given[12] as follows.

$$C_1 \cong 1 \tag{28}$$

$$C_\mu = \frac{K_{ab} + K_{vw} - K_{av} - K_{bw}}{2(K_{aw} + K_{bv})} \tag{29}$$

When w and v are both hydrogens, the negative H–H integral K_{vw} is of comparable magnitude with the positive Hund exchange integral, K_{ab}, and thus these two terms tend to cancel one another, thereby increasing the importance of the smaller K_{av} and K_{bw} integrals. Substitution of a halogen for a hydrogen might be expected to decrease the negative K_{vw} integral relative to the methylene case as the halogen σ-bond orbital has more directional characteristics than does the 1s hydrogen orbital. As the denominator in eq 29 is a negative quantity the effect of this change in K_{vw} with halogen substitution is to make C_μ more negative. This will result in an upfield shift as indicated by eq 27 as all other terms $[f_{1\mu}(p_{ab}) = +1, P^{ab} = +{}^1/_2]$ are positive quantities. If both v and w are halogens, even greater parallel spin correlation might be expected for the same reasons given above. The effect of altering electron spin pairing in this manner can be expected to result in an even greater upfield shift. Experimentally, this is the trend which is observed. The unavailability of values for the pertinent exchange integrals prevents, for the present, a quantitative calculation of the magnitude of this effect, but shifts of several parts per million were calculated in the alkanes[12] and the effects may be even greater in the halomethanes.

Acknowledgment. This work was supported by the Public Health Service under Grant GM O-8521 awarded by the National Institutes of Health. Discussions with Professor L. S. Bartell (University of Michigan) are acknowledged as they proved to be very helpful in formulating the section on steric effects.

Iodo- and Fluoropentaboranes. Nuclear Magnetic Resonance Comparison of 2-Pentaborane(9) Derivatives[1]

Anton B. Burg

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007. *Received August 17, 1967*

Abstract: Pentaborane(9) derivatives of the type 1-XB_5H_8 are more stable when X = heavier halogen, whereas 2-XB_5H_8 compounds are more stable when X = lighter halogen. The reason may be found in the different π-type interactions with the B_5 cage, and similar ideas explain some otherwise anomalous ^{11}B nmr chemical shifts. The catalytic isomerization of 1-IB_5H_8 to the far less stable new isomer 2-IB_5H_8 (mp −39°; bp 167° est) requires steady removal of this more volatile product. It is argued that halogen exchanges on the B_5 skeleton are done best by gas-flow processes at minimal pressure, as when $HgCl_2$ converts 1-IB_5H_8 to 1-ClB_5H_8 or SbF_3 converts 2-IB_5H_8 to the new 2-FB_5H_8 (mp −63°; bp 71° est). However, the analogous synthesis of 1-FB_5H_8 gave a product too unstable to be isolated. The ^{11}B nmr comparisons include all four of the 2-halogenated pentaboranes and 2-CH_3-B_5H_8, and accurate vapor-phase infrared spectra are reported for the five known XB_5H_8 compounds not previously so recorded.

Pentaborane derivatives of formula-type RB_5H_8 so far have been limited to R = hydrocarbon or halogen other than F. They usually are formed by substitution at the 1 (pyramid-peak) position, by methods suggestive of proton replacement by other positive ions (*e.g.*, CH_3^+ or X^+); then a catalytic skeletal rearrangement may lead to the 2-RB_5H_8 isomer. Replacement of one R by another apparently has been done only with halogens, often with yields far short of 100%.

The difficulty of such replacement may relate to the character of the pentaborane skeleton. The boron sites can be invaded only by strong bases, which tend to remove BH_3 groups[2] rather than displace hydride or halide. If X^+ were removed by some means, the remaining lone-pair electrons on boron would have strong-base character leading to extensive reaction with other pentaborane units. Or, if X^- were taken off, the opened boron site would have almost a hemisphere empty of electrons, with only strong Lewis-acid reactivity to relieve the strain; then an attack upon the XB_5H_8 substrate would be likely.

