thermic. As B_6H_{10} does not readily form from B_6H_{12},[16] there must be a substantial activation energy for reaction 2. On the other hand B_6H_{12} lies only 6 kcal below $BH_3 + B_5H_9$. As the addition reaction probably has an activation energy less than or equal to 6 kcal, B_6H_{12}, if formed, would not be stable enough to survive our conditions long enough to be detected. This would be in conflict with the known stability of B_6H_{12}.[16] Therefore we suggest that the hydrogen and boron rearrangement of the initial adduct illustrated in Figure 8 has a substantially higher barrier than the loss of an H_2 molecule. Thus it appears in this case that we are observing the direct reaction $BH_3 + B_5H_9 \rightarrow B_6H_{10} + H_2$.

As noted above these reactions of BH_3 do illustrate another aspect of the reactivity of this species. It is of interest to compare the rate constants for these reactions estimated above with those of other reactions of BH_3 that we have reported previously.[6-9] Before doing so it is necessary to point out that in this study we cannot exclude the possibility of some type of surface involvement in the formation of the addition products. In previous studies we have argued that the reactions observed were homogeneous on the basis of the large magnitude of the rate constants.[6] Here, however, products are observed only at very low levels, the rate constants are much smaller, and the arguments are much weaker. On the other hand the possibility of surface involvement does not affect the conclusion that the reaction of BH_3 with stable hydrides is substantially slower than the reaction with C_2H_4,[7] $N(CH_3)_3$,[8] and other species.[6,9]

An interesting comparison is the rate of reaction of BH_3 with C_2H_4 and B_2H_6. The rate constant for the former is at least 10^2 times larger than that for the latter.[7] It is clear that BH_3 addition to a carbon–carbon double bond followed by rearrangement is favored over BH_3 insertion into a boron framework. It has been suggested that there is a relationship between reactivity and the interaction of highest filled orbitals and lowest unfilled orbitals.[17] The highest filled orbital in C_2H_4 is a π MO ($1b_{2u}$) while in B_2H_6 it is a $1b_{2g}$ orbital, as the orbital corresponding to the π MO in C_2H_4 is the fourth lowest orbital in B_2H_6.[18] Assuming equal frequency factors for both reactions, the difference in rate constants would correspond to a difference in activation energies of 4 kcal. This in turn would indicate a total activation energy for the reaction of BH_3 with B_2H_6 of *ca.* 6 kcal.[7]

Acknowledgments.—This research was supported by the National Science Foundation under Grants No. GP 10199 and GP 28320. The aid of G. W. Mappes in setting up the apparatus is gratefully acknowledged. The helpful comments of the referees are appreciated.

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Mixed Tetrahaloborate Ions. Detection and Study by Nuclear Magnetic Resonance[1]

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BF_4^-, BCl_4^-, BBr_4^-, and BI_4^- undergo halogen exchange in methylene chloride solution to form the mixed tetrahaloborate ions, for which ^{19}F and ^{11}B nmr data are presented. A previous report of very rapid halogen exchange in the BF_4^-–BCl_4^- system is incorrect. Only in the BF_4^-–BI_4^- system is halogen redistribution so rapid that separate nmr signals are not observed for the mixed-halogen anions. Exchange with methylene halide solvents gives rise to ternary-halogen species such as BF_2ClBr^-. Additional methods of preparation of mixed tetrahaloborate anions are investigated. The nmr parameters of the mixed tetrahaloborate anions show trends which resemble those of the mixed boron trihalides. The trends can be interpreted in terms of the presence of boron–fluorine π bonding. The results of CNDO/2 calculations provide an alternative interpretation of the trends in chemical shifts. The ^{11}B and F^{19} chemical shifts of the tetrahaloborate anions are found to fit Malinowski's criteria of "pairwise additivity."

Introduction

Many boron–halogen compounds undergo halogen redistribution reactions to give mixed-halogen species. Although these reactions have been extensively studied for a number of types of boron–halogen compounds,[2-5] relatively little is known about the mixed tetrahaloborate anions.[5] Although there is evidence for the existence of several of the mixed tetrahaloborate ions in crystalline solids, only the chlorotrifluoroborate ion appears to have been well characterized.[5,6] A previous solution nmr study of the BF_4^-–BCl_4^- system in methylene chloride yielded only single averaged ^{19}F and ^{11}B nmr peaks, the peak position depending on the relative amounts of fluorine and chlorine in the system, and a very rapid halogen exchange *via* the mixed tetrahaloborate ions was postulated.[7] This behavior contrasted with the slower halogen-exchange reactions previously observed in BF_4^-,[8] the mixed

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boron trihalides,[9] and the dimethyl ether–mixed boron trihalide adducts.[10] As part of our study of donor–acceptor adducts of the mixed boron trihalides,[10,11] we have carried out nmr studies of systems which should contain mixed tetrahaloborate ions.

Experimental Section

Materials.—Tetra-*n*-butylammonium tetrafluoroborate was prepared by an ion-exchange method. An aqueous slurry of Dowex 50W X-8 (100–200 mesh) cation-exchange resin (J. T. Baker) in its silver form was treated with an excess of solid tetra-*n*-butylammonium bromide (Eastman). The resulting $(n\text{-}C_4H_9)_4N^+$ form of the resin and silver bromide precipitate were filtered off and rinsed with distilled water until the filtrate gave a negative silver nitrate test for bromide ion. The washed resin and AgBr were placed in a saturated aqueous solution of ammonium tetrafluoroborate (Alfa Inorganics) and extracted with successive portions of benzene. The benzene extract was filtered and evaporated to dryness on a steam bath. The resulting crude $(n\text{-}C_4H_9)_4N^+BF_4^-$ was recrystallized twice from ethanol–water mixtures. The monoclinic crystals were crushed and dried overnight under vacuum; mp 161.5–162.0° (lit.[12] mp 161.8°).

Tetraethylammonium tetrachloroborate was prepared by the direct addition of BCl_3 to tetraethylammonium chloride (Eastman). Finely ground anhydrous $(C_2H_5)_4N^+Cl^-$ was placed in a Pyrex trap which was evacuated and then immersed in a Dry Ice–acetone bath. Boron trichloride (Matheson) was distilled under vacuum from a 0° trap through Dry Ice–acetone and liquid nitrogen traps connected in series. The BCl_3 collected in the Dry Ice–acetone trap was distilled onto the $(C_2H_5)_4N^+Cl^-$ at 0° until an excess was present. After standing overnight at 0°, the excess BCl_3 was pumped off and the residue was dried at room temperature for 2 hr under vacuum, leaving a white, free-flowing powder.

Tetra-*n*-butylammonium tetrabromoborate was prepared from $(n\text{-}C_4H_9)_4N^+Br^-$ by a method analogous to that used for $(C_2H_5)_4N^+BCl_4^-$. After allowing $(n\text{-}C_4H_9)_4N^+Br^-$ to stand overnight with BBr_3 (Alfa Inorganics), excess BBr_3 was removed by pumping on the solid residue for 24 hr. The product was periodically broken up to facilitate drying. Both $(C_2H_5)_4N^+BCl_4^-$ and $(n\text{-}C_4H_9)_4N^+BBr_4^-$ were stored under vacuum in sealed ampoules until used.

Because previous attempts to isolate solid tetraalkylammonium tetraiodoborates proved unsuccessful,[13] tetra-*n*-butylammonium tetraiodoborate was prepared in solution by mixing BI_3 (Alfa Inorganics) and a 10% molar excess of tetra-*n*-butylammonium iodide (Eastman) in nmr sample tubes.

Trimethylsilyl chloride (Alfa Inorganics) was used without further purification. Trimethylsilyl iodide was prepared from hexamethyldisiloxane (NMR Specialties) using the method of Voronkov, *et al.*[14]

Reagent grade methylene chloride (British Drug Houses), tetramethylsilane (Stohler Isotope Chemicals), and trichlorofluoromethane (K & K Laboratories) were allowed to stand over Linde 4A Molecular Sieves and then vacuum distilled before use. Methylene bromide (Eastman), methylene iodide (Fisher), and hydrogen iodide (Matheson) were used without further purification. Trimethoxyboron (Chem Service) was prepared as a 10% v/v solution in CH_2Cl_2 and sealed in capillary tubes.

Preparation of Nmr Samples.—Manipulations of chemicals were carried out in a drybox. Tetrahaloborate solutions were prepared in precision nmr tubes, degassed by attachment to a high-vacuum system, and sealed off under high vacuum. Small amounts of $CFCl_3$ were condensed into the samples from the high-vacuum system to provide an internal ^{19}F reference. Samples containing BF_3 were prepared by condensation of known amounts of purified BF_3 from a calibrated volume on the high-vacuum system. Concentrations were approximately 1 *M*, except in some solutions where tetrahaloborates of the heavier halogens were not sufficiently soluble. In these cases, saturated solutions were used. In a few cases, precipitates formed on prolonged standing. These were not further investigated.

Nmr Measurements.—Fluorine-19 nmr spectra were measured with a Varian DA-60IL spectrometer operating at 56.4 MHz. Boron-11 nmr spectra were recorded using a Varian HA-100 spectrometer operating at 25.1 MHz. The spectra were calibrated by the audio-side-band method. Proton spectra were obtained on a Varian A-60 spectrometer.

Tensimetric and Electrical Conductivity Measurements.—A Beckman Model RC-18 conductivity bridge with an oscillator frequency setting of 1 kHz was used for conductivity measurements. The conductivity cell was of the variable-path-length type described elsewhere by Gillespie and coworkers.[15] Cell constants were compared before and after low-temperature titrations by thermostating a 0.2000 *M* KCl solution in conductivity water at 25.00 ± 0.05°. The cell constants did not change by more than ±1%.

Tensimetric and conductometric titrations of $(C_2H_5)_4N^+Cl^-$ in CH_2Cl_2 with BF_3 were carried out by condensation of known quantities of BF_3 into the tensimeter or conductivity cell at liquid nitrogen temperature. Measurements at −78.5° were made by immersing the frozen solution in a Dry Ice–acetone bath; the temperature of the bath was measured with a toluene-filled low-temperature thermometer and was held constant to within ±0.5°.

