Microwave Spectrum, Torsional Frequency and Barrier to Internal Rotation in Phenylboron Difluoride

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Microwave spectra of the ground and first three excited torsional states of $C_6H_5^{11}BF_2$ and for the ground and first two excited torsional states of $C_6H_5^{10}BF_2$ have been assigned. The variation of the inertial defect with torsional quantum number shows the molecule to be planar. The torsional frequency has been determined as $\nu = 49 \text{ cm}^{-1}$ and the barrier to internal rotation as $Y_2 = 1114 \text{ cm}^{-1}$ (13.3 kJ mol⁻¹). With the assumption of a regular benzene ring ($r_{C-C} = 1.397 \text{ Å}$ and $r_{C-H} = 1.084 \text{ Å}$) the geometry of the rest of the molecule is calculated to be $r_{C-B} = 1.551 \text{ Å}$, $r_{B-F} = 1.330 \text{ Å}$ and $FBF = 116.0^{\circ}$.

Organoboron compounds containing an aromatic group are of some interest because the electron deficient nature of the boron atom gives rise to possibilities of π bonding. In a valence bond picture of a molecule such as phenylboron diffuoride the structures (I)-(III) may be expected to contribute significantly to the overall state of the molecule and this would be reflected in such properties as the barrier to internal rotation about the carbon boron bond.



In order to see if this is the case we have studied the microwave spectra of the ground and torsionally excited states of phenylboron difluoride. In many respects phenylboron difluoride is similar to nitrobenzene, a molecule whose microwave spectrum has been studied in considerable detail.¹

EXPERIMENTAL

Phenylboron difluoride was prepared by the fluorination of phenylboron dichloride with antimony trifluoride,² the phenylboron dichloride being obtained by the reaction of tetraphenyl tin with boron trichloride.³ Spectra were observed using a conventional 100 kHz Stark modulation spectrometer and frequency measurements are generally accurate to within 0.1 MHz. In order to reduce sample decomposition the microwave absorption cell was cooled to -20° C. Intensity measurements were made using the Esbitt and Wilson method,⁴ but are of rather poor quality because of the dense nature of the spectrum and the consequent overlapping of lines and interference from Stark components.

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RESULTS AND DISCUSSION

ASSIGNMENT OF SPECTRA

Phenylboron difluoride is a near prolate rotor with a predictable asymmetry parameter $\kappa \sim -0.82$ and electric dipole moment constrained by symmetry to lie along the *a* inertial axis. A preliminary fast scan recording showed the bands of μ_a R branch lines characteristic of this type of rotor and gave $B + C \sim 1956$ MHz. Assignment of the spectrum was based on frequency predictions derived from a molecular model and qualitative considerations of Stark effects. The spectrum of $C_6H_5^{10}BF_2$ was assigned using a set of rotational constants obtained by correcting the observed moments of inertia of $C_6H_5^{11}BF_2$ with the isotopic shifts calculated from the molecular model.

TABLE 1.—OBSERVED LINE FREQUENCIES (MHz) AND DIFFERENCES BETWEEN OBSERVED AND CALCULATED LINE FREQUENCIES (MHz) FOR $C_6H_5^{11}BF_2$