By the latter argument, replacement of halide in XB_5H_8 should be most effective if a strong halide-exchange reagent were employed at pressures so low as to make XB_5H_8 only very poorly available to the $B_5H_8^+$ unit remaining after removal of halide. Otherwise, the reaction of $B_5H_8^+$ with XB_5H_8 must lead to a variety of polyboranes and resinous products.

In agreement with this hypothesis, a 105° sealed-tube reaction of 1-IB_5H_8 with $HgCl_2$ gave only a 7% yield of 1-ClB_5H_8 (with other volatiles and resins), whereas the same reactants in a 100° flow process at minimal pressure gave a 58% yield of 1-ClB_5H_8.

A similar low-pressure flow process was applied to the new isomer 2-IB_5H_8 with SbF_3, giving a 40% yield of the

---

(1) It is a pleasure to acknowledge the generous support of this research by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the U. S. Government. I am deeply grateful also to my colleague Dr. K. L. Servis for instruction and assistance in the use of the Varian HA-100 instrument, and to Dr. R. E. Williams of Space-General Corp., for full access to his experience with boron nmr spectra and the loan of a 32.1-Mc radiofrequency unit and probe.

(2) A. B. Burg, *J. Am. Chem. Soc.*, **79**, 2129 (1957).

first fluoropolyborane, 2-FB_5H_8. However, when the same method was tried with 1-IB_5H_8, a product having volatility near 1 mm at 0° may have been 1-FB_5H_8, but it was too unstable to be isolated; its decomposition products included diborane, boron fluoride, and probably a mixture of B_5H_9 and 2-FB_5H_8.

Extreme instability would be expected for 1-FB_5H_8 because the withdrawal of σ-bonding electrons from the 1-B atom would not be well compensated: adjustment of boron toward a planar form would be difficult, and the concentration of skeletal bonding electrons toward the 1-B position[3] would work against π-donor bonding from fluorine. On the other hand, the pyramid-base atoms (2, 3, 4, and 5 positions), with electron-deficient bonding in three directions from the B–F σ-bond axis, would welcome a π-bonding effect from the F atom. This argument (in principle similar to one used to explain the complete isomerization of 1-$CH_3B_5H_8$ to 2-$CH_3B_5H_8$)[4] would apply less effectively to larger halogen substituents, for which both σ-electron attraction and π-donor effect would decrease with increasing size. In fact, it appears that 2-ClB_5H_8 is more stable than 1-ClB_5H_8; the two BrB_5H_8 isomers are about equally stable;[4] and equilibration of the IB_5H_8 isomers provides very little of the 2-IB_5H_8 form.

Syntheses and Characterizations

Iodopentaboranes. Quantities of pentaborane(9) as large as 60 mmoles were heated in sealed tubes with equimolar proportions of iodine, reacting almost completely in less than 24 hr at 80–90°. The yields of 1-IB_5H_8 were in the range 93–96%. In one experiment a few grains of metallic aluminum were previously heated with iodine in the bomb tube; then the iodination of B_5H_9 was virtually complete in 11 hr at 68° No trace of 2-IB_5H_8 could be found from this run, although 58 mmoles of B_5H_9 reacted. However, both processes were appreciably more expeditious than the long runs described before.[5] The yields of HI were in the range 85–93%, with decomposition to H_2 and I_2 not always fully accounting for the deficiency. If the original amount of iodine were deficient, as in attempts to utilize the decomposition of HI as a means of conserving iodine, the yields of 1-IB_5H_8 might run as low as 46%.

The product 1-IB_5H_8 melted above 56° and conformed to the vapor-tension equation $\log P = 11.079 - 3448/T$ below the melting point (examples, in millimeters: 0.27 at 22.6°, 0.44 at 28.5°, 0.65 at 32.9°, 1.15 at 39.9°, and 2.56 at 50.0°; calcd: 0.26, 0.44, 0.65, 1.16, and 2.56, respectively).