Pressure measurements were made at equilibrium with a mercury manometer. The high-vacuum system employed was so designed that a minimum quantity of gas was outside the thermostated container. The system was calibrated by measuring the partial pressure of BF_3 over pure solvent at −78.5°; the resulting curve was nearly linear.

CNDO/2 Calculations.—Calculations using the CNDO/2 method were carried out with the CINDO–CNDO and INDO program provided by the Quantum Chemistry Program Exchange.[16] This program incorporates the theory outlined by Pople and coworkers.[17–19] The calculations were executed for the closed-shell configurations on an IBM 360 computer. Input data consisted of the wave function option, the open–closed shell option, the number of atoms, the molecular charge, the multiplicity, the atomic numbers of the atoms, and the cartesian coordinates of the atoms in their molecular geometry.

The B–F and B–Cl bond lengths in BX_3 molecules were taken as 1.291 and 1.74 Å, the experimentally determined distances in BF_3 and BCl_3, respectively.[20] Bond lengths in the BX_4^- ions were taken as the average B–F and B–Cl internuclear separations in the X-ray crystal structure of BF_4^-, 1.384 Å,[21] and BCl_4^-, 1.842 Å.[22] Ideal bond angles were assumed, *i.e.*, 120° X–B–X angles in BX_3 and 109° 28′ X–B–X angles in BX_4^-.

Results

Halogen scrambling among tetrahaloborate anions to give all of the possible mixed-halogen anions has been observed in most of the systems studied. Only in BF_4^-–BI_4^- systems was halogen exchange too rapid to allow the observation of separate nmr signals due to the individual mixed-halogen species. Nmr data for the mixed tetrahaloborate anions are given in Tables I and II.

BF_4^-–BCl_4^-.—The initial room-temperature ^{19}F and ^{11}B spectra of a solution of $(n\text{-}C_4H_9)_4N^+BF_4^-$ and $(C_2H_5)N^+BCl_4^-$ in methylene chloride showed only the peaks arising from BF_4^- and BCl_4^-. Heating the solution at 60° for several minutes led to the appearance of three new 1:1:1:1 quartets in the ^{19}F spectrum which

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TABLE I

^{19}F CHEMICAL SHIFTS AND ^{11}B–^{19}F COUPLING CONSTANTS OF BX_4^- IONS

BX_4^-	^{19}F chem shift,[a] ppm Obsd	^{19}F chem shift,[a] ppm Calcd[b]	^{11}B–^{19}F coupling constant, Hz Obsd	^{11}B–^{19}F coupling constant, Hz Calcd[b]
BF_4^-	151.3	151.5	1.0[c]	−1.5
BF_3Cl^-	124.6	123.9	25.2	25.7
BF_3Br^-	113.8	113.3	. . .	37.8
$BF_2Cl_2^-$	104.1	104.6	54.2	53.8
BF_2ClBr^-	95.7	96.3	65.1	65.2
$BFCl_3^-$	94.0	93.6	79.4	79.8
$BF_2Br_2^-$	88.2	88.9	76.1	75.9
$BFCl_2Br^-$	87.8	87.6	91.3	91.0
$BFClBr_2^-$	. . .	82.5	. . .	101.5
$BFBr_3^-$	78.6	78.3	111.3	111.3

[a] From internal $CFCl_3$ in CH_2Cl_2 solution. [b] From "pairwise interaction" parameters. [c] Splittings are visible only when no additional tetrahaloborates are present.

TABLE II

^{11}B CHEMICAL SHIFTS OF BX_4^- IONS

BX_4^-	^{11}B chem shift,[a] ppm Obsd	^{11}B chem shift,[a] ppm Calcd[b]	BX_4^-	^{11}B chem shift,[a] ppm Obsd	^{11}B chem shift,[a] ppm Calcd[b]
BCl_4^-	11.6[c]	11.5	BBr_4^-	42.4[c]	42.4
$BFCl_3^-$	11.8	12.1	$BClBr_2I^-$	. . .	57.2
$BF_2Cl_2^-$	13.8	13.7	$BCl_2I_2^-$	60.8	60.6
BCl_3Br^-	15.4	15.5	BBr_3I^-	62.8	63.2
BF_3Cl^-	16.6	16.3	$BClBrI_2^-$	. . .	72.8
BF_4^-	19.9[c]	20.0	$BBr_2I_2^-$	85.8	85.6
$BCl_2Br_2^-$	22.1	22.0	$BClI_3^-$	99.1	98.8
$BClBr_3^-$	30.9	31.0	$BBrI_3^-$	115.3	115.0
BCl_3I^-	30.9	31.5	BI_4^-	146.0[c]	146.0
BCl_2BrI^-	. . .	39.6			

[a] From external $(CH_3O)_3B$ (10% v/v in CH_2Cl_2) in CH_2Cl_2 solution. [b] From "pairwise interaction" parameters. [c] Literature values (ppm): BF_4^-, 20.0; BCl_4^-, 11.8; BBr_4^-, 42.3; BI_4^-, 146.0;[13] converted to $(CH_3O)_3B$ reference from $BF_3O(C_2H_5)_2$ by adding 18.3 ppm.

are assigned to BF_3Cl^-, $BF_2Cl_2^-$, and $BFCl_3^-$ (Figure 1). The ^{11}B spectrum became complex due to the overlapping of multiplets which arise from coupling of boron with the varying numbers of fluorines in the new species. By skewing the $BF_4^-:BCl_4^-$ ratio toward chlorine-containing species, it was possible to identify and assign multiplets in the ^{11}B spectra (Figure 2). ^{19}F and ^{11}B nmr parameters are given in Tables I and II, respectively. The ^{1}H spectra of the cations remained unchanged during halogen scrambling in this and all subsequent BX_4^- systems reported in this study.

BCl_4^-–BBr_4^-, BCl_4^-–BI_4^-, BBr_4^-–BI_4^-, and BCl_4^-–BBr_4^-–BI_4^-.—Exchange was found to be considerably faster in these systems than in the BF_4^-–BCl_4^- system. Thus the initial room-temperature ^{11}B spectra of mixtures of the respective tetraalkylammonium salts in methylene chloride showed the presence of equilibrium distributions of the mixed and unmixed tetrahaloborates, in accord with a near-random distribution of halogens. In the absence of fluorine each tetrahaloborate anion gives rise to a broad singlet. Thus two small peaks were observed having the chemical shifts of the BX_4^- and BY_4^- species,[13] and between these there were three additional ^{11}B peaks having chemical shifts which vary in a regular fashion from BX_4^- to BY_4^- (Table II). When the two tetrahaloborates are present in 1:1 proportions, the relative peak areas are in approximately the 1:4:6:4:1 proportions expected for random redistribution of halogen among BX_4^-, BX_3Y^-, $BX_2Y_2^-$, BXY_3^-, and BY_4^- (Figure 3).

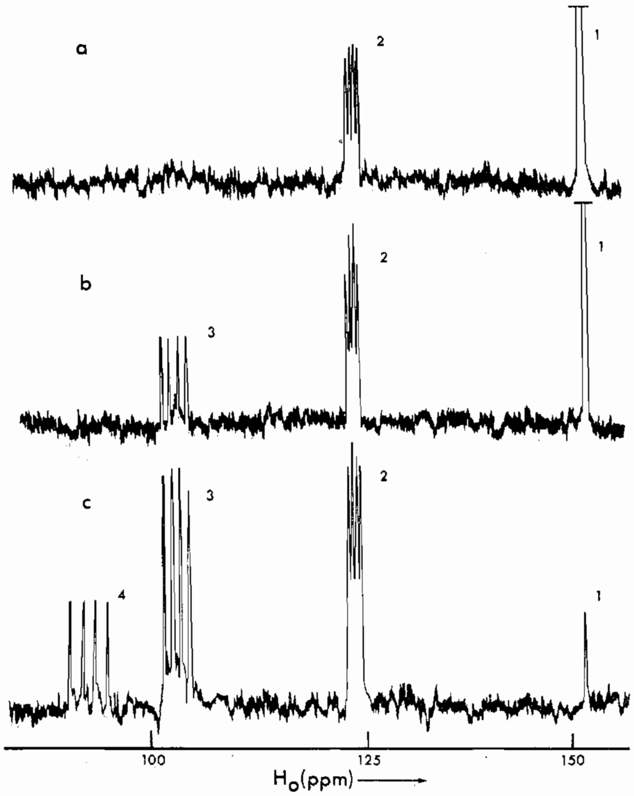

Figure 1.—^{19}F spectra of $(n\text{-}C_4H_9)_4N^+BF_4^-$–$(C_2H_5)_4N^+BCl_4^-$ (1:3 molar ratio in CH_2Cl_2), heated at 60° for (a) 5 min, (b) 10 min, and (c) 20 min. Peak assignments: 1, BF_4^-; 2, BF_3Cl^-; 3, $BF_2Cl_2^-$; 4, $BFCl_3^-$.

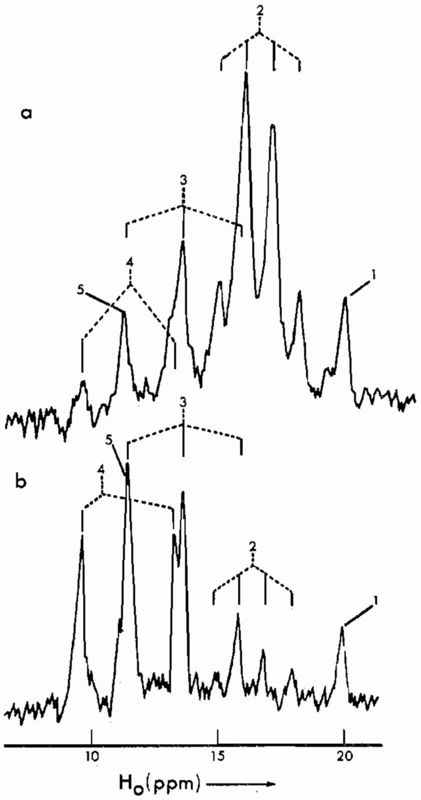

Figure 2.—^{11}B spectra of BF_4^-–BCl_4^- in CH_2Cl_2, in the molar ratios (a) 1:1 and (b) 1:3, after being heated at 60° for 30 min. Peak assignments: 1, BF_4^-; 2, BF_3Cl^-; 3, $BF_2Cl_2^-$; 4, $BFCl_3^-$; 5, BCl_4^-.