	$V_{\rm t}=0$		$V_{\rm t}=1$		$V_t = 2$		$V_{\rm t}=3$	
	observed	obs. – ca	lc. observed	obs cale.	. observed	obs. – calc.	observed	obs calc.
9 ₂₇ ← 8 ₂₆	18 528.26	0.11	18 503.18	0.12	18 477.61	0.15	18 451.71	0.13
$10_{0,10} - 9_{09}$	17 852.63	0.03	17 862.94	-0.16	17 873.63	0.16		
$10_{1,10} \leftarrow 9_{19}$	17 744.99	0.06	17 753.75	0.03	17 762.36	0.04	17 770.85	0.02
$10_{19} \leftarrow 9_{18}$	19 768.11	0.05	19 763.20	-0.08	19 758.11	0.01	19 752.56	0.13
10 ₂₉ ←9 ₂₈	19 040,42	0.10	19 036.13	-0.01	19 031.63	-0.01	19 026.93	0.03
$10_{28} \leftarrow 9_{27}$	20 609.01	0.06	20 583.05	-0.05	20 556.67	-0.00	20 529.95	0.09
10 ₃₇ ← 9 ₃₆	20 116.32	0.10	20 087.90	0.03	20 059.15	0.02	20 030.41	0.03
$11_{0.11} \leftarrow 10_{0.10}$	19 527.85	-0.08	19 539.82	0.04	19 551.38	0.12		
$11_{1,11} \leftarrow 10_{1,10}$	19 456.21	-0.04	19 466.72	0.05	19 476.99	0.09	19 487.18	0.14
$11_{1,10} \leftarrow 10_{19}$	21 493.77	-0.00						
$11_{2,10} \leftarrow 10_{29}$	20 847.09	0.05	20 844.29	0.02	20 841.14	-0.02	20 837.80	0.03
$11_{29} \leftarrow 10_{28}$	22 644.24	-0.06	22 618.99	0.06	22 592.98	0.07	22 566.42	0.02
11 ₃₈ ← 10 ₃₇	22 292.45	0.11	22 258.52	0.00	22 224.23	0.05	22 189.71	-0.08
11 ₄₇ ← 10 ₄₆	21 756.37	-0.07	21 733.72	0.09	21 710.39	-0.06		
11 (10)		-0.11		0.07				
$11_{75} - 10_{74}$	21 526.50	-0.11	21 509.86	0.07				
1174~1073)								
$12_{0,12} \leftarrow 11_{0,11}$	21 208.48	0.03	21 221.48	-0.12	21 234.59	-0.02	21 247.43	-0.10
$12_{1,12} \leftarrow -11_{1,11}$	21 162.02	0.04	21 173.99	-0.03	21 185.84	-0.03	21 197.63	0.02
$12_{1,11} \leftarrow 11_{1,10}$	23 174.01	0.05	23 177.20	0.05	23 180.09	0.06	23 182.41	-0.02
$12_{2,11} \leftarrow 11_{2,10}$	22 632.88	0.04	22 631.77	0.02	22 630.31	-0.00	22 628.59	0.02
$12_{2,10} \leftarrow 11_{29}$	24 625.35	-0.12	24 601.94	-0.01	24 577.87	0.17	24 552.78	-0.07
$12_{3,10} \leftarrow 11_{39}$	23 482.83	0.02	23 468.04	-0.02	23 452.84	0.02	23 437.26	-0.01
12 ₃₉ ←11 ₃₈	24 487.72	-0.00	24 449.18	-0.10	24 410.14	-0.04	24 370.94	0.03
$13_{0,13} \leftarrow 12_{0,12}$	22 893.27	0.02	22 907.74	0.04	22 922.00	0.01	22 936.23	0.03
$13_{1,13} \leftarrow 12_{1,12}$	22 863.80	0.06	22 877.41	0.04	22 890.86	0.06	22 904.34	0.21
$13_{1,12} \leftarrow 12_{1,11}$	24 827.01	-0.01	24 833.53	0.20	24 839.35	-0.04	24 845.00	-0.03
$13_{2,12} \leftarrow 12_{2,11}$	24 399.35	-0.00						
$13_{2,11} \leftarrow 12_{2,10}$	26 544.44	0.01	26 523.98	-0.26	26 503.08	-0.20	26 481.48	-0.08
$13_{3,11} \leftarrow 12_{3,10}$	25 385.03	-0.05	25 370.98	0.04	25 356.20	-0.07	25 341.19	0.04
$13_{3,10} \leftarrow 12_{39}$	26 680.12	-0.05	26 638.61	-0.00	26 596.17	-0.08	26 553.50	-0.06
140,14 - 130,13	24 581.12	-0.10	24 597.00	0.00			24 627.93	-0.18
$14_{1,14} \leftarrow 13_{1,13}$	24 562.74	-0.04	24 577.90	-0.08	24 592.88	-0.08	24 607.74	-0.11

