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VIBRATIONAL SPECTRA AND NORMAL COORDINATE ANALYSIS OF CF_3 COMPOUNDS

XXXIV *. THE BIS(TRIFLUOROMETHYL)DIFLUOROBORATE ANION: X-RAY STRUCTURE OF $Cs[(CF_3)_2BF_2]$

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Summary

The ^{10}B and ^{11}B IR and Raman spectra of the $[(CF_3)_2BF_2]^-$ anion are reported, assigned, and used to determine a quadratic local symmetry force field via a normal coordinate analysis. The crystal structure of $Cs[(CF_3)_2BF_2]$ ($P2_1/m$, a 5.958(1), b 7.628(1), c 8.2997(9) Å, β 100.50(1)°, $Z = 2$, d_c 2.863 g cm^{-3}) has been determined by X-ray diffractometry. The most important force constants are f(BC) 3.68 × 10^2, f(BF) 4.17 × 10^2 and f(CF) 4.85 × 10^2 N/m, the respective mean bond lengths being 1.618, 1.391 and 1.353 Å. The F—B—F and C—B—C bond angles are 108.1(4) and 113.6(5)°, respectively. Apparently because of Cs···F(B, C) interactions, one B—C bond has a staggered and the other an eclipsed conformation in the solid state.

Introduction

We recently reported [2] the first synthesis of salts containing the $(CF_3)_2BF_2$ anion, the first compounds in which more than one CF_3 group is bonded to a B atom. Indeed, B is the only element, E, of main Groups I, II and III known to form CF_3—E linkages.

Among other features, our interest in CF_3B compounds centers on the nature of the C—B bond. Possessing an electronegativity below 2.5, B would be expected to bind less tightly to a CF_3 group than to a CH_3 group in the light of a comparison of CF_3—E and CH_3—E bond lengths with the electronegativity of E [3]. This behavior was not confirmed by our structural and spectroscopic investigation of $K[CF_3BF_3]$, but comparative data were scant [4]. The latter

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* For Part XXXIII, see Ref. 1.

study [4] revealed a clear analogy between the vibrational spectra of $CF_3BF_3^-$ and CF_3CF_3. We now report a vibrational spectroscopic investigation of $(CF_3)_2BF_2^-$, compare the spectrum with that of the isoelectronic $CF_3CF_2CF_3$ [5], and describe the structure of $Cs[(CF_3)_2BF_2]$ as determined by X-ray diffraction.

X-ray structure analysis of $Cs[(CF_3)_2BF_2]$

X-ray data collection

The needle-shaped crystals used in the X-ray study were glued to glass fibers. Precession and Weissenberg photographs indicated that the crystals belong to the monoclinic system, space groups $P2_1$ or $P2_1/m$. Precise lattice constants were determined by a least-squares method from 50 θ values measured with a CAD-4 diffractometer, which was also used for the intensity measurements. During data collection, the variations of three periodically-monitored standards were less than ±3% of their mean intensities. After an absorption correction, the intensities were converted into $|F_0|$'s. Crystal data and details of data collection and reduction are given in Table 1.

Solution and refinement

Coordinates for the Cs atom were derived from a Patterson map. A difference Fourier synthesis calculated assuming space group $P2_1$ revealed that the remaining atoms were arranged as required by space group $P2_1/m$. Thus the latter symmetry was used in all further calculations. The structure was refined by least-squares techniques, the function $\Sigma w\Delta^2$, $\Delta = ||F_0| - |F_c||$, being mini-

TABLE 1

CRYSTAL DATA FOR $Cs[(CF_3)_2BF_2]$

crystal system	monoclinic
a	5.958(1) Å
b	7.628(1) Å
c	8.2997(9) Å
β	100.50(1)°
Z	2
d_c	2.863 g/cm^3
t	20°C
Systematic absences	$0k0$ $k = 2n + 1$
space group	$P2_1/m$
Quadrant measured	hkl, $\bar{h}kl$
λ	0.7107 Å (Mo-K_α)
Monochromator	graphite
Maximum θ	30°
Scan technique	$\omega - 2\theta$
Scan width (ω)	1.2° + 0.34° tan θ
Scan speed (2θ)	0.45—5.00°/min
Reflections measured	1219
Unique reflections	1099
Observed ($\lvert F_0\rvert \geqslant 6\sigma(\lvert F_0\rvert)$)	999
Weights w observed	$[\sigma^2(\lvert F_0\rvert) + 0.0009\,\lvert F_0\rvert^2]^{-1}$
unobserved	0
Crystal size	0.06 × 0.10 × 0.58 mm
μ(Mo-K_α)	51 cm^{-1}
Transmission factors	0.590—0.738

mized. Dispersion-corrected [6a] relativistic Hartree Fock scattering factors [6b] were used for all atoms. Anisotropic refinement including an extinction correction converged * with $R = \Sigma\Delta/\Sigma|F_0| = 0.028$ and $Rw = [\Sigma w\Delta^2/\Sigma w|F_0|^2]^{1/2} = 0.042$ for the 999 observed reflections.

On the final cycle no parameter (Table 2) shifted more than 0.04 σ. The peaks (1.0 to —0.6 $e/Å^3$) on the final difference map confirmed the structure, only one feature (0.6 $e/Å^3$) greater than 0.4 $e/Å^3$ not being near the Cs atoms. Plots of $(w\Delta^2)^{1/2}$ versus $|F_0|$, sin θ/λ and various groupings of the Miller indices verified the relative validity of the weighting scheme. The numbering scheme is specified in Fig. 1. Selected distances and angles are listed in Table 3. The computer programs have been described previously [4].