The isomerization of 1-IB_5H_8 to 2-IB_5H_8 was accomplished by catalysts such as hexamethylenetetramine or (less conveniently) 2,6-lutidine. Most expeditiously, one makes from a 25-mm wide Pyrex tube a vertical reflux system with an alembic form near the top. The blown bulb at the bottom is supplied with a small quantity of freshly sublimed $(CH_2)_6N_4$ and a generous amount of 1-IB_5H_8. Heating up to 90° under 20-mm pressure of dry nitrogen (with the system attached to the high-vacuum manifold) causes the relatively volatile liquid 2-IB_5H_8 to collect in the rim of the alembic, from which it can be distilled into the vacuum system for purification. As the process goes forward, the pressure rises with the formation of hydrogen and polyboranes, among which B_5H_9 was definitely identified. Base-inclusive resins also are formed, tending to consume the catalyst. *Warning:* At temperatures above 100°, the catalyst hexamethylenetetramine may develop a rapid reaction with the iodopentaboranes, causing an explosion.

The purification of the product 2-IB_5H_8 was done in a high-vacuum microcolumn with reflux at 0°. A middle fraction melted very sharply at −39.3° and gave a vapor-phase molecular weight value of 189.3 (calcd 189.0). Its vapor tensions are shown in Table I. It proved stable enough for practical study, but small impure samples showed major formation of resinous material on long standing at 25°. Like 1-IB_5H_8, it showed no reaction with mercury.

Table I. Volatility of Liquid 2-IB_5H_8
($\log P = 6.7038 + 1.75 \log T - 0.0052T - 2712/T$)
($t_{760} = 167.2°$; Trouton constant = 21.2 eu)

Temp, °C	30.55	36.23	41.80	48.77	62.17	71.31	77.90
P_{obsd}, mm	3.47	4.87	6.71	9.87	19.59	30.14	40.48
P_{calcd}, mm	3.46	4.87	6.72	9.86	19.58	30.16	40.49

The Chloride–Iodide Replacements. A 0.374-mmole sample of 1-IB_5H_8 was wholly consumed by heating with 365 mg of $HgCl_2$ in a sealed tube (70 min, 105°), producing (mmoles) 0.373 H_2, 0.491 HCl, 0.002 B_2H_6, 0.67 BCl_3, and 0.026 1-ClB_5H_8 (7% yield). In a more gentle process, 1.053 mmoles of 1-IB_5H_8, intermittently heated with 2.055 mmoles of $HgCl_2$, with frequent removal of the volatile products, was 51% consumed to give (in mmoles) 0.152 H_2, 1.312 HCl, 0.045 B_2H_6, 0.834 BCl_3, and 0.117 1-ClB_5H_8 (22% yield).

For the low-pressure flow process, $HgCl_2$ was spread out in a six-turn helix of 14-mm o.d. Pyrex tubing (neatly fitting into a 1-l. beaker), and 1.173 mmoles of 1-IB_5H_8 sublimed from a tube at 25° through the helix at 100°. An automatic Sprengel pump continuously removed hydrogen through a −196° trap. Two 3-hr passes consumed 1.124 mmoles (96%) of the 1-IB_5H_8, forming (mmoles) 0.103 H_2, 1.773 HCl, 0.307 B_2H_6, 0.415 BCl_3, and 0.647 1-ClB_5H_8 (57.5% of 1.124). For all such experiments, the 1-ClB_5H_8 was identified by its known volatility,[6] rough hydrolytic analyses, and mass spectra.[7]

Fluoropentaborane. The same glass helix was supplied with freshly sublimed and powdered SbF_3; then 1.682 mmoles of 2-IB_5H_8, evaporating at 0°, passed through the helix at 100° with a −196° trap and high vacuum beyond. The process was repeated five times with the recovered 2-IB_5H_8, each pass requiring about 1 hr. The consumption of 2-IB_5H_8 amounted to 1.553 mmoles, forming 1.08 BF_3, 0.18 B_5H_9, a trace of B_5H_{11} (infrared peak at 2495 cm^{-1}), and 0.325 of 2-FB_5H_8 (21% yield).

Larger runs employed 5.2 mmoles of 2-IB_5H_8 with the helix at 105° and each of eight passes requiring about 5 hr. The consumption of 2-IB_5H_8 now was 2.4

---

(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 110.

(4) A. B. Burg and J. S. Sandhu, *J. Am. Chem. Soc.*, **87**, 3787 (1965).

(5) L. H. Hall, V. V. Subbanna, and W. S. Koski, *ibid.*, **86**, 3969 (1964).