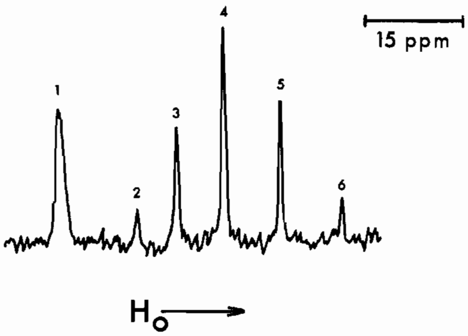

Figure 3.—The ^{11}B spectrum of BCl_4^-–BBr_4^- (1:1 molar ratio in CH_2Cl_2). Peak assignments: 1, external $(CH_3O)_3B$; 2, BCl_4^-; 3, BCl_3Br^-; 4, $BCl_2Br_2^-$; 5, $BClBr_3^-$; 6, BBr_4^-.

In the BBr_4^-–BI_4^- system there is negligible halogen exchange with methylene chloride on standing for a brief time at room temperature; no additional peaks were observed which could be assigned to chlorine-containing tetrahaloborate anions.

Solubility problems were especially serious in the BCl_4^-–BBr_4^-–BI_4^- system, so that only a very weak ^{11}B spectrum could be obtained. There appeared to be more ^{11}B signals present than would arise from the possible BX_4^- and $BX_nY_{4-n}^-$ species, and thus the ternary-halogen species were probably present. However, because the spectra were extremely weak, assignments of the peaks were not attempted.

BF_4^-–BBr_4^-.—The ^{19}F spectra of methylene chloride solutions of the $(n\text{-}C_4H_9)_4N^+$ salts of BF_4^- and BBr_4^- likewise showed that halogen exchange had occurred readily at room temperature. However, the spectra were complex and contained more peaks than could be accounted for by the presence of all of the species $BF_nBr_{4-n}^-$. The presence of a CH_2ClBr peak in the ^1H spectra indicated that some halogen exchange with the solvent had occurred and resulted in the formation of ternary-halogen tetrahaloborate anions which are discussed in the next section.

Simpler spectra were obtained from solutions of BF_4^- and BBr_4^- in methylene bromide as solvent, since halogen exchange with this solvent cannot result in the formation of additional tetrahaloborate anions (Figure 4). However, only when the solution had been supercooled to −57°, could the expected four resonances due to BF_4^-, BF_3Br^-, $BF_2Br_2^-$, and $BFBr_3^-$ be observed. Above this temperature the collapse of the BF_4^- and BF_3Br^- peaks indicates rapid chemical exchange of fluorine between these two environments. At −57° the ^{19}F chemical shifts (ppm) were as follows: BF_4^-, 143.8; BF_3Br^-, 113.2; $BF_2Br_2^-$, 86.9; $BFBr_3^-$, 77.8. Except for BF_4^- these values differ only slightly from the values found in methylene chloride (Table I). The BF_4^- peak was broad and weak (only about 5% of the BF_3Br^- peak intensity) and its anomalous low-field position is attributed to chemical exchange between BF_4^- and BF_3Br^- still being quite rapid at −57°.

At low temperatures none of the peaks show splitting due to boron–fluorine coupling. The $BF_2Br_2^-$ and $BFBr_3^-$ peaks do show these splittings at higher temperatures, so quadrupole relaxation of boron,[23] rather than rapid chemical exchange, is responsible.

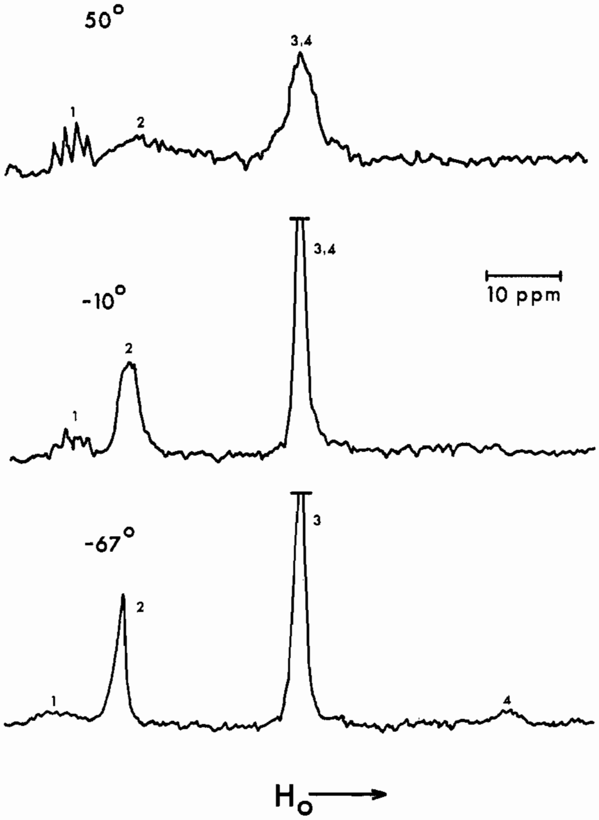

Figure 4.—Temperature dependence of the ^{19}F spectrum of BF_4^-–BBr_4^- (1:1 molar ratio in CH_2Br_2). Peak assignments: 1, $BFBr_3^-$; 2, $BF_2Br_2^-$; 3, $BFBr_3^-$; 4, BF_4^-.

The $BF_2Br_2^-$ peak shows splittings due to boron–fluorine coupling only in a narrow temperature range near −10° and the quartet is never well resolved. Above this temperature range chemical exchange occurs and by +50° the $BF_2Br_2^-$ peak is on the verge of coalescence with the BF_3Br^-–BF_4^- peak (Figure 4). Since boron–fluorine splittings are still sharp in the $BFBr_3^-$ resonance at +50°, fluorine exchange is much slower in this species. The splittings due to boron–fluorine coupling in BF_3Br^- are collapsed at *all* temperatures, due to rapid chemical exchange and/or rapid quadrupole relaxation of boron, and it has not been possible to determine the boron–fluorine coupling constant in BF_3Br^-.

BF_4^-–BCl_4^-–BBr_4^-.—The ^{19}F spectra obtained from BF_4^-–BBr_4^- solutions in methylene chloride are very similar to those obtained from BF_4^-–BCl_4^-–BBr_4^- solutions. At least two 1:1:1:1 quartets are present in addition to those arising from the $BF_nCl_{4-n}^-$ and $BF_nBr_{4-n}^-$ series and are assigned to two of the three possible ternary-halogen species, BF_2ClBr^- and $BFCl_2Br^-$. These assignments are supported by good agreement of the observed shifts with chemical shifts calculated from "pairwise interaction" constants as described in a later section. In BF_4^-–BBr_4^- solutions in methylene chloride, exchange of bromine for the chlorine of methylene chloride must occur fairly rapidly since freshly prepared solutions give rise to a small CH_2ClBr peak in their proton spectra. Heating of the samples at 60° causes an intensification of the CH_2ClBr signal, and after 5 hr of heating the ^{19}F spectrum shows the presence of the series $BF_nCl_{4-n}^-$ but not the series $BF_nBr_{4-n}^-$. However, unlike the simple

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BF_4^-–BCl_4^- system discussed earlier, the $BF_nCl_{4-n}^-$ peaks are collapsed at room temperature, and separate peaks are obtained only at low temperatures. Halogen exchange is thus more rapid with bromine present and might involve the $BCl_nBr_{4-n}^-$ species which cannot be detected by ^{19}F nmr.

Initial room-temperature ^{19}F spectra of methylene chloride solutions of either BF_4^-–BBr_4^- or BF_4^-–BCl_4^-–BBr_4^- were complex and showed not only that mixed tetrahaloborate anions had formed rapidly but also that halogen exchange among certain of the species is rapid on the nmr time scale. A quartet which did not undergo chemical exchange collapse at room temperature was identified as $BFCl_3^-$. The spectra were very temperature dependent between room temperature and −20° (Figure 5). The BF_3Cl^- and BF_3Br^- peaks were collapsed at 0° but separated at −10°, but even at temperatures well below this, splittings due to boron–fluorine coupling were not observed on these peaks. Chemical exchange appears to be quite rapid. Since no BF_4^- peak could be observed, BF_4^- undergoes rapid exchange as in the BF_4^-–BBr_4^- system. In the −20 to −70° temperature range no changes were observed in the spectra except for the broadening and collapse of some of the boron–fluorine splittings due to quadrupole relaxation of boron.[23] The ^{11}B spectra were too complex for interpretation although BBr_4^- and $BClBr_3^-$ were clearly present.

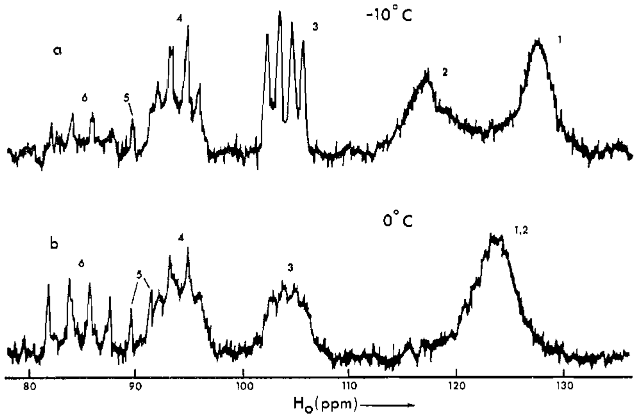

Figure 5.—^{19}F spectra of BF_4^-–BCl_4^-–BBr_4^- (1:1:1 molar ratio in CH_2Cl_2) after heating at 60° for 15 min. Peak assignments: 1, BF_3Cl^-; 2, BF_3Br^-; 3, $BF_2Cl_2^-$; 4, BF_2ClBr^-; 5, $BFCl_3^-$; 6, $BFCl_2Br^-$.