Description of the structure

The successful refinement to relatively low discrepancy indices affords further justification for our choice of space group, $P2_1/m$. Therefore with $Z = 2$, each ion must possess either crystallographic m or $\bar{1}$ symmetry; in fact, the former symmetry was found for both ions, the anion atoms B, C(1), C(2), F(1) and F(3) occupying the mirror plane. Because the conformation of B—C(1) is staggered while that of B—C(2) is eclipsed, the symmetry of the anion, which might otherwise have been as high as $mm2$ (C_{2v}), is no higher than m (C_s), in the solid state. Possible structural effects of the difference in conformation will be delineated later.

Bond lengths and angles in various borate structures are tabulated in Table 7. The similarity of the average values for $Cs[(CF_3)_2BF_2]$ and $K[CF_3BF_3]$ [4] is striking. Except for the 1.8(6)° smaller F—B—F angle in the Cs salt, none of the variations are statistically significant. Furthermore, substituting one or two F atoms of BF_4^- by CF_3 groups has no apparent influence on the remaining B—F bond lengths. The B—C distances in Table 7 are relatively constant ** and are similar to the 1.620(5) Å value found in three diethylbis(1-pyrazolyl)borato (Et_2Bpz_2) complexes [8]. The C(1)—B—C(2) angle, 113.6(5)°, compares well with those reported in the Et_2Bpz_2 complexes (114.0(4)°) [8] and in CF_3CFI-CF_3 (113.2(12)°) [9].

The most surprising structural feature is the different conformation of the two B—C bonds. Steric repulsions along B—C(2) must be greater than those along B—C(1), and the anion displays several distortions which can be related to this difference. First, the B—C(2) bond length is significantly longer, 0.029(12) Å, than the B—C(1) bond. Second, Fig. 2 shows that the plane through F(3), F(4), $F(4)^I$ is 0.051(8) and 0.026(11) Å further removed from the B and bonded C atom, respectively, than the F(1), F(2), $F(2)^I$ plane is ***. Third, as measured by the mean F···F distances in the same CF_3 group, the F

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* To reduce the chances of refining to a false minimum, the B—C distances were equalized and the CF_3 geometries were optimized assuming local 3 m symmetry before anisotropic refinement was commenced.

** The B—C(CF_3) distances in the Cs and K salt are 0.01—0.02 Å shorter than the mean B—C(CH_3) bond lengths in $LiB(CH_3)_4$ [7]; however, the latter bonds display variations which might be due to the two different types of CH_3···Li interactions present. Thus for the linearly bridged B—CH_3···Li fragments, the X-ray results [7] yield a B—C bond length, 1.626(8) Å, which agrees well with the B—C(CF_3) distances.

*** Corresponding distances in $K[CF_3BF_3]$ are 2.165(5) and 0.539(4) Å respectively.

TABLE 2

POSITIONAL [a] AND THERMAL [b] PARAMETERS [c] FOR $Cs[(CF_3)_2BF_2]$

Atom	*x*	*y*	*z*	*U*(1,1) [d]	*U*(2,2)	*U*(3,3)	*U*(1,2)	*U*(1,3)	*U*(2,3)
Cs	1987(6)	25000	22237(4)	589(2)	434(2)	446(2)	0	96(1)	0
B	6832(10)	2500	7928(7)	43(2)	56(3)	39(2)	0	6(2)	0
C(1)	4312(13)	2500	8350(12)	52(3)	87(5)	88(5)	0	28(3)	0
C(2)	6867(11)	2500	5960(7)	60(3)	60(3)	45(3)	0	9(2)	0
F(1)	4277(12)	2500	9962(8)	116(5)	137(6)	102(4)	0	74(4)	0
F(2)	3040(8)	3913(7)	7722(7)	102(3)	157(4)	159(4)	80(3)	44(3)	31(4)
F(3)	4923(11)	2500	4913(7)	85(3)	165(6)	59(2)	0	−15(2)	0
F(4)	8058(8)	3886(5)	5511(4)	157(4)	89(2)	68(2)	−43(2)	37(2)	6(2)
F(5)	7945(5)	3976(4)	8666(3)	85(2)	74(2)	62(2)	−32(2)	17(1)	−14(1)

[a] For Cs × 10^5, otherwise × 10^4. [b] For Cs × 10^4, otherwise × 10^3. [c] Equation of extinction correction is $|F_c|^* = |F_c|(1 - x|F_c|^2/\sin\theta)$ where $x = 4(1) \times 10^{-7}$. [d] Form of anisotropic thermal ellipsoid is $\exp[-2\pi^2(h^2a^{*2}U(1,1) + \ldots + 2klb^*c^*U(2,3))]$.

