	1131 R 1125 P s	1128 m, p	ν_4, CF_2 sym str
1102 vw		1098 vw, p			
	1040 vw	1050 vw, p			$2 \times \nu_8 = 1064$?
1009 m			1028 R 1022 P s		ν_5, B-C str
973 sh					
958 vs	956 vw	972 vw, p	986 R 980 P vs	981 vw	ν_6, BCl_2 antisym str
883 sh					
879 m			884 sh		ν_7, $^{10}BCl_2$ sym str
			872 R		
868 sh	860 vw, p		868 Q vs		ν_7, $^{11}BCl_2$ sym str
859 s			864 P		
844 sh			845 sh		
839 m					
	650 w	655 sh		649 w	$2\nu_{10} = 658$ or $2\nu_{15} = 646$
	638 m	640 sh			
634 m	633 s	632 s, dp	634 Q m		ν_{14}, CF_2 wag
	536 sh		536 R		ν_8, CF_2 rock (^{10}B)
	532 m	533 w, dp	532 Q w	535 w, p	ν_8, CF_2 rock (^{11}B)
			530 P		
	522 w				
	520 sh	524 vw, dp			$\nu_{15} + \nu_{11} = 551$ (A″)
	407 s	403 vs, p	401 vw	404 vs, p	ν_9, BCl_2 scissors
	402 m, sh				
	398 w, sh				
	334 m	333 w, dp		329 w	ν_{10}, CF_2 scissors
	323 vw		323 w		ν_{15}, CF out-of-plane bend
	255 vw				
	247 m	245 w, dp	248 w	244 w	ν_{16}, BCl_2 wag
	220 m	218 s, p	217 vw	213	ν_{11}, CF in-plane bend
	160 vw			163 w, p	ν_{12}, BCl_2 rock
	143 w	138 m, p	139 R 132 P vw	135 m, p	ν_{13}, CCB bend
				90 w	ν_{17}, CF_2 twist
	67 s				Lattice modes and ν_{18}, BCl_2 torsion
	52 m				
	37 m				
	22 s				

[a] For abbreviations used, see Table I.

teristic and unaffected by the boron isotopic masses.

Our assignment of the C–B stretching vibrations in the range 1000–1050 cm^{-1} is in contrast to the corresponding assignment made previously near 1360 cm^{-1}.[7] By comparing the V_fBF_2 and V_fBCl_2 molecules we feel that the peaks in the 1300-cm^{-1} region arise from C–F (or B–F) stretching vibrations. It is possible though that we have switched the CF_2 symmetric stretch and the C–B stretch. Again, mixing is expected to be important and these designations may be arbitrary. For V_fBCl_2 the C–B stretch may give rise to the very weak Raman line at 1040 cm^{-1}, with the infrared band at 1023 cm^{-1} being the $^{10}BCl_2$ antisymmetric stretch. Judging from intensities and band contours, we prefer the assignment given in Table IV, but with the present data, it is impossible to decide unequivocally between the two assignments.

The calculation of the normal modes of vibrations and force constants was not carried out for a number of reasons. We expected the mixing to be an important factor because of the relative masses of the atoms and the low symmetry of the molecules. Furthermore, the force field necessary for describing these molecules involves more force constants than frequencies. This introduces nonuniqueness into the force field and severely limits the credibility of the calculations. The various problems with the force field have been previously discussed.[2] A further problem regarding the uniqueness of the calculations is that we have only one isotopic species per molecule whose assignments are definitive.