BF_4^-–BI_4^-.—Very rapid exchange occurred in methylene chloride solutions containing 1:1:1 and 1:2:1 proportions of BI_3–$(n\text{-}C_4H_9)_4N^+I^-$–$(n\text{-}C_4H_9)_4N^+BF_4^-$ so that even at −90° an averaged ^{19}F signal at 133 ppm was obtained. Warming of these samples at 0° for 30 sec resulted in the rapid evolution of BF_3 and after warming the −90° spectra contained an additional broadened peak (about 5% of the total fluorine intensity) at 66.4 ppm while the high-field peak shifted to 123.2 ppm. Liquid HI solutions of 1:1:1 BI_3–$(n\text{-}C_4H_9)_4N^+I^-$–$(n\text{-}C_4H_9)_4N^+BF_4^-$ at −40° gave a large broadened peak at 119 ppm and a small broadened peak at 44.6 ppm; unfortunately solvent effects do not permit a direct comparison of results obtained in HI with those obtained in CH_2Cl_2. The low-field peaks in these systems might be due to $BF_2I_2^-$ or BFI_3^- or to products of decomposition reactions.

BX_4^-–CH_2Y_2 and X^-–CH_2Y_2.—Solutions of CH_2Br_2 and CH_2I_2 in CH_2Cl_2 undergo halogen exchange with BX_4^- (X = Cl, Br, I). The utility of this reaction in preparing mixed tetrahaloborates was briefly explored. Table III[24] lists the ^1H nmr evidence for exchange in these systems. Even after standing for 2 months at room temperature and further heating at 90° for several more hours, BBr_4^- did not exchange halogen with CH_2Cl_2. However, exchange took place readily upon warming to 90° for 15 min in the presence of BF_4^- or BCl_4^-. These solvent-exchange experiments sometimes gave rise to crystalline materials, which were not further investigated.

TABLE III

^1H NMR EVIDENCE FOR HALOGEN EXCHANGE IN BX_4^-–CH_2Y_2 SYSTEMS[a]

X	CH_2Y_2[b]	^1H chem shift of the new signal, δ	Assignment[c]
F	Cl	. . .	. . .
F	Br	. . .	. . .
F	I	. . .	. . .
Cl	Br	5.17	CH_2ClBr
Cl	I	4.99	CH_2ClI
Br	Cl	. . .	. . .
Br	I	4.50	CH_2BrI
F–Br	Cl	5.15	CH_2ClBr
Cl–Br	Cl	5.18	CH_2ClBr

[a] Exchange was effected by heating at 90° for 15 min; systems which did not exchange after 15 minutes did not exchange when heated an additional 2 hr at 90°. [b] Solutions 10% v/v in CH_2Cl_2. [c] Reference 24.

Solutions of the corresponding tetra-*n*-alkylammonium halides in neat dihalomethane solvents also underwent exchange (Table IV).

TABLE IV

^1H NMR EVIDENCE FOR HALOGEN EXCHANGE IN X^-–CH_2Y_2 SYSTEMS[a]

X	CH_2Y_2	^1H chem shift(s) of the new signals(s)	Assignment(s)[b]
Cl	Br	5.16, 5.33	CH_2ClBr, CH_2Cl_2
Cl	I	4.97, 5.33	CH_2ClI, CH_2Cl_2
Br	I	4.48	CH_2BrI
I	Br	4.49	CH_2BrI
Br	Cl	5.18	CH_2ClBr[c]
I	Cl	5.00	CH_2ClI[c]

[a] Solutions were heated for 1 hr at 80°. [b] Reference 24. [c] Only very small amounts were formed.

BF_4^-–$(CH_3)_3SiY$.—Mixed fluorohaloborates can be prepared by halogen exchange between BF_4^- and a trimethylhalosilane at room temperature. Thus, in the case of $(CH_3)_3SiCl$–BF_4^- in CH_2Cl_2, the ^1H spectrum gave a sharp doublet attributed to $(CH_3)_3SiF$ at δ 0.21, $J_{^1H-^{19}F}$ = 7.4 Hz,[25] and a singlet corresponding to unreacted $(CH_3)_3SiCl$ at δ 0.42. The ^{19}F spectrum showed three signals—a decet (eight peaks resolved) corresponding to $(CH_3)_3SiF$ at 159.0 ppm,[26] $J_{^1H-^{19}F}$ = 7.4 Hz; a BF_3Cl^- quartet at 125.0 ppm, $J_{^{11}B-^{19}F}$ = 25.0 Hz; and a peak due to unreacted BF_4^-.

Tetrafluoroborate was found to undergo rapid halogen exchange with $(CH_3)_3SiI$. The room-temperature ^1H spectrum contained an exchange-averaged

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[24] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High-Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Oxford, 1966, Appendix B.

[25] H. Schmidbaur, *J. Amer. Chem. Soc.*, **85**, 2336 (1963).

[26] R. B. Johannesen, F. E. Brinckman, and T. D. Coyle, *J. Phys. Chem.*, **72**, 660 (1968).

signal just to low field of TMS. At −40° exchange was slowed sufficiently to observe a sharp $(CH_3)_3SiF$ doublet and a singlet at δ 0.80 corresponding to unreacted $(CH_3)_3SiI$. The room-temperature and −40° ^{19}F spectra contained a $(CH_3)_3SiF$ signal with the expected fine structure and a peak at 146.0 ppm. The latter peak is somewhat to low field of the BF_4^- peak position; this indicates rapid fluorine exchange among BF_4^- and the $BF_nI_{4-n}^-$ species which are present in relatively small amounts. Cooling to −90° failed to slow the exchange process sufficiently to observe peaks that might be attributed to the individual fluoroiodoborates.

BF_3–X^-.—In agreement with previous work,[27] both tensimetric and conductometric data indicate that direct addition of BF_3 to CH_2Cl_2 solutions of $Et_4N^+Cl^-$ results in the uptake of 1 mol of BF_3. The −80° ^{19}F spectra of solutions having 1:1 proportions of BF_3–$(C_2H_5)_4N^+Cl^-$ and of BF_3–$(n\text{-}C_4H_9)_4N^+Br^-$ gave peaks corresponding to the BF_4^-, BF_3X^-, and $BF_2X_2^-$ species. In both systems the BF_4^- peak corresponded to about 30% of the total fluorine intensity. The relative peak areas of the trifluoro and difluoro compounds were $BF_3X^-:BF_2X_2^- = 3:1$. Direct addition of BF_3 to $(n\text{-}C_4H_9)_4N^+I^-$ solutions gave a broad, exchange-averaged ^{19}F peak at 131 ppm similar to one observed previously in BI_3–I^-–BF_4^- systems. A small broadened peak at 66.9 ppm was observed at −90° as well.

Discussion

Formation of the Mixed-Halogen Anions.—Mixed tetrahaloborate anions have been prepared in solution by (i) halogen redistribution between BX_4^- and BY_4^-, (ii) reaction of a boron trihalide BX_3 with a halide ion Y^-, (iii) halogen exchange with methylene halide solvents, and (iv) halogenation of BF_4^- with trimethylsilyl halides. None of these methods leads to a single mixed tetrahaloborate anion under our conditions. The initial reaction to form BX_3Y^- is followed by disproportionation. Many of the possible mixed tetrahaloborate ions have been identified by ^{19}F and/or ^{11}B nmr (Tables I and II).

Rates of halogen exchange in BF_4^-–BX_4^- solutions increase by several orders of magnitude as X is changed from Cl to Br to I. Thus warming of the solution is required to carry out halogen exchange in BF_4^-–BCl_4^-, while the exchange is rapid enough in BF_4^-–BBr_4^- that temperature-dependent ^{19}F spectra are observed, and the exchange is so rapid in BF_4^-–BI_4^- that it is not possible even at −90° to observe separate ^{19}F signals from the individual mixed adducts $BF_nI_{4-n}^-$. In the fluorine-containing systems ^{19}F nmr gives the best evidence for the formation of mixed tetrahaloborate anions. When chemical exchange is slow on the nmr time scale, each fluorine-containing species $BF_nX_{4-n}^-$ gives rise to the 1:1:1:1 quartet which is characteristic of coupling to boron-11 ($I = {}^3/_2$). Thus in the BF_4^-–BCl_4^- system the three new quartets which appear (Figure 1) are assigned to BF_3Cl^-, $BF_2Cl_2^-$, and $BFCl_3^-$. Because the chemical shifts are large compared to the coupling constants, the quartets are readily identified. Lowering of the temperature causes the peaks of the quartets to broaden and eventually collapse, due to quadrupole relaxation of boron.[23] Broadening due to quadrupole relaxation is easily distinguished from broadening due to chemical exchange because the broadening becomes more pronounced as the temperature is *decreased;* also the coalescence pattern is somewhat different from that which results from chemical exchange.[23] ^{19}F resonances in the BF_4^-–BBr_4^- and BF_4^-–BCl_4^-–BBr_4^- systems are affected by rapid chemical exchange at higher temperatures and rapid quadrupole relaxation of boron at lower temperatures, so that the quartets are never as well resolved as in the BF_4^-–BCl_4^- system.

^{11}B chemical shifts are smaller than ^{19}F chemical shifts in these systems, so that the multiplets arising from boron–fluorine coupling overlap (Figure 2). However, multiplets arising from all of the $BF_nCl_{4-n}^-$ species could be identified. In systems which do not contain fluorine, the initial room-temperature ^{11}B spectra show separate broadened singlets arising from the mixed- and unmixed-halogen species which have rapidly reached their equilibrium concentrations (Figure 3). In these systems the distribution of halogens is near-random.