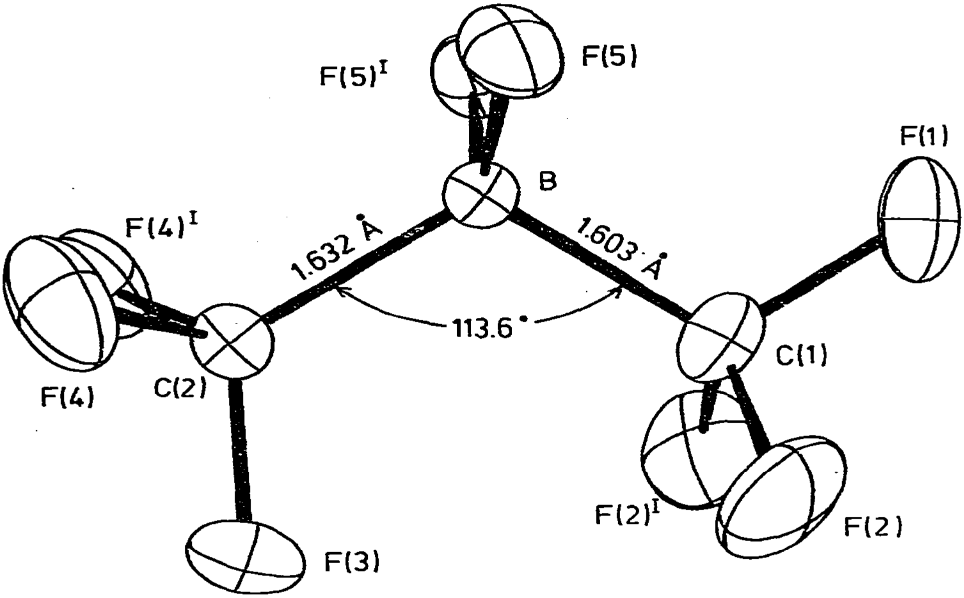

Fig. 1. Perspective drawing of the anion in Cs[$(CF_3)_2BF_2$] using 20% probability thermal ellipsoids.

atoms of C(2) (2.122(4) Å) are forced closer together than are those of C(1) (2.158(5) Å). For comparison, the mean value in K[CF_3BF_3] is 2.129(5) Å. Indications of angular distortions were obtained by examining the acute angles (Fig. 2) formed by the B—C vectors and by the normals to the F(1), F(2), F(2)^I and F(3), F(4), F(4)^I planes, P_1 and P_2, respectively, with the normal to the B, F(5), F(5)^I plane P_3. The following observations can be made. First, while P_1 is essentially colinear with B—C(1), P_2 deviates by 4.1° from colinearity with B—C(2) †. Second, since $\measuredangle(P_2, P_3)$ is 2.0° larger than $\measuredangle(P_1, P_3)$, the F substituent plane of C(2) tilts slightly further away from the borate F atoms than does that of C(1). Third, B—C(2) is inclined 6.2° more steeply to P_3 than is B—C(1). The second and third points are consistent with the relatively short C(2)—F(3) bond length, 1.318(8) Å, and the large B—C(2)—F(3) bond angle, 119.5(6)°. Despite these distortions, the F(4)···F(5) contact, 2.632(4) Å, is considerably less than the fluorine van der Waals diameter, 2.94 Å [10], as well as the F(1)···F(5) distance, 2.839(7) Å, and nearly equal to the shortest F···F distance between different CF_3 groups in the overcrowded $N(CF_3)_3$, 2.60(4) Å [11].

Interestingly, since the contacts C(1)···C(2) (2.71(1) Å), F(3)···C(1) (2.94(1) Å) and F(2)···F(3) (2.967(8) Å) are not unusually short, nonbonded repulsions between CF_3 groups are certainly not severe. To evaluate the nonbonded repulsions in a structure with both CF_3 groups staggered relative to the BF_2 fragment, distances were calculated after rotating the F atoms bonded to C(2) by 180° around the B—C(2) bond. Because of the above-mentioned

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† Correspondingly, no significant deviation from $3m$ symmetry is found for the bond distances and angles of C(1) while those of C(2) would show significant deviations (χ^2 tests) even if the σ's are underestimated by a factor of two.

TABLE 3

SELECTED DISTANCES (Å) AND ANGLES (°) IN Cs[(CF$_3$)$_2$BF$_2$]

B—C(1)	1.603(9)	Cs—F(1)$^{\mathrm{II}}$ [b]	3.330(7)
B—C(2)	1.632(8)	Cs—F(2)$^{\mathrm{III}}$	3.354(5) [a]
B—F(5)	1.391(4) [a]	Cs—F(3)	3.258(6)
C(1)—F(1)	1.342(11)	Cs—F(4)$^{\mathrm{IV}}$	3.385(4) [a]
C(1)—F(2)	1.365(6) [a]	Cs—F(4)$^{\mathrm{V}}$	3.391(4) [a]
C(2)—F(3)	1.318(8)	Cs—F(5)$^{\mathrm{V}}$	3.048(3) [a]
C(2)—F(4)	1.365(5) [a]	Cs—F(5)$^{\mathrm{VI}}$	3.216(3) [a]

C(1)—B—C(2)	113.6(5)	F(1)—C(1)—F(2)	105.8(5) [a]
C(1)—B—F(5)	107.1(4) [a]	F(2)—C(1)—F(2)$^{\mathrm{I}}$	104.3(8)
C(2)—B—F(5)	110.3(3) [a]	B—C(2)—F(3)	119.5(6)
F(5)—B—F(5)$^{\mathrm{I}}$	108.1(4)	B—C(2)—F(4)	112.2(3) [a]
B—C(1)—F(1)	113.8(7)	F(3)—C(2)—F(4)	101.6(6) [a]
B—C(1)—F(2)	113.2(5) [a]	F(4)—C(2)—F(4)$^{\mathrm{I}}$	104.8(4)