(6) D. F. Gaines, *ibid.*, **88**, 4528 (1966).

(7) Thanks are due to Dr. J. F. Ditter (of Space-General Corp.), who obtained all such mass spectra for me at the facility of West Coast Technical Services, San Gabriel, Calif.

mmoles and the yield of $2\text{-}FB_5H_8$ was 0.96 mmole, or 40%. The recovered $2\text{-}IB_5H_8$ was contaminated with an unstable impurity which precipitated a yellow solid on standing; this impurity was easily eliminated and was not involved in the estimate of the yield of $2\text{-}FB_5H_8$.

For purification, the $2\text{-}FB_5H_8$ was first allowed to stand at 25° to decompose the B_5H_{11} impurity; then a slow high-vacuum fractional condensation through a trap at −65° (with B_5H_9 passing a −78° trap) gave a product melting very sharply at −63.6°. Its vapor-phase molecular weight was 80.7 (calcd, 81.1). The normal character of its vapor-tension curve (Table II) confirms its purity.

Table II. Volatility of Liquid $2\text{-}FB_5H_8$
($\log P = 6.0979 + 1.75 \log T - 0.0055T - 1981/T$)
($t_{760} = 70.5°$; Trouton constant = 21.2 eu)

Temp, °C	−74.9	−59.8	−40.2	−33.97	−15.9	0.00	15.15
P_{obsd}, mm	0.10	0.53	2.85	4.61	15.9	40.3	88.3
P_{calcd}, mm	0.11	0.52	2.85	4.60	15.9	40.4	88.2

For analysis, a 0.0831-mmole sample of $2\text{-}FB_5H_8$ (measured in the gasometer where hydrogen would be collected later by the automatic Sprengel pump) was hydrolyzed in a sealed tube during 8 hr at 50°, yielding 0.9228 mmole of H_2 (11.1 mmoles of H_2 per $2\text{-}FB_5H_8$). Titration by standard base in the presence of mannitol gave 5.25 mmoles of H^+ per mmole, indicating that some B–F bonds were retained, contrary to the simple equation

$$FB_5H_8 + 15H_2O \longrightarrow 11H_2 + HF + 5B(OH)_3$$

Digestion with dilute calcium chloride brought the H^+ up to 5.6 per molecule.

The Chloropentaborane Approach. The preparation of useful quantities of $2\text{-}IB_5H_8$ is difficult enough to suggest the use of $2\text{-}ClB_5H_8$ instead, for syntheses such as that of $2\text{-}FB_5H_8$. It proved quite easy to make $2\text{-}ClB_5H_8$ by mixing nearly equal gaseous streams of B_5H_9 and Cl_2 at 3 mm pressure, with the mixture passing through a 2-l. bulb, followed by a −78° trap to remove B_5H_9 and ClB_5H_8 from the stream of unused Cl_2 (trapped beyond at −196°)—thus avoiding formation of a highly explosive liquid–solid Cl_2–B_5H_9 mixture. With 13% conversion, the yield of $2\text{-}ClB_5H_8$ was 72%; of $1\text{-}ClB_5H_8$, less than 10%. Nonvolatile products also appeared.

A minimal-pressure stream of $2\text{-}ClB_5H_8$, passing some 30 times over SbF_3 in the glass helix at 100–120°, with frequent removal of the volatile products, was 24% consumed, and only 15% of this 24% appeared as $2\text{-}FB_5H_8$. Better conditions might be found, but at present the chloropentaborane process seems less effective than the use of $2\text{-}IB_5H_8$. Pentaborane(9) itself failed to react either with SbF_3 during low-pressure flow at 167° or with $HgCl_2$ in a closed tube at 200°.

Nuclear Magnetic Resonance Spectra

The ^{11}B nmr spectra of the 2-substituted pentaboranes were recorded at 32.1 Mc by the Varian HA-100 instrument, which was used also for ^{19}F at 94.1 Mc and protons at 100 Mc. Table III compares the ^{11}B chemical shifts δ, measured upfield from trimethyl borate, and J in cycles per second. The italicized data from the very recent literature[8] were converted from the boron trifluoride etherate reference point by adding 18.2 ppm.