Except for the $BF_nI_{4-n}^-$ system where exchange is especially rapid, all of the members of all of the possible binary-halogen systems $BX_nY_{4-n}^-$ have been detected. The complexity of the spectra when more than two halogens are present makes the identification of signals arising from the ternary-halogen anions more difficult and only a few of these have been detected. The two most firmly established species, BF_2ClBr^- and $BFCl_2Br^-$, have been detected by ^{19}F nmr. Weak ^{11}B signals which probably arise from ternary Cl–Br–I species have been detected, but the signals were so weak due to solubility limitations in the BCl_4^-–BBr_4^-–BI_4^- system that assignments were not attempted. Our data are consistent with halogen scrambling among all of the possible tetrahaloborate ions.

Only in the BF_4^-–BCl_4^- system, where the formation of the mixed tetrahaloborate anions is the slowest, were we able to observe the approach to an equilibrium distribution of the $BX_nY_{4-n}^-$ species. The first mixed species to appear is BF_3Cl^-, followed by $BF_2Cl_2^-$ and finally by $BFCl_3^-$ (Figure 1). A simple halogen exchange between BF_4^- and BCl_4^- would be expected to give equal amounts of BF_3Cl^- and $BFCl_3^-$ initially, followed by $BF_2Cl_2^-$. In the absence of more detailed studies we can only suggest that the $BFCl_3^-$ which should be formed initially may be especially subject to rapid disproportionation, and its concentration does not build up until large amounts of the other species have formed.

We find that halogen exchange in the BF_4^-–BCl_4^- system is *slower* than in the corresponding boron trihalides, not faster as was reported by Kemmitt, Milner, and Sharp.[7] Thus instead of observing only single averaged ^{19}F and ^{11}B nmr signals, we find that heating of the solutions is required to form the mixed-halogen species and that these species give rise to separate, well-defined nmr signals. It is not clear why such a rapid halogen exchange should have been observed in the BF_4^-–BCl_4^- system in Kemmitt, Milner, and Sharp's nmr study. They used the triphenylmethyl cation whereas we used tetraalkylammonium cations, and Brownstein[28] has postulated that these two types

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(27) I. Wharf and D. F. Shriver, *J. Inorg. Nucl. Chem.*, **32**, 1831 (1970).

(28) S. Brownstein, *Can. J. Chem.*, **45**, 2403 (1967).

of cation can have markedly different effects upon halogen disproportionation in species such as BF_3Cl^-. This seems plausible since the triphenylmethyl cation is a weak Lewis acid and might complex with halide ion to some extent, leaving an excess of boron trihalide in solution to catalyze exchange. However, we find that neither free boron trihalide, halide ion, nor water has such an effect on the exchange rate. The presence of a large amount of an impurity in their solutions seems likely, especially since their reported ^{11}B chemical shift of 6.6 ppm between BF_4^- and BCl_4^- does not agree with a literature value (8.13–8.29 ppm, depending on concentration[13]) or with our value (8.3 ppm).

Waddington and coworkers have reported the synthesis and isolation of salts of certain of the mixed tetrahaloborate ions BX_3Y^- by the reaction of a boron trihalide BX_3 with a halide ion Y^- in the hydrogen halide solvent HY.[5,6] The best characterized of Waddington's mixed species, BF_3Cl^-,[6] is in the chloride–fluoride system in which halogen redistribution is shown in the present work to be especially slow. However, the reported[6] chloride analysis is low, suggesting that some halogen redistribution may have occurred and that the material which was isolated may have been contaminated with BF_4^-. Our work indicates that the mixed chlorofluoroborates are sufficiently stable to disproportionation that their separation and purification should be possible but that temperatures well below room temperature may be necessary. Wharf and Shriver[27] have presented tensimetric and infrared evidence for the formation of BF_3Cl^- by low-temperature additions of BF_3 to methylene chloride solutions of $SnCl_3^-$, $GeCl_3^-$, and Cl^-. In the BF_3^-–Cl^- system they inferred the existence of a considerable amount of BF_4^-. Brownstein[28] has postulated the disproportionation of initially formed BF_3Cl^- in methylene chloride to give BF_4^- and BCl_4^-. Our tensimetric and conductometric studies confirm the reported 1:1 association of BF_3 and Cl^- to give BF_3Cl^-.[5,27,28] However, ^{19}F spectra show that the initially formed BF_3Cl^- ion readily undergoes disproportionation to give BF_4^- and $BF_2Cl_2^-$. Other BX_3Y^- species have been reported to form in the same fashion,[5] and our ^{19}F nmr results are consistent with the formation of BF_3Br^- and BF_3I^- from BF_3 and Br^- or I^-, followed by disproportionation which is especially rapid in the BF_3I^- case. ^{19}F nmr is a particularly sensitive technique for distinguishing between ions of the $BF_nCl_{4-n}^-$ and $BF_nBr_{4-n}^-$ series.

The methylene halides CH_2X_2 (X = Cl, Br, I) tend to undergo halogen exchange with halogens other than fluorine when these are present either in tetrahaloborate anions or as halide ions (Tables III and IV). Although none of these methylene halides will exchange their halogen for fluorine when BF_4^- is present, the presence of BF_4^- can accelerate the exchange of the heavier halogens between solvent and tetrahaloborate (Table III). This has complicated some of our studies, in particular those of the BF_4^-–BBr_4^- system in methylene chloride, by introducing a third halogen. In contrast, the BBr_4^-–BI_4^- system which was also studied in methylene chloride did not appear to undergo solvent exchange on standing at room temperature. Solvent exchange can be a useful method for obtaining ternary-halogen anions such as BF_2ClBr^-.

The chlorinating agent trimethylsilyl chloride has been used to obtain various tungsten(VI) chloride fluorides by stepwise chlorination of WF_6[29] and has a similar effect on BF_4^-, giving BF_3Cl^- initially. Subsequent halogen redistribution reactions give the other $BF_nCl_{4-n}^-$ species. Trimethylsilyl iodide is an effective iodinating agent and exchanges iodine for fluorine of BF_4^-. In keeping with very rapid exchange in fluoride–iodide systems, a temperature-dependent coalescence of $(CH_3)_3SiF$ and $(CH_3)_3SiI$ peaks is observed in the proton spectrum. Rapid halogen exchange among the $BF_nI_{4-n}^-$ ions is indicated in the ^{19}F spectrum, but the exchange with $(CH_3)_3SiF$ is much slower since a separate ^{19}F resonance is observed for $(CH_3)_3SiF$.

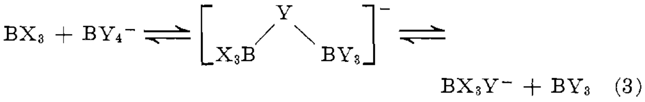
Proposed Exchange Mechanisms.—In an excellent review of redistribution reactions, Lockhart has discussed probable mechanisms of substituent redistribution in three-coordinate and four-coordinate boron compounds.[3] In three-coordinate compounds, redistribution of substituents which are good donor groups should be possible *via* a doubly bridged, four-coordinate transition state B_2X_6. Since an initial breaking of bonds is not required, such an exchange mechanism should have a low activation energy. Thus in systems such as the free boron trihalides[2,3,5] and diboron tetrahalides[4] halogen exchange is rapid enough to prevent the isolation of the mixed-halogen species but is slow on the nmr time scale so that separate resonances can be observed for the mixed and unmixed species. In tetrahedral boron compounds such as BX_4^- a preliminary dissociation of one of the ligands is probably required as a first step in the exchange

$$BX_4^- \rightleftharpoons BX_3 + X^- \qquad (1)$$

Exchange of substituents could then occur by more than one possible mechanism, as discussed by Lockhart for the BX_4^- ions.[3] The most plausible mechanisms would appear to be (i) the recombination of BX_3 with a different halide ion Y^-

$$BX_3 + Y^- \rightleftharpoons BX_3Y^- \qquad (2)$$

and (ii) exchange *via* a singly halogen-bridged intermediate analogous to the known species $B_2F_7^-$ [30,31] and $Al_2X_7^-$ (X = Cl, Br, I)[32]



$$BX_3 + BY_4^- \rightleftharpoons \left[X_3B{-}Y{-}BY_3 \right]^- \rightleftharpoons BX_3Y^- + BY_3 \qquad (3)$$

An additional mechanism suggested by Lockhart, nucleophilic attack of X^- on BY_4^-, seems less likely because of the double negative charge in the transition state but would likely be important in exchange reactions of neutral donor–acceptor adducts of the boron trihalides.

The requirement for an initial dissociation step in halogen redistribution reactions of tetrahedral boron compounds implies that the rates of redistribution should be highly dependent on the ease of dissociation

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[29] G. W. Fraser, C. J. W. Gibbs, and R. D. Peacock, *J. Chem. Soc. A*, 1708 (1970).

[30] S. Brownstein and J. Paasivirta, *Can. J. Chem.*, **43**, 1645 (1965).

[31] J. J. Harris, *Inorg. Chem.*, **5**, 1627 (1966).

[32] G. M. Begun, C. R. Boston, G. Torsi, and G. Mamontov, *ibid.*, **10**, 886 (1971).

of at least one of the boron substituents. This should be true regardless of which of the possible exchange mechanisms is dominant in the later stages of the redistribution reaction. This expectation is confirmed in our studies of the formation of donor–acceptor adducts of the mixed boron trihalides by halogen exchange[10,11,33]

$$D\cdot BX_3 + D\cdot BY_3 \rightleftharpoons D\cdot BX_2Y + D\cdot BXY_2 \qquad (4)$$

In the absence of excess Lewis acid the ability to exchange halogen between $D\cdot BX_3$ and $D\cdot BY_3$ appears to have an inverse relationship with the strength of the donor–acceptor bond. Thus trimethylamine adducts, which have an exceptionally strong donor–acceptor bond, do not exchange halogen at all under these conditions,[11] whereas the much weaker dimethyl ether adducts rapidly undergo reaction 4.[10] Dissociation to give a trigonal-boron species appears to be the essential first step. In the presence of excess boron trihalide *both* of the Me_3N and Me_2O adduct systems undergo a very rapid halogen redistribution reaction.[10,11] Thus when a trigonal-boron species is present already in large amount a reaction such as (3) can occur much more readily, since there is no need for an initial bond-breaking step.