[a] Two such mirror-related values. [b] Coordinates r of primed atoms are related to those of the asymmetric unit as follows: $r^{\mathrm{I}} = x, 0.5 - y, z$; $r^{\mathrm{II}} = x, y, 1 - z$; $r^{\mathrm{III}} = -x, y - 0.5, 1 - z$; $r^{\mathrm{IV}} = x - 1, y, z$; $r^{\mathrm{V}} = 1 - x, y - 0.5, 1 - z$; $r^{\mathrm{VI}} = x - 1, y, z - 1$.

angular distortions, this model will place the F atoms of C(2) somewhat too far from F(5) and somewhat too near C(2) and F(2) than expected for an anion with exact $mm2$ symmetry. Since the model yields F(5)···F(C(2)) distances all greater than 2.96 Å while shortest F(2)···F(C(2)) and C(1)···F(C(2)) contacts are 2.86 and 3.08 Å respectively, nonbonded repulsion would appear to favor a staggered conformation over that found in the crystal. However, such a model is incompatible with the observed anion packing because of an impossibly short F(C(2))···F(C(2)) contact (1.89 Å) over the inversion centre at 1/2, 0, 1/2. In the real structure, the shortest contact between anions is F(4)···F(4) ($2 - x$, $1 - y$, $1 - z$), 3.111(8) Å.

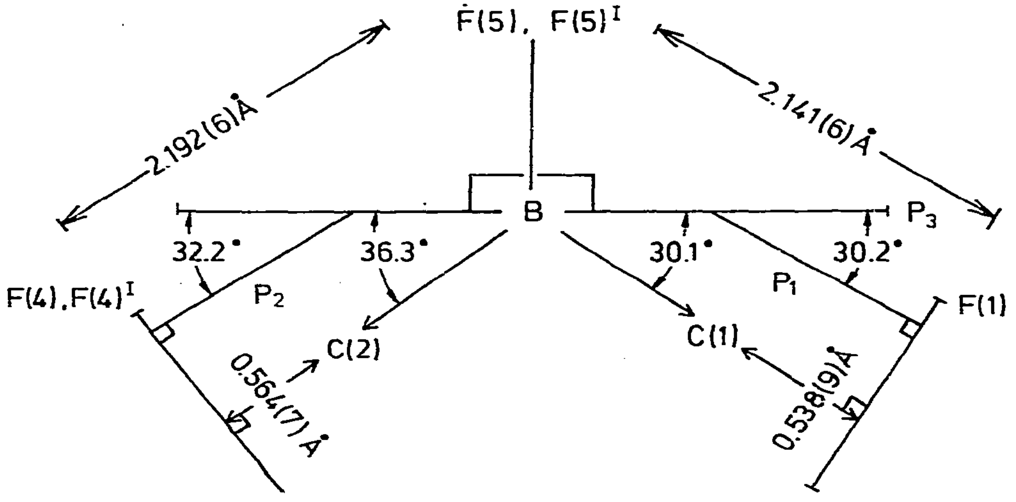

Fig. 2. Projection down b of B—C(1) and B—C(2) vectors and of plane normals P_1, P_2 and P_3.

These observations imply that the anion conformation is dictated by the requirements of best possible anion packing about the cations. The Cs cations make twelve contacts (Table 3) shorter than 3.68 Å with F atoms in eight different anions. Of these, the shortest four (2 × 3.048(3) Å, 2 × 3.216(3) Å) are with boron-bonded F atoms, which may be compared with eight such distances (3.11(1)—3.211(8) Å) reported for $CsBF_4$ [12]. That five of the remaining eights Cs···F contacts are with substituents of C(2) further indicates that Cs···F interactions favor the observed anion conformation.

Vibrational spectra

General. In the discussion of the $CF_3BF_3^-$ anion [4], the relationship between the isoelectronic species $CF_3BF_3^-$ and CF_3CF_3 proved to be very useful for the interpretation of the vibrational spectra, and analogous behavior might be expected for the isoelectronic species $(CF_3)_2BF_2^-$ and $CF_3CF_2CF_3$ which were studied recently [5]. Since the structure determination of $Cs[(CF_3)_2BF_2]$ established that the anion conformation in the solid state is probably influenced by the cation, ideal C_{2v} symmetry appears to be justified for the solution spectra and for the normal coordinate analysis (NCA). The notation of the normal vibrations of $(CF_3)_2BF_2^-$ $\Gamma vib = 9a_1 + 5a_2 + 7b_1 + 6b_2$ is that of Table 1 in Ref. 5. The notation is also indicated in Table 4 of this paper. The vibrational spectra of $(CF_3)_2{}^{11}BF_2^-$ (natural abundance 80.4% ^{11}B) and of $(CF_3)_2{}^{11}BF_2^-$ (92.4% ^{10}B; Oak Ridge National Laboratory) are reproduced in Table 5. Fig. 3 shows the Raman spectra of aqueous $(CF_3)_2BF_2^-$ and of C_3F_8. Fig. 4 shows the IR spectrum. From Fig. 3 it is evident that not only the intensity