The assignments for the torsional vibrations are very tentative. The reduced moments for these motions have been calculated from the assumed structures and $F = 0.479$ and

Table III. Fundamental Vibrational Frequencies (cm^{-1}) for Gaseous Perfluorovinyldifluoroborane and Perfluorovinyldichloroborane

Approx description	F_2CCFBF_2		$F_2CCFBCl_2$	
	A′			
C=C str	ν_1	1725	ν_1	1694
CF str	ν_2	1410	ν_2	1290
CF_2 antisym	ν_3	1390	ν_3	1352
BX_2 antisym str	ν_4	1323	ν_6	981
CF_2 sym str	ν_5	1179	ν_4	1128
B-C str	ν_6	1040	ν_5	1023
BX_2 sym str	ν_7	709	ν_7	864
CF_2 rock	ν_8	679	ν_8	532
BX_2 scissors	ν_9	584	ν_9	404
CF_2 scissors	ν_{10}	370	ν_{10}	329
BX_2 rock	ν_{11}	351	ν_{12}	163
CF bend	ν_{12}	248	ν_{11}	217
CCB bend	ν_{13}	138	ν_{13}	135
	A″			
CF_2 wag	ν_{14}	682	ν_{14}	632
BX_2 wag	ν_{15}	596	ν_{16}	245
CF bend	ν_{16}	335	ν_{15}	323
CF_2 twist	ν_{17}	123	ν_{17}	90
BX_2 torsion	ν_{18}	(69)	ν_{18}	(30)

0.237 cm^{-1} for V_fBF_2 and V_fBCl_2, respectively. If the torsional fundamental for V_fBF_2 is 69 cm^{-1}, the twofold barrier to internal rotation is near 7 kcal/mol, but if this frequency represents double jumps, the barrier would be close to 2 kcal/mol. For V_fBCl_2 a torsional frequency of 30 cm^{-1} corresponds to ~2.7 kcal/mol.

Conclusion

The vibrational spectra of perfluorovinyldifluoroborane and perfluorovinyldichloroborane indicate that both molecules have a plane of symmetry and are probably planar in the fluid and solid phases. It is difficult to determine directly from the vibrational frequencies whether there is π delocalization along the C–B bond. Unfavorable steric factors can be explained by invoking a degree of delocalization.

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation by Grants No. CHE 74-04805-AO2 and No. MPS 74-12241-AO.

Registry No. V_fBF_2, 1511-68-8; V_fBCl_2, 758-99-6.

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Reactions of Tetraborane(10) with Mono- and Dimethylamine

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Received May 5, 1977 AIC703221

The reactions of tetraborane(10) with mono- and dimethylamine were found to give $H_2B(CH_3NH_2)_2{}^+B_3H_8{}^-$ and $H_2B[(CH_3)_2NH]_2{}^+B_3H_8{}^-$, the unsymmetrical cleavage products of tetraborane(10), exclusively. As in the reaction of tetraborane(10) with ammonia, the fast deprotonation of tetraborane(10) proceeds to produce $B_4H_9{}^-$ ion first and the competing reaction to form the final product proceeds slowly. The latter reaction becomes fast at about −40 °C. The mechanism of the reactions that leads to the exclusive unsymmetrical cleavage of tetraborane(10) by these amines is discussed with reference to the reactions of diborane(6) with the same amines, where both symmetrical and unsymmetrical cleavage products are produced. The strong affinity of the B_3H_7 group toward the bridge hydrogen in the intermediate $H_2B(amine)–H–B_3H_7$ is thought to be responsible for the exclusive formation of the $B_3H_8{}^-$ salts.

Introduction

Two types of cleavage products, "symmetrical" and "unsymmetrical", are known to form in different proportions in the reactions of diborane(6) with the series of methylamines. Ammonia gives the unsymmetrical cleavage product, $H_2B(NH_3)_2{}^+BH_4{}^-$, virtually exclusively under carefully controlled conditions.[1] With increasing methyl substitution on amine nitrogen the amounts of symmetrical cleavage products in the reaction products increase,[2,3] and trimethylamine gives only the symmetrical cleavage product $(CH_3)_3N·BH_3$.[4] The observed variation has been correlated with the increasing steric requirement of the amine ligands and the steric effect is considered to be a predominant factor that determines the type of cleavage product in this series of diborane reactions.[2,5]