The reported[13] concentration dependence of the ^{11}B chemical shifts of BCl_4^-, BBr_4^-, and BI_4^- suggests that these ions are partially dissociated in methylene chloride solution according to eq 1 and that the extent of dissociation varies in the order $BI_4^- > BBr_4^- > BCl_4^-$. Our observation of halogen exchange in X^-–CH_2Y_2 and BX_4^-–CH_2Y_2 systems (Tables III and IV) supports the postulate of tetrahaloborate dissociation. BF_4^- has been reported to undergo insufficient dissociation to have any effect on its ^{11}B spectrum,[13] and we find that no fluorine is transferred to the solvent. Dihalomethanes should undergo nucleophilic attack by halide ion, the expected order of nucleophilicity being $I^- < Br^- < Cl^-$ and the expected order of leaving ease being $I^- > Br^- > Cl^-$. Dissociation of X^- from BX_4^-, followed by attack of X^- on CH_2Y_2, is the most plausible mechanism for BX_4^-–CH_2Y_2 halogen exchange. Thus since bromide ion displaces chloride in CH_2Cl_2 only with difficulty (Table IV), BBr_4^- is not expected to exchange halogen with methylene chloride to a significant extent (Table III). In systems which do not contain fluorine the rates of halogen exchange are moderate, *i.e.*, too fast to allow isolation of the individual mixed-halogen species but slow on the nmr time scale at room temperature. These ions are analogous in their BX_4^-–BY_4^- and BX_4^-–CH_2Y_2 exchange reactions to the corresponding tetrahaloaluminate systems.[34,35] The predominant mode of halogen exchange, beyond eq 1, is not known in these systems; variable-temperature ^{11}B spectra might provide further information.

Systems containing BF_4^- are very different in their exchange behavior, the major unique features being (i) halogen redistribution can be either exceptionally slow (BF_4^-–BCl_4^-) or exceptionally fast (BF_4^-–BI_4^-), (ii) fluorine does not exchange with the halogen of the methylene halide solvents, and (iii) halogen exchange between *other* tetrahaloborates and the solvent occurs much more rapidly when BF_4^- is present. The last point indicates that the $BF_nX_{4-n}^-$ species are not intermediate between BF_4^- and BX_4^- in their halogen-exchange properties. ^{19}F studies on the BF_4^-–BBr_4^- and BF_4^-–BCl_4^-–BBr_4^- systems are especially informative.

Table V summarizes the relative lifetimes of fluorine on the various possible fluorine-containing tetrahaloborates in the BF_4^-–BCl_4^-–BBr_4^- system, as inferred from variable-temperature ^{19}F spectra (Figure 5). The trends can be explained if reaction 1 is necessary to initiate exchange. The central columns of Table V show the most probable dissociation products of each of the tetrahaloborate ions assuming that the ability of the halogens to function as the leaving group varies in the order Br > Cl ≫ F. The extent to which dissociation will occur will depend on the ease of formation of both of the products BX_3 and X^-. Stabilization due to π bonding is important in the boron trihalides and is more effective in boron–fluorine bonds than in other boron–halogen bonds.[36,37] The stability of the BX_3 fragment should therefore increase in the order $BX_3 < BX_2F < BXF_2 < BF_3$. In other words, the Lewis acid strength of the BX_3 species decreases as the number of fluorines increases; this is confirmed by the ^1H complexation shifts of dimethyl ether and trimethylamine adducts of these mixed boron trihalides.[10,11]

TABLE V

RELATIVE RATES OF FLUORINE REDISTRIBUTION AMONG TETRAHALOBORATE ANIONS IN THE BF_4^-–BCl_4^-–BBr_4^- SYSTEM, AS OBSERVED BY ^{19}F NMR

BX_4^-	Most probable dissociation products (eq 1)		Rate of fluorine redistribution
	BX_3	X^-	
BF_4^-	BF_3	F^-	Fast
BF_3Cl^-	BF_3	Cl^-	
BF_3Br^-	BF_3	Br^-	
$BF_2Cl_2^-$	BF_2Cl	Cl^-	Intermediate
BF_2ClBr^-	BF_2Cl	Br^-	
$BF_2Br_2^-$	BF_2Br	Br^-	
$BFCl_3^-$	$BFCl_2$	Cl^-	Slow
$BFCl_2Br^-$	$BFCl_2$	Br^-	
$BFBr_3^-$	$BFBr_2$	Br^-	

BF_4^- should not dissociate readily in spite of the π stabilization of BF_3 because F^- is a poor leaving group, and when fluorine is the only halogen present, the fluorine redistribution reaction has been shown to be slow.[8] In contrast, the dissociation of BF_3X^- species should be especially favored because both products of dissociation are favored; X^- is a good leaving group while BF_3 has the maximum π stabilization. The $BF_2X_2^-$ and BFX_3^- species have good leaving groups, but the BF_2X and BFX_2 fragments are successively stronger Lewis acids and hence the dissociation becomes successively less favorable than in the BF_3X^- species.

Whereas BF_4^- undergoes a *slow* fluorine redistribution when no other tetrahaloborate anions are present,[8] it is involved in a very fast reaction in the BF_4^-–BBr_4^- and BF_4^-–BCl_4^-–BBr_4^- systems, in which fluorine is

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[33] Unpublished results from this laboratory.

[34] R. H. Bradley, P. N. Brier, and D. E. H. Jones, *J. Chem. Soc. A*, 1397 (1971).

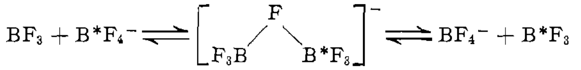
[35] R. G. Kidd and D. R. Truax, *J. Amer. Chem. Soc.*, **90**, 6867 (1968).

[36] P. J. Bassett and D. R. Lloyd, *J. Chem. Soc. A*, 1551 (1971).

[37] D. R. Armstrong and P. G. Perkins, *ibid.*, 1218 (1967).

apparently transferred between BF_4^- and BF_3X^- species. Thus in the BF_4^-–BBr_4^- system the BF_4^- and BF_3Br^- peaks are separated only at the lowest temperatures attainable (Figure 4), whereas $BF_2Br_2^-$ and in particular $BFBr_3^-$ undergo much slower exchange. The sequence of eq 5 can explain the results.

$$BF_3Br^- \rightleftharpoons BF_3 + Br^-$$



$$BF_3 + B^*F_4^- \rightleftharpoons \left[F_3B{-}\overset{}{F}{-}B^*F_3\right]^- \rightleftharpoons BF_4^- + B^*F_3 \qquad (5)$$

$$B^*F_3 + Br^- \rightleftharpoons B^*F_3Br^-$$

$B_2F_7^-$, which should have a symmetrical fluorine bridge, is the only known $B_2X_7^-$ ion and has moderate stability.[30,31] It allows fluorine exchange from BF_4^- without the necessity for dissociation of fluoride ion. $B_2X_7^-$ ions containing heavier halogens may form less readily, although the analogous $Al_2X_7^-$ species are known,[32] and if so, halogen exchange in $BF_2X_2^-$ and BFX_3^- ions would be slower. Reaction scheme 5 does not occur rapidly enough to cause collapse of ^{19}F peaks in the BF_4^-–BCl_4^- system. However, in the BF_4^-–BCl_4^-–BBr_4^- system the BF_3Cl^- peak undergoes a chemical exchange collapse which must be attributed to the presence of bromine (Figure 5). Rapid exchange is occurring among BF_4^-, BF_3Cl^-, and BF_3Br^- environments. Dissociation of BF_3Cl^- to give BF_3 and Cl^- may be fast even in the BF_4^-–BCl_4^- system, but if recombination of the fragments occurs much more frequently than reaction sequence 5, the ^{19}F spectrum would not show chemical exchange collapse. The presence of BF_3Br^-, and hence a considerable concentration of Br^-, appears to lead to the frequent recombination of BF_3 with a different heavier halogen.

These halogen-exchange reactions are complex and our studies are not sufficiently detailed to deal with all of the possibilities. However, the emerging pattern is consistent with very different exchange behavior when fluorine is present in the system. Even the exchange of heavier halogens between tetrahaloborate ions and solvent is affected by the presence of fluorine. An especially favorable dissociation of BF_3X^-, to give higher concentrations of X^- than can be obtained from BX_4^- alone, can explain why the heavier halogen X exchanges especially rapidly with the solvent when fluorine is present.

Nmr Parameters.—Figure 6 compares trends in ^{19}F chemical shifts and ^{11}B–^{19}F coupling constants in the mixed tetrahaloborates with those in the mixed boron trihalides.[38] In both series, replacement of fluorine by heavier halogens causes a low-field shift of the remaining fluorines and an increase in the magnitude of the ^{11}B–^{19}F coupling constant. The trend in the chemical shifts, which is especially pronounced in the free boron trihalides, has been explained in terms of π bonding from fluorine to boron in these compounds.[5,38] Since the same trend exists but is less pronounced in the BX_4^- series, it would seem that π bonding is not completely destroyed but merely reduced when the planar BX_3 takes on an additional ligand to form the tetrahedral BX_4^-. It has frequently been assumed[5] that little or no π bonding can occur in species such as BF_4^-. However, it has been suggested on theoretical grounds by Armstrong and Perkins[37] and by Brown, Drago, and Bolles[39] that when a planar BX_3 takes on an additional ligand, the π bonding is merely reduced rather than destroyed. It has been proposed that the amount of π bonding destroyed depends on the donor;[39] in agreement with this, trends in ^{19}F chemical shifts and ^{11}B–^{19}F coupling constants which are similar to but not identical with the trends in the tetrahaloborates have been observed in mixed boron trihalide adducts of dimethyl ether[10] and other donors.[33] In the transition from three-coordinate to four-coordinate boron the loss of the mirror plane causes the distinction between σ and π orbitals to vanish, and it has been pointed out that strictly speaking we should use the term "multiple bonding" rather than "π bonding" to describe the additional boron–halogen bonding in the tetrahedral case.[37] However, the term "π bonding" will probably continue in general use.