TABLE 4

VIBRATIONAL SPECTRA (cm^{-1}) OF THE $(CF_3)_2BF_2^-$ ANION

Raman (natural B)	IR $^{11}B/^{10}B$	Assignment
	~70s	Lattice Vibration
	122(sh)	ν_8 (a_1)
	180m	ν_{26} (b_2)
	234m	ν_{13}, ν_{21} (a_2, b_1)
286sp	286w	ν_6 (a_1)
305(sh)		ν_{12} (a_2)
311m	310vw	ν_{19} (b_1)
334mp	334m	ν_5 (a_1)
430vw	429vw	ν_{24} (b_2)
515mp	514m	ν_4 (a_1)
553(sh)		ν_{18} (b_1)
	~560vw	
564m		ν_{23} (b_2)
595mp	595m	ν_9 (a_1)
689w	689/691s	ν_{16} (b_1)
725vsp	725w	ν_2 (a_1)
	880/907vs	ν_{20}, ν_{25} (a_1, b_2)
1010vw	1011/1038vs	ν_7 (a_1)
~1055w	~1050s	ν_{17}, ν_{10} (b_1, a_2)
	~1090vs	ν_3 (a_1)
~1095m	~1100/1120vs	ν_{22} (b_2)
1319mp	1320/1334s	ν_{15} (b_1)

TABLE 5

NON-ZERO SYMMETRY FORCE CONSTANTS F_{ij} (10^2 N/m) FOR THE $(CF_3)_2BF_2^-$ ANION, SCALED TO 1 Å

	F_{ij}, ij =		F_{ij}, ij =	
$\nu_s(CF_3)$	11 = 1515	6.65	12 = 1516	0.60
$\delta_s(CF_3)$	22 = 1616	1.80	16 = 1520	0.25
$\nu_{as}(CF_3)$	33 = 1010 = 1717 = 2222	3.95	26 = 1620	−0.25
$\delta_{as}(CF_3)$	44 = 1111 = 1818 = 2323	1.80	34 = 1011 = 1718 = 2223	−0.75
$\rho(CF_3)$	55	0.90	35 = 1012 = 1719 = 2224	0.40
$\nu_s(BC_2)$	66	3.96	38	0.08
$\nu_s(BF_2)$	77	5.56	45 = 1112 = 1819 = 2324	−0.25
$\delta_s(BC_2)$	88	1.18	48	−0.08
$\delta_s(BF_2)$	99	1.20	57	−0.20
δ(FCB)	1212	0.99	67	0.20
δ(FBC)	1313	0.80	68	0.10
$\rho(CF_3)$	1919	1.17	69	−0.30
$\nu_{as}(BC_2)$	2020	3.40	78	−0.60
δ(FBC)	2121	0.60	79	0.60
δ(FCB)	2424	1.35	89	0.25
$\nu_{as}(BF_2)$	2525	2.78	1213	0.05
δ(FBC)	2626	0.66	1920	0.10
			1921	0.18
			2021	0.24
			2425	−0.23
			2426	−0.04
			2526	0.53

pattern but also the absolute and relative positions of the Raman lines are surprisingly consistent for both species, though there is a general shift to lower frequencies in the anion.

a_1 Vibrations. Six of the nine a_1 vibrations are immediately recognized from

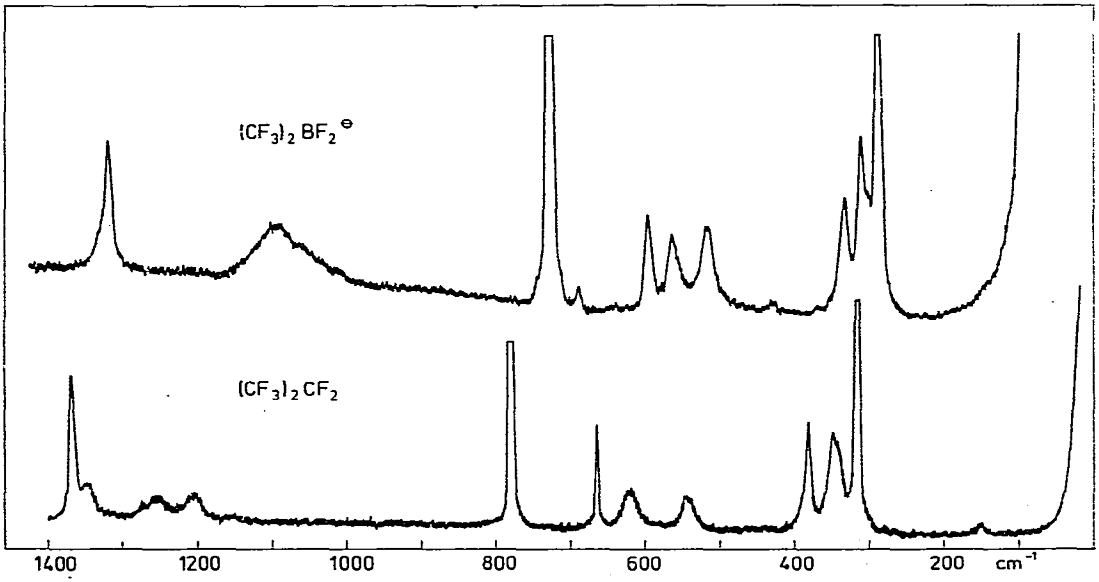

Fig. 3. Raman spectra of $Cs[(CF_3)_2BF_2]$, ~50% aqueous solution, and of liquid C_3F_8.