The excited torsional states were assigned with the help of a number of microwavemicrowave double resonance experiments. Vibrational satellites of two other excited states at approximately 150 cm^{-1} and 350 cm^{-1} were also observed but no accurate measurements were made. Rotational constants were obtained from the observed line frequencies using a rigid rotor least squares fitting procedure. The line frequencies and rotational constants for the ground and first three excited torsional states of $C_6H_5^{11}BF_2$ are

TABLE 2.—ROTATIONAL CONSTANTS ^a AND INERTIAL DEFECTS ^b FOR C₆H₅¹¹BF₂

	$V_{t}=0$		$V_{\rm t} = 1$		$V_t = 2$		$V_t = 3$	
A/MHz	3686.14	(0.07)	3685.40	(0.10)	3684.95	(0.10)	3684.15	(0.10)
B/MHz	1099.431	(0.002)	1097.401	(0.002)	1095.342	(0.002)	1093.266	(0.002)
C/MHz	847.199	(0.001)	847.924	(0.002)	848.642	(0.002)	849.362	(0.002)
∆/a.m.u. Ų	-0.2465	6 (0.0028)	-1.6343	(0.0039)	-3.0211	(0.0039)	-4.4319	(0.0041)

^a Standard errors are given in parentheses; ^b calculated using the conversion factor 5.05376×10^5 MHz a.m.u. Å².

given in tables 1 and 2 and for the ground and first two excited torsional states of $C_6H_5{}^{10}BF_2$ in tables 3 and 4. The standard errors on the A rotational constants are much larger than those on the B and C constants, but the A constants are determined with sufficient accuracy for the present calculations.

It has not been possible to derive the electric dipole moment or the boron nuclear quadrupole coupling constants since none of the observed lines showed resolved Stark effects or nuclear hyperfine structure.

Table 3.—Observed line frequencies (MHz) and differences between observed and calculated line frequencies (MHz) for $C_6H_5{}^{10}BF_2$

	$V_t = 0$		$V_t =$	1	$V_{ m t}=2$	
	observed	obs calc.	observed	obs calc.	observed	obscalc.
$10_{1,10} \leftarrow 9_{19}$	17 823.80	0.16	17 832.61	0.13		
10 ₁₉ ←9 ₁₈	19 857.58	0.03	19 853.06	0.01	19 847.97	0.06
10 ₂₉ ← 9 ₂₈	19 130.88	0.10	19 126.68	0.08		
$10_{28} \leftarrow 9_{27}$	20 720.36	0.10	20 694.34	0.16	20 667.65	-0.02
10 ₃₇ ← 9 ₃₆	20 231.57	-0.04	20 202.50	-0.07	20 173.48	-0.12
$11_{0.11} \leftarrow 10_{0.10}$	19 612.11	0.00	19 623.86	-0.18	19 635.83	-0.12
$11_{1,10} \leftarrow 10_{19}$	21 587.46	-0.20				
$11_{2,10} \leftarrow 10_{29}$	20 944.77	0.07			20 938.94	-0.00
$11_{29} \leftarrow 10_{28}$	22 763.41	0.08	22 737.66	-0.19		
$11_{47} \leftarrow 10_{46}$	21 874.68	-0.11	21 851.25	-0.16		
11 10		0.15		0.08		0.18
$11_{75} \leftarrow 10_{74}$ $11_{74} \leftarrow 10_{73}$	21 638.81	0.15	21 621.57	0.08	21 604.37	0.18
$12_{0,12} \leftarrow 11_{0,11}$	21 300.19	-0.03			21 326.86	0.18
$12_{1,12} \leftarrow 11_{1,11}$	21 254.90	-0.15				
$12_{1,11} \leftarrow 11_{1,10}$	23 272.66	0.03	23 276.05	-0.15	23 279.02	-0.08
$12_{2,10} \leftarrow 11_{29}$	24 750.93	0.14	24 727.51	0.20		
$12_{3,10} \leftarrow 11_{39}$	23 600.87	-0.04	23 585.92	-0.09		
$12_{39} \leftarrow 11_{38}$	24 630.15	-0.11	24 591.07	-0.01		
$13_{0,13} \leftarrow 12_{0,12}$	22 992.57	-0.04	23 007.22	0.08		
$13_{1,13} \leftarrow 12_{1,12}$	22 964.24	0.20	22 977.73	-0.02	22 991.47	-0.20
$13_{1,12} \leftarrow 12_{1,11}$	24 931.42	0.01	24 938,14	0.08	24 944.08	-0.03
$13_{2,12} \leftarrow 12_{2,11}$	24 510.69	-0.04				
$13_{2,11} \leftarrow 12_{2,10}$	26 674.35	-0.14	26 654.49	-0.05		
$13_{3,11} \leftarrow 12_{3,10}$	25 511.03	-0.03				
$13_{3,10} \leftarrow 12_{39}$	26 833.96	-0.07	26 791.87	0.03	26 749.30	-0.08
$14_{0,14} \leftarrow 13_{0,13}$	24 688.00	-0.13			24 719.79	-0.09
$14_{1,14} \leftarrow 13_{1,13}$	24 670.32	-0.03				