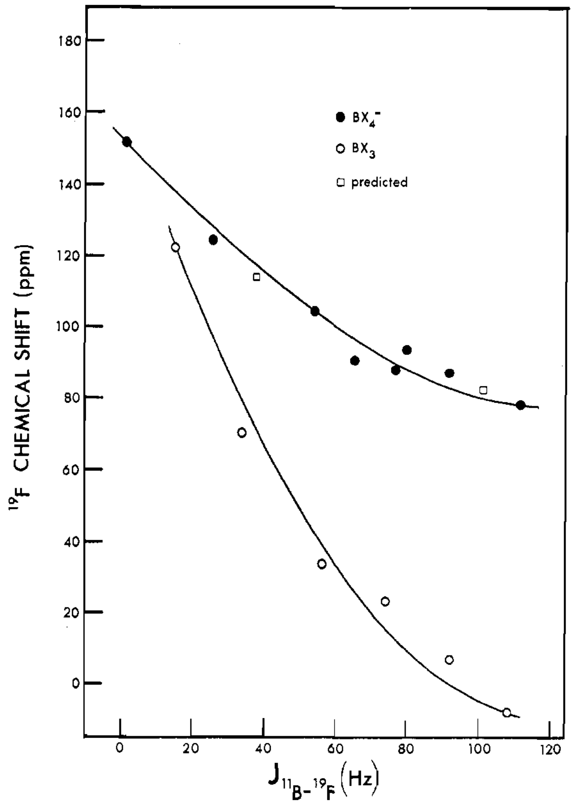


Figure 6.—Variation of ^{19}F chemical shifts and ^{11}B–^{19}F coupling constants of the boron trihalides[5] BX_3 and the tetrahaloborates BX_4^- (X = F, Cl, Br).

Müller and coworkers[40] have noted a linear relationship between the ^{19}F chemical shifts and the sums of the electronegativities of the substituents about boron in the mixed boron trihalides. A similar, almost linear relationship holds for the ^{19}F shifts of the mixed tetrahaloborates. When the substituent electronegativity sum is plotted against the ^{11}B chemical shift in the tetrahaloborate series and in the boron trihalide series, two widely differing trends are seen (Figure 7). In both series, fluorine-containing species are clearly

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[38] The coupling constant in BF_3 may be of opposite sign to that in the other boron trihalides, giving a straight-line relationship of chemical shift *vs.* coupling constant: S. A. Fieldhouse and I. R. Peat, *J. Phys. Chem.*, **73**, 275 (1969).

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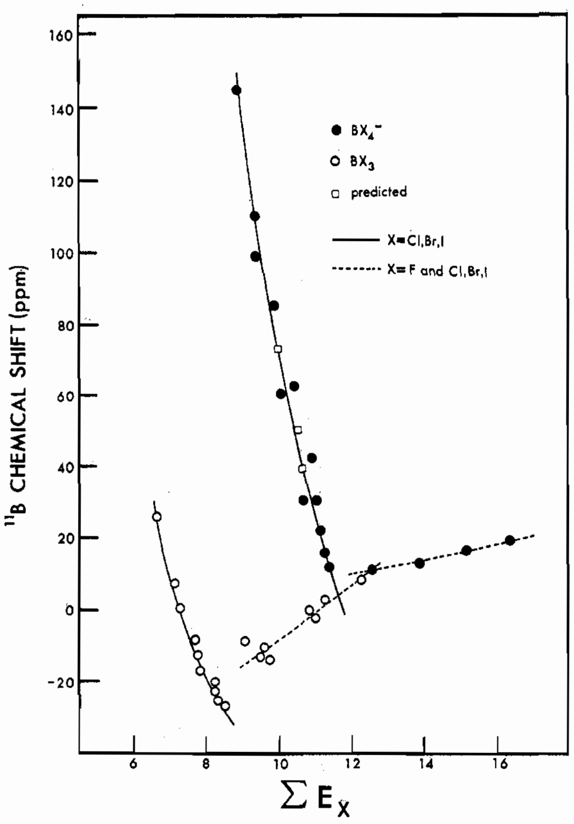

Figure 7.—Plot of ^{11}B chemical shifts of the boron trihalides[6] and the tetrahaloborates *vs.* the sums of the electronegativities of the halogen substituents (using the values of Allred and Rochow).

anomalous on the basis of electronegativity considerations alone. The anomalously high shielding in these species can be interpreted in terms of boron–fluorine π bonding. As with the ^{19}F data, the existence of the same trends in BX_4^- and BX_3 suggests similar bonding.

The tetrahaloborate ions are isoelectronic with the tetrahalomethanes in which the nature of the bonding has long been controversial. Similar trends in ^{19}F chemical shifts and in ^{13}C–^{19}F coupling constants have been observed in the tetrahalomethanes, and carbon–fluorine multiple bonding has been invoked to explain them.[41] Carbon–halogen multiple bonding in the halomethanes, probably arising from the filling of antibonding orbitals,[42] has been postulated to explain anomalies in a number of properties in addition to nmr parameters.[42,43] These concepts remain controversial. A recent interpretation of nqr and Mössbauer data on organohalostannanes, where multiple tin–halogen bonding is indicated, suggests that even in tin–halogen systems where back-bonding to the d orbitals of tin is possible, the sp^3 orbitals of tin are more important than the d orbitals in back-bonding.[44] Thus there appears to be considerable support for the possibility of multiple bonding to tetrahedral carbon, where d orbitals are not available, and hence to tetrahedral boron as well. The BX_4^- series is likely to be of value in the study of multiple bonding to four-coordinate first-period elements since direct comparisons can be made to the parallel series of BX_3 compounds in which π bonding is well established.

Calculation of Chemical Shifts from Pairwise Additivity Constants.—In nmr spectroscopy, nuclear spin–spin coupling constants and chemical shifts of various nuclei have been observed which are pairwise additive with respect to the substituent groups.[45] That is, the chemical shift (or spin–spin coupling) can be expressed as

$$\delta = \sum \eta_{i,j} \tag{6}$$

where $\eta_{i,j}$, is a parameter associated with substituents i and j and independent of all other substituents. The sum is taken over all substituents about a central atom, excluding the nucleus observed in the nmr experiment. In the case of $BF_2Cl_2^-$

$$\begin{aligned} \delta^{11}\text{B} &= \eta_{\text{F,F}} + 4\eta_{\text{F,Cl}} + \eta_{\text{Cl,Cl}} \\ \delta^{19}\text{F} &= 2\eta_{\text{F,Cl}} + \eta_{\text{Cl,Cl}} \end{aligned} \tag{7}$$

where $\eta_{i,j}$ is different for each nucleus observed.

Theoretical justification of the pairwise additivity rule for chemical shifts and nuclear spin–spin couplings can be found in the work of Vladimiroff and Malinowski.[45] Pairwise contributions arise because the wave function of each substituent group suffers a linear correction due to the presence of each neighboring substituent group. In general, chemical shifts are expected to be at least pairwise additive. If the substituent is far removed from the nucleus in question, then direct additivity is expected. Some insight into the type of coupling mechanism involved can also be deduced by considering substituent effects. The local nature of the Fermi contact term reduces a pairwise rule to a direct additivity rule. On the basis of the above generalizations and observed additivity behavior in a wide range of systems, Malinowski and Vladimiroff have been able to arrive at two sets of criteria for assessing the nature of the spin–spin coupling: (i) if the coupling is directly additive and the chemical shifts of both of the coupled nuclei are pairwise additive, the Fermi contact term is dominant for this coupling; (ii) if the chemical shifts of both of the coupled nuclei and their spin–spin coupling constant obey the same type of additivity rules, the Fermi contact term is not dominant.

The observation by Malinowski[46] of pairwise additivity in the ^{27}Al chemical shifts of the mixed tetrahaloaluminate ions has demonstrated the utility of this principle in confirming tentative chemical shift assignments. Pairwise parameters for ^{11}B chemical shifts of some of the non-fluorine-containing mixed boron trihalides have been presented by Vladimiroff and Malinowski.[45] The present study reveals that the chemical shifts and B–F coupling constants of BX_4^- systems can be correlated by pairwise additivity relations and provide useful confirmations of their assignments. The empirical parameters were calculated using a least-squares technique. Calculated values are compared to the observed values to give an estimate of the reliability of the correlation (Tables I and II). The parameters are also presented (Table VI) since they can be used to estimate the chemical shifts of yet unmeasured ions.

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Table VI

Pairwise Substituent Parameters for the ^{19}F and ^{11}B Nmr Parameters of BX_4^- Ions

	$\eta_{i,j}$				$\eta_{i,j}$		
Substituents i, j	Chem shift, ppm ^{19}F	Chem shift, ppm ^{11}B	^{11}B–^{19}F coupling constant, Hz	Substituents i, j	Chem shift, ppm ^{19}F	Chem shift, ppm ^{11}B	^{11}B–^{19}F coupling constant, Hz
F, F	50.5	3.34	−0.5	Br, Br	26.1	7.07	37.1
F, Cl	36.7	2.11	13.6	Cl, I	...	8.60	...
F, Br	31.4	...	19.4	Br, I	...	14.0	...
Cl, Cl	31.2	1.91	26.6	I, I	...	24.3	...
Cl, Br	28.2	3.25	32.2				

On the basis of the criteria set forth by Malinowski and Vladimiroff, the B–F coupling constants in the fluorinated tetrahaloborates do not arise from a dominant Fermi contact term, and the remaining orbital and spin–dipolar contributions must be considered. Similarly, the contact term is probably not dominant in ^{13}C–^{19}F couplings, since ^{19}F chemical shifts[45] and ^{13}C–^{19}F coupling constants[47] are both pairwise additive. Recently a self-consistent field perturbation theory has been applied to calculate the orbital and spin–dipolar terms as well as the contact term of ^{13}C–^{19}F coupling constants in the fluorinated methanes.[48] The results confirm that the Fermi contact term is incapable by itself of reproducing the experimental trends of ^{13}C–^{19}F values in a wide range of molecules. It is only when the other two usually neglected terms are included that the experimental trends are obtained.