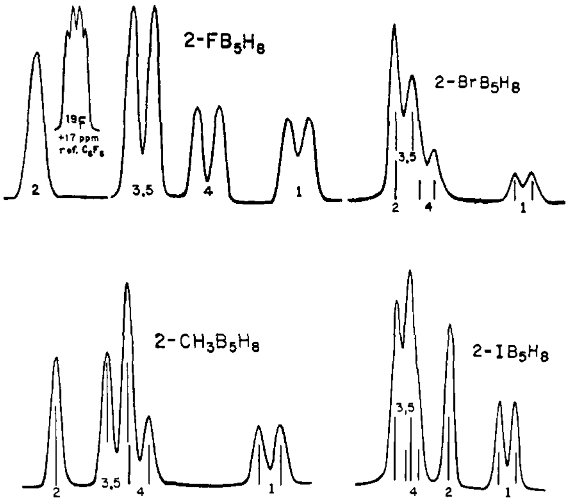

Figure 1. Boron nmr spectra of four $2\text{-}RB_5H_8$ compounds.

Table III. Comparison of ^{11}B Spectra of 2-Pentaboranes

	Skeletal position						
	1		2	3,5		4	
	δ	J	δ	δ	J	δ	J
B_5H_9	71.5	178		31.7	163		
	70.0	*178*		*30.7*	*161*		
$2\text{-}FB_5H_8$	74.7	175	10.1	36.4	160	52.4	167
$2\text{-}CH_3B_5H_8$	69.7	168	16.7	32.0	165	37.4	161
	68.6	*176*	*16.0*	*30.9*	*160*	*36.3*	*160*
$2\text{-}ClB_5H_8$	*69.2*	*179*	*17.7*	*30.7*	*177*	*40.2*	*178*
$2\text{-}BrB_5H_8$	70.6	180	29	32	170?	38	170?
	71.7	*180*	*29*	*33*	*170*	*38*	*170*
$2\text{-}IB_5H_8$	65.9	171	46.1	29.5	155	29.5?	?

Figure 1 shows most of these spectra, making it clear that differences from the literature can be ascribed to errors in judging the exact positions of the peaks. Especially the profile for $2\text{-}BrB_5H_8$ is difficult to analyze. In the present study the value $J = 170$ cps was assumed as a compromise between two methods for estimating the positions of the overlapping peaks and then used to correct the value of δ as measured from one peak of each doublet. The independent estimates in ref 8 show a remarkable agreement which still might be fortuitous.

In XB_5H_8 compounds the ^{11}B spectra usually do not reveal B–X coupling (for X other than H), for the boron quadrupoles destroy the resolution. We now find that this rule applies not only to X = Cl, Br, or I, but also to the magnetically simpler ^{19}F. However, the ^{19}F spectrum at 94.1 Mc (insert in Figure 1) does show a somewhat blurred quartet. The apparent coupling constant here is $J = 60$ cps.

An apparent anomaly in the ^{11}B spectra is the trend of chemical shifts for the 4-B atom. Measuring from basal boron in B_5H_9, we have the following δ values (ppm): −2 for $2\text{-}IB_5H_8$, +6 for $2\text{-}CH_3B_5H_8$, +7 for $2\text{-}BrB_5H_8$, +10 for $2\text{-}ClB_5H_8$, and +21 for $2\text{-}FB_5H_8$. The halogens here obviously show a trend just opposite

---

[8] T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1466 (1967); prior literature cited.