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TABLE 4.--ROTATIONAL CONSTANTS ^a AND INERTIAL DEFECTS ^b FOR C₆H₅¹⁰BF₂

	$V_t = 0$	$V_{t} = 1$	$V_t = 2$	
4/MHz	3685.80 (0.11)	3685.51 (0.15)	3684.31 (0.18)	
B/MHz	1105.685 (0.003)	1103.629 (0.003)	1101.549 (0.004)	
C/MHz	850.900 (0.002)	851.626 (0.004)	852.361 (0.004)	
∆/a.m.u. Ų	-0.2537 (0.0046)	-1.6224 (0.0063)	-3.0433 (0.0074)	

 a Standard errors are given in parentheses ; b calculated using the conversion factor 5.053 76×10^5 MHz a.m.u. Ų.

Table 5.— σ_1 values for some monosubstituted benzenes ⁵ and relevant distortions ^{*a*} to the benzene ring in these compounds

	F	ОН	CN	NO ₂	BF_2
σ_1	0.51	0.27	0.52	0.64	0.16
C_1C_2	1.383	1.396	1.388	1.375	1.397
C_2C_3	1.395	1.396	1.396	1.403	1.397
C_3C_4	1.397	1.396	1.397	1.396	1.397
$\langle C_6 C_1 C_2$	123.4	120.0	121.8	125.0	120.0
ref.	13	14	15	1	assumed in this work

^a Bond lengths in Å, angles in degrees.

STRUCTURAL CONSIDERATIONS

The inertial defects ($\Delta = I_c - I_a - I_b$) are given in tables 2 and 4 and the variation of Δ with torsional quantum number (V_t) is shown in the figure. Although the ground state inertial defects are negative, extrapolation to the hypothetical torsionless state ($V_t = -\frac{1}{2}$) gives $\Delta = +0.447$ a.m.u. Å² and leaves little doubt that phenylboron diffuoride, like nitrobenzene,¹ is a planar molecule.



FIG. 1.—Variation of inertial defect (Δ) with torsional quantum number (V_t) for C₆H₅¹¹BF₂.

The distance of the boron atom from the centre of mass of $C_6H_5^{11}BF_2$ is calculated to be $a_B = 1.6090$ Å using Kraitchman's equations and the relevant ground vibrational state moments of inertia. In order to derive any further structural

information about the molecule, a number of assumptions must be made. Substitution structures are now available for a number of simple benzene derivatives and some of these are summarized in table 5. Significant distortions to the benzene ring only

occur to $r_{C_1-C_2}$ and $C_2C_1C_6$ and it has been pointed out ^{13, 15} that these are primarily caused by effects in the carbon substituent σ bond. As can be seen from table 5 there is a reasonable correlation between the amount of distortion to the benzene ring and the Taft σ_1 parameters.⁵ The value of σ_1 for the BF₂ group indicates that the benzene ring in phenylboron diffuoride is not likely to be seriously distorted, and in the structural calculations described below a regular benzene ring with $r_{C-C} = 1.397$ Å and $r_{C-H} = 1.084$ Å ⁶ has been assumed.