Both the expression for the orbital contribution and the spin–dipolar contribution consider only the 2p functions.[49,50] The resulting p_σ–p_σ and p_π–p_π bond order terms in the expressions determine the degree of mixing of the ground and excited states. Furthermore, the orbital contribution is nonzero only if there is multiple bonding between the coupled atoms. If the observed trends in ^{11}B–^{19}F (and ^{13}C–^{19}F) coupling constants truly reflect boron–fluorine (and carbon–fluorine) p_π–p_π bonding, the relative p_π–p_π contributions in the theoretical expressions should be dominant.

CNDO Calculation of Chemical Shifts.—The ^{19}F and ^{11}B chemical shifts for the $BF_nCl_{4-n}^-$ and BF_nCl_{3-n} series have been calculated by a CNDO treatment, using molecular orbital theory developed by Karplus and Pople for the calculation of ^{13}C chemical shifts.[51,52] A CNDO treatment is intermediate in complexity between full LCAO–SCF calculations and the simple Hückel approach. It is of particular value since it includes all valence electrons, rather than just π electrons, permitting a full treatment of σ and π electrons in planar molecules and application of the theory to nonplanar molecules where σ–π separation is not possible. In the CNDO calculations no simple hybridization scheme is assumed; boron and halogen atomic orbitals are distributed according to their energies and overlap properties, but always consistent with the symmetry of the molecule. Trends rather than exact chemical shifts should be compared as discrepancies between calculated and observed chemical shifts can be due to the nature of the calculation itself as well as to the inherent sensitivity of the method to the chosen geometry.

If differences in ^{11}B and ^{19}F chemical shifts are determined mainly by the paramagnetic term of the screening tensor, σ_p^{AA}, then by second-order perturbation theory, σ_p^{AA} can be expressed in terms of ground-state molecular orbitals. It is inversely proportional to a mean excitation energy ΔE, *i.e.*

$$(\sigma_p^{AA})_{av} = \frac{-e^2h^2}{2m^2c^2(\Delta E)}\langle r^{-3}\rangle_{2p}(Q_{AA})_{av} + \sum_{B(\neq A)}(Q_{AB})_{av} \tag{8}$$

where $\langle r^{-3}\rangle_{2p}$ is the mean inverse cube of the 2p-orbital radial function on the nucleus observed in the nmr experiment, $(Q_{AA})_{av}$ is a charge density term, and

$$\sum_{B(\neq A)}(Q_{AB})_{av}$$

is a π bond order term. The terms Q_{AB}, which can occur only if atom B possesses available p atomic orbitals, contain the p_π–p_π contributions to the chemical shift.

The term σ_p^{AA} is the sum of contributions from all the excited states of $p_x \rightarrow p_y$ type (for the lighter elements other than hydrogen), which are mixed with the ground state. The degree of mixing increases with a decrease in the excitation energy ΔE. This mixing is due to unquenching of the orbital angular momentum in the applied field. This circulation of charge around the nucleus deshields it by a reinforcement of the field at the nucleus. As in previous calculations on the boron trihalides,[53] the change in ΔE from species to species was taken into account by using the calculated singlet–singlet transition energies

$$\Delta E = \epsilon_j - \epsilon_i \tag{9}$$

where ϵ_i is the energy corresponding to the highest occupied molecular orbital and ϵ_j is the energy corresponding to the lowest unoccupied molecular orbital.

The parameters needed in eq 8 to calculate the local paramagnetic contribution σ_p^{AA} are listed in Table VII. Calculated values of σ_p^{AA} were scaled by a factor of 1/1.60 in the case of ^{19}F chemical shifts and 1/2.50 in the case of ^{11}B chemical shifts. Contributions other than the paramagnetic contribution were assumed to be constant in both series and were evaluated by taking the difference between the calculated (scaled) BF_3 chemical shift and the observed BF_3 chemical shift (^{19}F, 122.2 ppm from $CFCl_3$; ^{11}B, 6.7 ppm from external $(CH_3O)_3B$). This difference was then added to the scaled theoretical chemical shift values of the remaining BX_3 and BX_4^- species to give the plots in Figures 8 and 9.

The main features of the results given in Figures 8 and 9 arise from changes with excitation energy ΔE (Table VII), though the terms Q_{AB} and Q_{AA} also give negative contributions to the paramagnetic shift with decreasing numbers of fluorine substituents. The ability of this method to predict the correct trends in ^{11}B and ^{19}F chemical shifts suggests that assessment of boron–fluorine p_π–p_π bonding in these systems in terms of ^{11}B and ^{19}F chemical shifts may be better understood if the nature of the dominant term, ΔE, is known.

^{11}B chemical shifts of fluorine-containing systems are

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TABLE VII

CALCULATED PARAMETERS (IN AU) FOR THE PARAMAGNETIC CONTRIBUTIONS TO THE ^{19}F AND ^{11}B CHEMICAL SHIFTS

Molecule or ion	ΔE	Fluorine-19 $(Q_{AA})_{av}$	Fluorine-19 $\sum_{B(\neq A)} (Q_{AB})_{av}$	Fluorine-19 q_A	Boron-11 $(Q_{AA})_{av}$	Boron-11 $\sum_{B(\neq A)} (Q_{AB})_{av}$	Boron-11 q_A
BF_3	0.9016	0.6667	0.1958	0.2324	1.5752	0.5499	−0.6971
BF_2Cl	0.6415	0.7060	0.2112	0.1940	1.6157	0.5619	−0.5645
$BFCl_2$	0.5407	0.7480	0.2268	0.1544	1.6711	0.6246	−0.4171
BCl_3	0.5140	...	...	...	1.7412	0.6603	−0.2522
BF_4^-	0.9717	0.5233	0.1394	0.4015	1.6243	0.5544	−0.6059
BF_3Cl^-	0.6862	0.5680	0.1492	0.3609	1.6386	0.5607	−0.5560
$BF_2Cl_2^-$	0.5924	0.6080	0.1554	0.3241	1.6657	0.5657	−0.4795
$BFCl_3^-$	0.5687	0.6480	0.1618	0.2902	1.7059	0.5654	−0.3781
BCl_4^-	0.5564	...	...	...	1.7570	0.5492	−0.2539

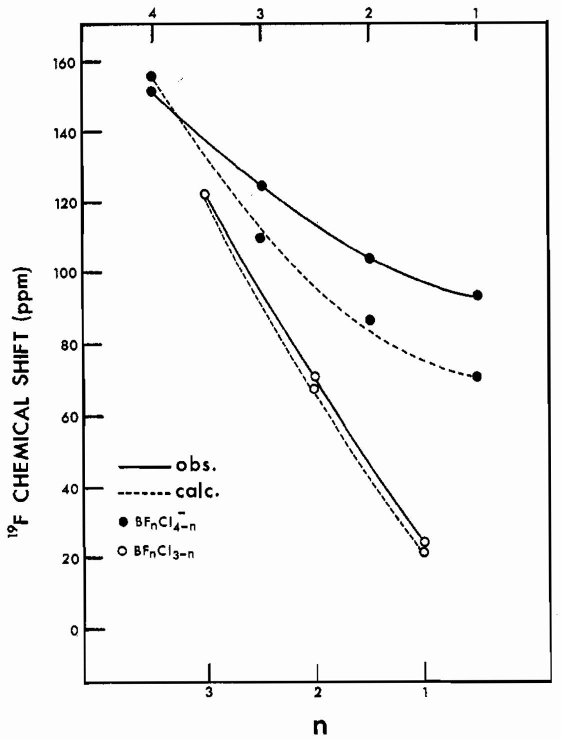

Figure 8.—Comparison of experimental and calculated (CNDO/2) ^{19}F chemical shifts of the boron trihalides BF_nCl_{3-n} and the tetrahaloborates $BF_nCl_{4-n}^-$.

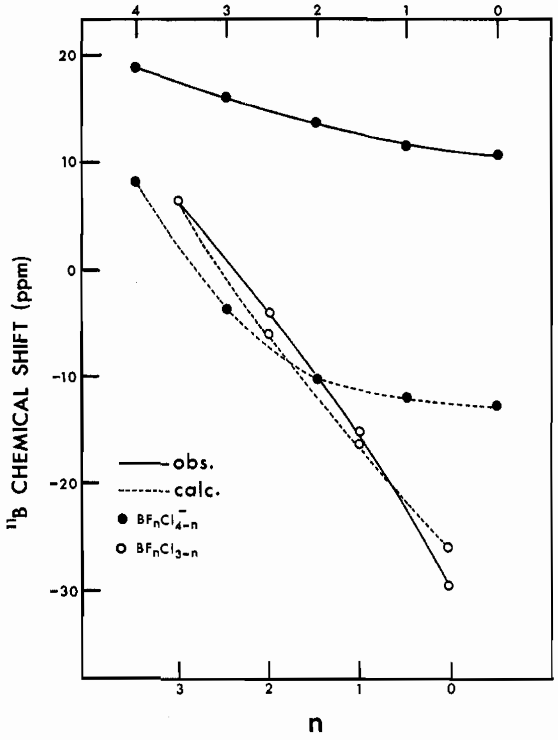

Figure 9.—Comparison of experimental and calculated (CNDO/2) ^{11}B chemical shifts of the boron trihalides BF_nCl_{3-n} and the tetrahaloborates $BF_nCl_{4-n}^-$.

clearly anomalous by electronegativity considerations alone, with the observed shifts occurring to much higher field than those expected on the basis of substituent electronegativities (Figure 7). This could be a result of ΔE being anomalously large in the fluorine cases; the nature of the excitation may be different when only fluorine is present. The highest occupied molecular orbital in both BF_3 and BCl_3 appears to be a σ orbital.[36] The large drop in ΔE upon going from BF_3 to BF_2Cl (or from BF_4^- to BF_3Cl^-) and subsequent smaller changes as more chlorines are substituted for fluorines suggest that ΔE is dominated by low-lying unoccupied d orbitals on chlorine when chlorine is present. A similar rationale might be extended to ^{19}F chemical shift trends in these systems. Analogous trends in adducts of the mixed boron trihalides[10] and in the isoelectronic tetrahalomethanes[41] might be explained in the same way.

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