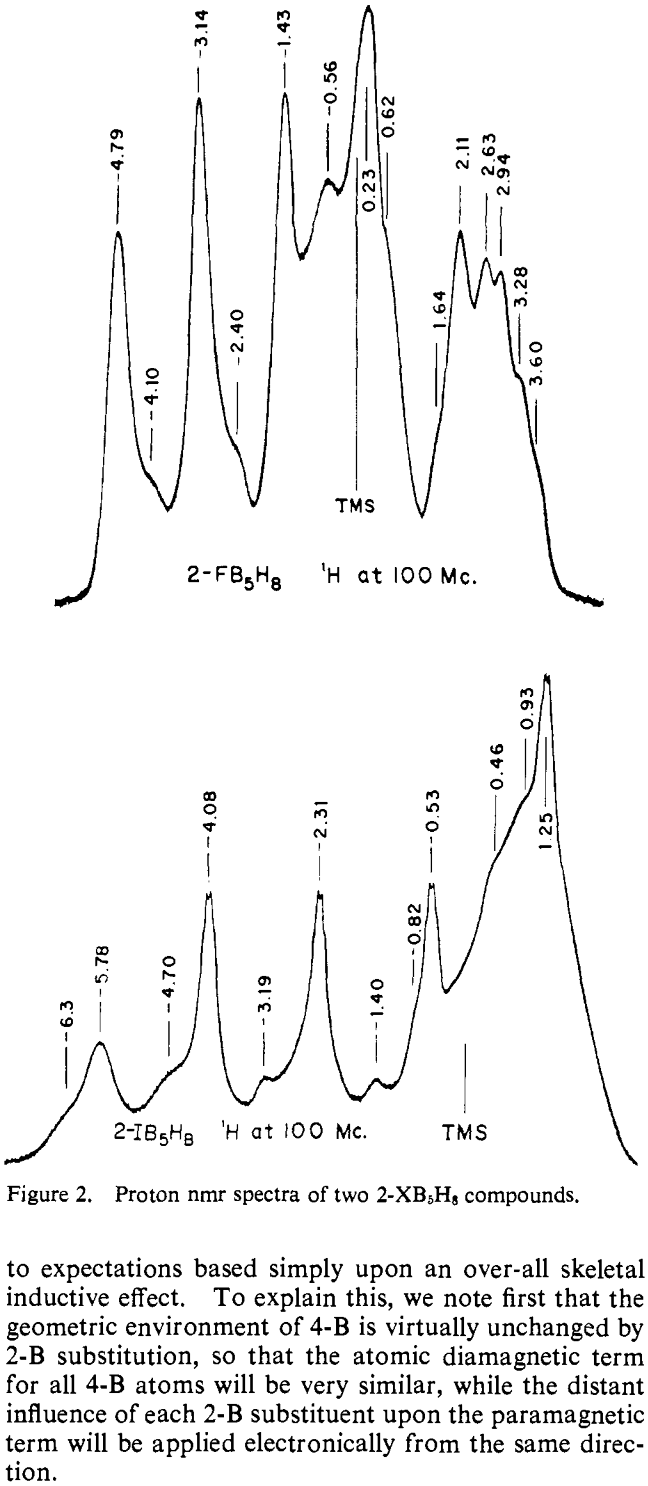

Figure 2. Proton nmr spectra of two 2-XB_5H_8 compounds.

to expectations based simply upon an over-all skeletal inductive effect. To explain this, we note first that the geometric environment of 4-B is virtually unchanged by 2-B substitution, so that the atomic diamagnetic term for all 4-B atoms will be very similar, while the distant influence of each 2-B substituent upon the paramagnetic term will be applied electronically from the same direction.

The nature of this influence can be discussed simply by reference to an early molecular-orbital description,[9] according to which a 2,1,4 three-center bond employs a bent 1-B atomic orbital having mostly 2p character. This highly electron-deficient situation should attract F_{2p} π electrons, releasing electron density toward the 4-B atom, where penetration *via* a nearly perfect sp^3 hybrid would account for a sharp increase of nuclear shielding. The 1-B atom would get little effect through its 2p orbital, and the 2-B atom also would be little affected by F_{2p} applied in the manner of the top half of a π bond. Indeed, the direct σ withdrawal of electrons from 2-B toward F accounts for a δ value of -22 ppm relative to basal boron in B_5H_9, *vs.* $+21$ ppm for 4-B. Both the π action pushing electrons toward 4-B and the σ withdrawal from 2-B should decrease regularly from F to Cl to Br to I, in agreement with the observed trend of chemical shifts.

The 3,1,5 three-center bond would be orthogonal to the 2,1,4 three-center bond, so that only a second pair of halogen π electrons would affect the 3,5-B atoms, indirectly across the B–H–B bridges. The net effect here seems to be a small upfield trend of δ for smaller halogens at the 2-B position.