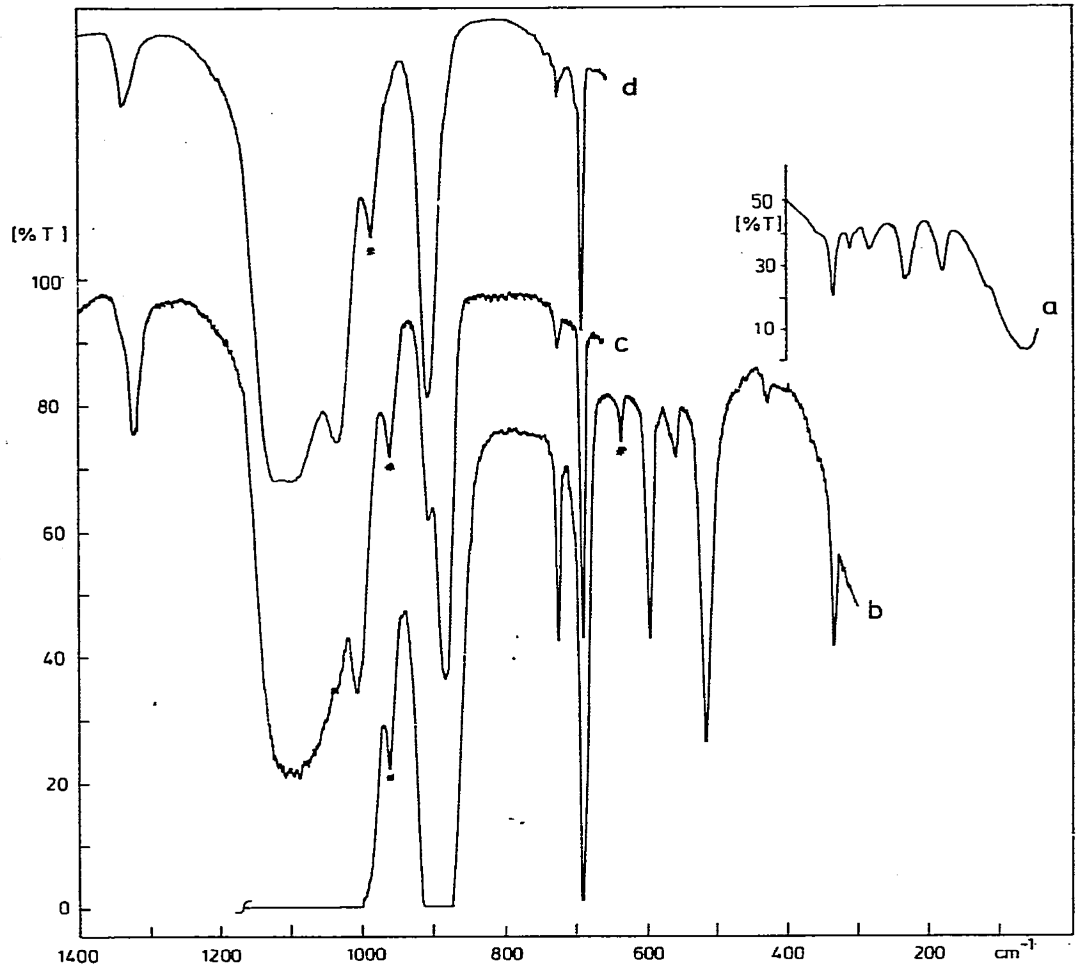

Fig. 4. Infrared spectra of Cs[$(CF_3)_2BF_2$]; a, polyethylene disc, natural B; b, c, KBr disc, natural B; d, KBr disc, ^{10}B, $CF_3BF_3^-$ impurities are marked with asterisks.

their polarized Raman lines at 286, 334, 515, 725 and 1319 cm^{-1}. Their counterparts in C_3F_8 are observed at 318, 389, 547, 665, 781 and 1369 cm^{-1}. The three a_1 vibrations still missing correspond to the C_3F_8 vibrations at 151, 1151 and 1262 cm^{-1}. Assuming a decrease of the C_3F_8 frequencies in $(CF_3)_2BF_2^-$, and taking into account the results of the NCA and the expected $^{10}/^{11}B$ shifts, the IR absorptions observed at 122 cm^{-1} for the CBC bending and at 1038/1011 and ~1100/~1090 cm^{-1} ($^{10}/^{11}B$) for the BF and CF stretch, respectively, are most likely to be associated with the missing a_1 vibrations. The mixing of the two latter vibrations, as indicated by the $^{10}/^{11}B$ shift, should be noted.

b_1 Vibrations. The seven b_1 vibrations which are symmetrical to the CBC plane should be associated with IR absorptions. In C_3F_8 these are observed at 276, 337, 537, 731, 1008, 1210 and 1350 cm^{-1}. These correspond to IR absorptions of $(CF_3)_2BF_2^-$ at 234, 310, 553, 691/689, 907/880, 1055 and 1334/1320 cm^{-1}. This assignment is supported by the NCA results. From these

it is concluded that the CBC stretch (ν_{20}) associated with the absorption at 907/880 cm^{-1} accidentally coincides with the BF stretch ν_{25}, which again exhibits the same $^{10}/^{11}$B shift.

b_2 Vibrations. The nontorsional b_2 fundamentals of C_3F_8 are located at 219, 461, 618, 1155 and 1268 cm^{-1}. Taking into account the accidental coincidence of ν_{20} and ν_{25} and the expectation that the b_2 vibrations are active both in the IR and Raman effect, the vibrations observed at 180, 430, 564, 907/880 and 1100 cm^{-1} are assigned to b_2.

a_2 Vibrations. As in C_3F_8, the a_2 vibrations, which are only Raman active, are barely observable. Either their intensities are very low or they coincide with fundamentals of other symmetry species, a shoulder on the Raman line at 305 cm^{-1} being the only experimental evidence for an a_2 vibration. From the NCA the nontorsional frequencies are calculated to be 236, 305, 558 and 1050 cm^{-1}, which compares well with the a_2 fundamentals of C_3F_8 for which 276, 347, 537 and 1369 cm^{-1} were calculated [5].