The remaining structural parameters (r_{C-B} , r_{B-F} and FBF) have been determined using a least squares fitting procedure ⁷ to the ground vibrational state moments of inertia of $C_6H_5^{11}BF_2$ and the differences of the ground vibrational state moments of $C_6H_5^{11}BF_2$ and $C_6H_5^{10}BF_2$. In this procedure the inertial differences are given a weight of ten compared to a weight of unity for the moments of inertia. The resulting

parameters are $r_{C-B} = 1.551$ Å, $r_{B-F} = 1.330$ Å and $FBF = 116.0^{\circ}$. The distance of the boron atom from the centre of mass of $C_6H_5^{11}BF_2$ is $a_B = 1.6093$ Å in excellent agreement with the value calculated using Kraitchman's equations. The effect of

small distortions of the benzene ring was investigated by changing $\tilde{C}_2 C_1 C_6$ by $\pm 1^{\circ}$ and repeating the least squares calculations. Changes of ± 0.007 Å in r_{C-B} ,

in r_{B--F} and $\mp 0.2^{\circ}$ in FBF were found and a_B was found to differ by ± 0.002 Å from the value calculated using Kraitchman's equations.

The geometry of the BF₂ group in C₆H₅BF₂ may be compared with that in CH₃BF₂ ($r_{B-F} = 1.30 \pm 0.02$ Å, FBF = 118°),⁸ NH₂BF₂ ($r_{B-F} = 1.325$ Å, FBF = 117.9°),⁹ OHBF₂ ($r_{B-F} = 1.323$ Å, FBF = 116.5°).¹¹ The boron carbon bond in C₆H₅BF₂ is between that in CH₃BF₂ ($r_{C-B} = 1.60 \pm 0.03$ Å,)⁸ and that in HCCBF₂ ($r_{C-B} = 1.513$ Å).¹¹ More examples of accurately determined related structures are needed before such geometries can be used as indications of the extent of π -bonding, in comparison with other factors, such as hybridization and valency shell population.

TORSIONAL FREQUENCY AND BARRIER TO INTERNAL ROTATION

The almost linear variations in the rotational constants and inertial defects with torsional quantum number show that the torsional vibration in its lowest states is essentially harmonic and that the barrier to internal rotation is high. Intensity measurements on 11 transitions gave a value of $64 \pm 30 \text{ cm}^{-1}$ for the $1 \leftarrow 0$ torsional frequency, but probably a more accurate value can be obtained from the inertial defects.¹ For a harmonic vibration the difference in the inertial defect in the first excited torsional and ground states is related to the torsional frequency v (expressed as a wavenumber) by the approximate equation

$$\Delta(V_t = 1) - \Delta(V_t = 0) = -4 \left(\frac{h}{8\pi^2 c}\right)^{\frac{1}{2}}.$$

For both isotopic species of phenylboron difluoride this equation gives $v = 49 \text{ cm}^{-1}$.

If the internal rotation is assumed to be hindered by a simple two-fold potential

$$V(\alpha) = \frac{V_2}{2}(1 - \cos 2\alpha)$$

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where α is the angle between the plane of the BF₂ group and that of the phenyl group, then, with the assumption that the torsion is a harmonic vibration, the barrier height is given by ¹

$$V_2 = 2\pi^2 c v^2 I_{\rm red} / h$$

where

 $I_{\rm red} = I_{\rm BF2} \times I_{\rm Ph} / I_a$

and I_{BF_2} and I_{Ph} are the moments of inertia of the BF₂ and phenyl groups about the *a* axis. With the molecular structure derived above

$$V_2 = 1114 \pm 200 \text{ cm}^{-1}$$
 or $13.3 \pm 2.4 \text{ kJ mol}^{-1}$

The barrier height is similar to that in nitrobenzene ($V_2 = 1030 \text{ cm}^{-1}$)¹ and phenol $(V_2 = 1213 \text{ cm}^{-1})^{12}$ and is further indication that in molecules of this type V_2 may be taken as a measure of the π interaction between the substituent and the benzene ring.

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