The effect of methyl should be somewhat like that of a halogen, because it can apply its C–H electrons similarly in the well-known "hyperconjugative" manner, but it would have been difficult to predict an effect upon δ_4 comparable to that of bromine. A more striking effect is apparent from a listing of δ values for 2-B (again measured from B_5H_9): F, -22; CH_3, -15; Cl, -14; Br, -2; and I, $+15$. The halogens are in the expected order, but CH_3 seems to have more σ-electron withdrawing effect than Cl. One may argue that a movement of electrons from the C–H bonds toward the B_5 skeleton would widen the HCH bond angle. Then the far side of the carbon atom would develop an electron deficiency which must be at least partially compensated by drawing σ-electron density from the 2-B nuclear region. For the halogens, this specific effect would be less important because any π-type action by the second and third electron pairs would have little effect upon the nonbonding fourth pair, having largely s character in any case.

It is more difficult to explain why bromine has nearly the same effect upon the 2-B atom as hydrogen, while iodine actually gives it decidedly more nuclear shielding. The more deformable halogen might allow easier compensation of the electron deficiency at a basal position; and iodine might even accept a small assignment of skeletal electrons into its fairly effective 5d orbitals. However, the latter effect should be more important at the 1-B position, where iodine causes only a $+3$ δ shift relative to hydrogen.

The proton spectra of 2-IB_5H_8 and 2-FB_5H_8 are shown in Figure 2, with the indicated δ values (ppm measured from tetramethylsilane) related by a factor of 100 to a cps scale for coupling constants. The chief recognizable feature of each spectrum is a strong quartet with J values respectively 178 and 168 cps. Most plausibly, these quartets would be assigned to terminal protons in the 3 and 5 positions, with much superposition of weaker features such as 1-H and 4-H quartets, two BHB bridge septuplets, and even a broad, low-intensity background due to the ^{10}B isotope.

The main quartet for 2-IB_5H_8 has individual peaks in the form of blurred quartets with $J = 4.6 \pm 0.2$ cps. No such effect could be observed for 2-FB_5H_8, and the reason is not apparent.

Infrared Spectra

The vapor-phase infrared spectra of five XB_5H_8 compounds were recorded in the same manner as described earlier for the BrB_5H_8 and $CH_3B_5H_8$ isomers.[4] Spectrum complexity correlated with volatility, partly because higher pressures permitted detection of weaker

---

[9] W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, 22, 989 (1954). It is suggested that any more precise quantitative theory of B_5H_9 bonding would have the same qualitative import for the present purpose.

bands, but more because the wider ranges of rotational transitions in the lighter molecules would lead to more superposition of bands and more points of reinforcement; also, the lower symmetry of the more volatile 2-XB_5H_8 isomers led to a wider variety of bands. For example, the most intense band for 2-FB_5H_8, having a wide maximum at 1332 cm^{-1}, ranged from 1150 to 1550 cm^{-1}, with B–F stretching and BHB bridging modes superposed to develop many shoulders, either blunt or sharp. For compact description, such broad and diffuse bands will be identified by the letter d, while c indicates a complex peak having several maxima not easily recognized or resolved. As usual, sh means a shoulder and the relative intensities appear in parentheses. These intensity values lack absolute accuracy, but their short-range relations can be used to infer the shapes of the bands. No exact account of all of the spikes and shoulders of any band can have much meaning, for wider or narrower slit programs must lead to a considerable variation of each band envelope. Accordingly, only the most reproducible features appear in the following listing of frequencies (cm^{-1}) of peaks and shoulders.

2-Fluoropentaborane: 2622 (8.8), 2614 (10), 2606 (7.8), 2514 sh (0.03), 2495 sh (0.06), 2487 (0.08), 2480 sh (0.05), 2390 (0.016), 1969 d (0.87), 1852 d (0.74), 1826 d (0.70), 1776 d (0.55), 1636 d (0.28), 1603 d (0.22), 1332 d (10), 1126 (0.11), 1028 cd (0.35), 834 c (1.1), 798 c (0.16), 790 (0.14), 755 c (0.2), 730 c (0.12), 675 c (1.15), 595 cd (2.6), 564 (1.2), 556 (1.0), 517 (0.70), 512.5 (0.74), 507.5 (0.81), 502 sh (0.6), 425 c (0.3).