There is no experimental evidence for the torsions ν_{14} and ν_{27} for which a frequency of ~50 cm^{-1} is most likely. From intensity considerations the strong IR absorption at 70 cm^{-1} is assigned to a lattice mode.

TABLE 6

OBSERVED AND CALCULATED VIBRATIONAL FREQUENCIES, $^{10/11}$B SHIFTS (cm^{-1}) AND POTENTIAL ENERGY DISTRIBUTION $V(k)$ [a] FOR THE $(CF_3)_2{}^{11}BF_2$ ANION

	$\nu_{obs}{}^{11}B$	$\Delta\nu_{obs}(^{10}B - {}^{11}B)$	$\nu_{calc}{}^{11}B$	$\Delta\nu_{calc}$ $(^{10}B - {}^{11}B)$	$V(k)$ [a] (^{11}B)
a_1	1319		1311	8	44(2), 43(6), 38(1)
	725		725		52(1), 26(2)
	~1090		1084	6	74(3), 24(4), 17(5), 16(8)
	595		600	2	21(3), 14(4), 10(7), 10(9)
	515		520	1	47(4), 25(9), 13(6)
	1011	27	1014	23	83(7), 13(9)
	334		329		64(9), 11(5)
	286		286		44(5), 27(6), 14(4), 12(2)
	122		122		77(8), 24(5)
a_2			1050		91(10), 27(11), 13(12)
			558		60(11), 16(10)
		305	305		71(12), 25(11), 19(13)
			236		75(13), 22(12)
b_1	1320	14	1319	12	52(20), 40(16), 35(15)
	689	2	693	3	49(16), 30(15)
	1050		1047	1	86(17), 25(18), 18(19)
	553		551		65(18), 13(17)
	880	27	880	26	37(15), 37(20), 18(21)
	311		311		86(19), 18(18)
	234		234	1	77(21)
b_2	~1100	~20 [b]	1110	7	69(22), 30(24), 22(23), 11(26)
	564		560		47(23), 19(22), 10(25)
	880	27	880	28	88(25), 17(22), 14(26), 12(24)
	180		179		86(26), 26(24)
	430		428	1	39(23), 36(24), 13(25)

[a] $V(k) = F_{dia}L_{ik}^2\,100/\Sigma_{ij}F_{ij}L_{ik}L_{jk}$ for $V(k) \geqslant 10$. [b] Uncertain.

Normal coordinate analysis

In order to gain support for the assignment mainly based on comparison with C_3F_8, a NCA was undertaken to obtain force constants for the interpretation of the bonding in the $(CF_3)_2BF_2^-$ anion, particularly in comparison with $CF_3BF_3^-$, and to describe the vibrational behavior properly. Following the FG matrix method a G matrix was calculated [13] assuming C_{2v} symmetry with staggered orientation of the CF_3 groups and averaged bond lengths and bond angles taken from the X-ray data. A starting F matrix following the principle of the quadratic local symmetry force field [14] was adopted transferring force constants from the $CF_3BF_3^-$ anion [4]. This force field reproduced both experimental frequencies and $^{10}/^{11}B$ shifts very satisfactorily. It was refined according to the following criteria:

(i) exact fit with fundamental frequencies obtained from solution spectra whenever possible,

(ii) precise reproduction of experimental $^{10}/^{11}B$ shifts,

(iii) reduction of the F matrix multiplicity according to the principle of meaningful potential energy distribution [15]. F_{ij}'s corresponding to identical G_{ij}'s were given the same value, and F_{ij}'s corresponding to $G_{ij} = 0$ were taken as zero. In classes a_2 and b_2 the torsions were not considered.

The final non-zero symmetry force constants are given by Table 5. Experimental and calculated vibrational frequencies for the ^{10}B and ^{11}B species as well as the calculated potential energy distribution in terms of diagonal force constants (not eigenvectors) are collected in Table 6. Calculated frequencies and $^{10}/^{11}B$ shifts are in acceptable agreement with observation.

Discussion

That the force constants for $Cs[(CF_3)_2BF_2]$ are normal is shown by the comparisons given in Table 7. A qualitative correlation at least between the force constants and bond lengths may be discerned if one assigns an uncertainty to the force constants of about 0.2 [10^2 N/m].

In contrast to *f*(BF), *f*(BC) appears to be less sensitive to the coordination number of the B atom; similarly, the change from borane to borate influences *r*(BF) more than *r*(BC). The substitution effect of the CF_3 group on B—C and B—F bond lengths appears to be relatively small. Thus investigations of further CF_3—B compounds will be necessary before a weakening or strengthening of the B—C bond in CF_3—B compounds with respect to analogous CH_3—B species can be detected with certainty.

In general, large cations are believed to have little influence on anion geometry. In $K[CF_3BF_3]$, only 8° deviations of the F—C—B—F torsion angles from exactly staggered values were found [4]. However in $Cs[(CF_3)_2BF_2]$, anion—cation packing forces appear to determine the conformation of the anion. While the anion—cation interactions must be essentially electrostatic in nature, their effect on structure is clearly not negligible and difficult to predict.

Experimental

$Cs[(CF_3)_2BF_2]$ was prepared according to Ref. 2, the ^{10}B sample being obtained from $^{10}B_2O_3$. Raman spectra of an aqueous solution in a 1 mm i.d. capil-

TABLE 7

COMPARISON OF FORCE CONSTANTS [a] AND GEOMETRIES [b]

	∡(FCF)	∡(BCF)	∡(FBF)	∡(CBF)
$Cs[(CF_3)_2BF_2]$ [c]	104.5	114.0	108.1	108.7
$K(CF_3BF_3]$ [d]	104.9	113.7	109.9	109.1

	$f(BC)$	$f'(BC)$	$r(BC)$	$f(BF)$	$f'(BF)$	$r(BF)$	$f(CF)$	$f'(CF)$	$r(CF)$
$Cs[(CF_3)_2BF_2]$ [c]	3.68	0.28	1.618	4.17	1.39	1.391	4.85	0.90	1.353
$K[CF_3BF_3]$ [d]	3.63	—	1.625	4.19	0.84	1.391	4.85	0.90	1.343
$K[BF_4]$				4.85 [e]	0.65	1.386 [f]			
BF_3				7.28 [g]	0.77	1.311 [h]			
$Li[(CH_3)_4B]$ [i]	3.4 [j]	0	1.646 [k] 1.634 [l]						
$(CH_3)_3B$	3.84 [j]	0.13	1.578 [m]						
$(CF_3)_2CF_2$ [n]	4.87	0.38		6.10	0.85		6.22	0.89	

[a] In 10^2 N/m. [b] Distances (Å) and angles (°). [c] This work. [d] Ref. 4. [e] Ref. 16. The experimental $^{10/11}B$ shifts of ν_3 was determined to be 40.5 to 41.0 cm^{-1} for BF_4^- [17]. Owing to anharmonicity effects and Fermi resonance of ν_3 with $2\nu_4$, which is stronger for the ^{11}B than the ^{10}B species, the experimental shift should be corrected. Corrections for both effects would indicate that the true shift, about 42 cm^{-1}, is larger than observed, which is in excellent agreement with that calculated using Becher's force constant [16]. [f] Ref. 18. [g] Ref. 19. [h] Ref. 20. [i] Ref. 7. [j] Ref. 21. [k] Neutron results. [l] X-ray results. [m] Ref. 22. [n] Analogous force constants from ref. 5.

lary were recorded with a Cary 82 instrument, excitation Kr^+ 6471 Å, 200 mW at the sample, spectral slit width 3 cm^{-1}, wavenumber accuracy ±1—2 cm^{-1}. IR spectra were obtained from KBr and polyethylene discs employing a Beckman IR 12 (2000—200 cm^{-1}) and a Nicolet Series 8000 FT instrument (500—50 cm^{-1}). Wavenumber accuracy ±1—2 cm^{-1}.

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References

1 A. Ruoff and H. Bürger, Spectrochim. Acta A, 36 (1980) 171.
2 G. Pawelke, F. Heyder and H. Bürger, J. Organometal. Chem., 178 (1979) 1.
3 A. Yokozeki and S.H. Bauer, Top. Curr. Chem., 53 (1975) 71.
4 D.J. Brauer, H. Bürger and G. Pawelke, Inorg. Chem., 16 (1977) 2305.
5 H. Bürger and G. Pawelke, Spectrochim. Acta A, 35 (1979) 525.
6 (a) J.A. Ibers and W.C. Hamilton, Ed., International Tables for X-ray Crystallography, Vol. IV, The Kynoch Press, Birmingham, 1974, Table 2.3.1 (b) ibid., Table 2.2B.
7 W.E. Rhine, G. Stucky and S.W. Peterson, J. Amer. Chem. Soc., 97 (1975) 6401.
8 B.W. Davies and N.C. Payne, J. Organometal. Chem., 102 (1975) 245; F.A. Cotton, T. La Cour and A.G. Stanislowski, J. Amer. Chem. Soc., 96 (1974) 754; F.A. Cotton, B.A. Fenz and A.G. Stanislowski, Inorg. Chim. Acta, 7 (1973) 503.
9 A.L. Andreassen and S.H. Bauer, J. Chem. Phys., 56 (1972) 3802.
10 A. Bondi, J. Phys. Chem., 68 (1964) 441.
11 H. Bürger, H. Niepel, G. Pawelke and H. Oberhammer, J. Mol. Struct., 54 (1979) 159.
12 M.J.R. Clark and H. Lynton, Can. J. Chem., 47 (1969) 2579.
13 P. Pulay, G. Borossay and F. Török, J. Mol. Struct., 2 (1968) 336; P. Pulay and W. Sawodny, J. Mol. Spectrosc., 26 (1968) 150.
14 T. Shimanouchi in H. Eyring, D. Henderson and W. Jost, (Eds.), Physical Chemistry, An Advanced Treatise, New York, N.Y., 1970, p. 233.
15 H.J. Becher, Fortschr. Chem. Forsch., 10 (1968) 156.
16 H.J. Becher, Colloq. Intern. CNRS, Paris, 191 (1970) 187.
17 H. Bonadeo and E. Silberman, J. Mol. Spectrosc., 32 (1969) 214.
18 G. Brunton, Acta Crystallogr., B, 25 (1969) 2161.
19 J.L. Duncan, J. Mol. Spectrosc., 22 (1967) 247.
20 K. Kuchitsu and S. Konaka, J. Chem. Phys., 45 (1966) 4342.
21 H.J. Becher and F. Bramsiepe, Spectrochim. Acta, A, 35 (1979) 53.
22 L.S. Bartell and B.L. Carroll, J. Chem. Phys., 42 (1965) 3076.