1-Chloropentaborane: 2620 (13), 1847 d (1.7), 1787 d (0.86), 1625 d (0.5), 1560 d (0.5), 1513 d (0.8), 1443 d (3.7), 1386 d (3.8), 1212 (2.85), 1205 (2.85), 1198 (2.85), 1171 (3.6), 1165 (3.7), 1145 sh (2.4), 1140 sh (2.3), 1073 (1.1), 1043 d (0.9), 909 d (2.7), 857–884 d (1.3), 781 R (0.93), 773 Q (1.4), 765 P (0.88), 644 (3); lower frequencies not sought.

2-Chloropentaborane: 2623 sh (8.8), 2618 c (10.0), 2608 sh (8.4), 2060 d (0.08), 1924 d (0.32), 1855 d sh (0.43), 1804 d (0.88), 1725 d (0.49), 1668 d (0.18), 1603 d (0.27), 1423 d sh (2.5), 1384 (6.5), 1334 c (1.2), 1327 (1.1), 1301 c (0.62), 1264 (0.56), 1185 d (0.08), 1129 (2.4), 1124 (2.4), 1120 sh (1.9), 1070 c sh (2.6), 1044 c (6.9), 995 (0.54), 988 (0.55), 945 d (0.26), 884 c (5.7), 834 d (0.56), 761 c (0.6), 685 (0.76), 677 (0.64), 635 sh (1.68), 630 (1.91), 625 (1.99), 602 c (1.36), 573 (0.48), 564 (0.48), 471 (1.02), 466 (1.02), 392 c (0.48).

1-Iodopentaborane: 2618 c (15), 1844 c (4.1), 1802 d (1.7), 1617 d (0.5), 1500 d sh (1.05), 1443 d (4.2), 1379 d (2.5), 1315 d (0.46), 1270 d (0.14), 1187 c (1.3), 1140 (4.6), 1136 (4.7), 1047 d (0.55), 1028 d (0.4), 907 (3.5), 865 (2.4), 752 c (1.6), 656 c (3.6); nil down to 300 cm^{-1}. These spectra were recorded at temperatures as high as 103° (*ca.* 24 mm pressure, corrected to 25°) by means of a KBr-windowed cell in a transite box with a heater-blower, wholly within the dry cell-chamber of the Beckman IR7 instrument.

2-Iodopentaborane: 2620 c (14), 2614 (14), 2487 d (1.4), 1800 d (0.6), 1525 d sh (0.7), 1490 sh (3.0), 1469 (4.7), 1445 d (3.2), 1415 d sh (6.4), 1388 (14), 1345 d sh (1.5), 1247 (0.85), 1113 d (0.67), 1017 c (6.4), 920 d sh (0.75), 884 c (6.5), 840 c (3.3), 765 c (1.4), 644 sh (4.0), 637 (4.3); lower frequencies not sought.

Low-Temperature Spectra. The infrared spectra of 2-FB_5H_8, 2-IB_5H_8, and 1-IB_5H_8, in the form of thin microcrystalline films on a silver chloride window at −196°, were recorded by my colleague Dr. David A. Dows, using a Perkin-Elmer 521 instrument. The low temperature virtually eliminated the P and R rotational branches, so that each peak represented a nearly pure vibrational energy transition. This technique served to resolve some of the vapor-phase bands labeled c or d, although some new complexities could be attributed to the solid state. Among the more interesting results was the resolution of the especially diffuse 1332-cm^{-1} band of 2-FB_5H_8 into at least eight main features. Each of the peaks at 1267 and 1318 cm^{-1} is accompanied by shoulders on the high-frequency side, with spacing (4–6 cm^{-1}) wider than expected for a ^{10}B isotopic effect upon a BHB bridging mode; most probably these peaks correspond to two different ways of coupling the B–F stretching with the B_5 skeleton. Isotopic effects appeared also in the low-temperature spectra of the iodopentaborane isomers; however, their occurrence cannot be understood until a full theoretical analysis, combined with further experience with RB_5H_8 spectra, clarifies all of the assignments.